Nanomechanical Systems with Small Dissipation

by

Ye Tao

B.A., Harvard University (2009)
S.M., Massachusetts Institute of Technology (2011)

Submitted to the Department of Chemistry
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

September 2015

© Massachusetts Institute of Technology 2015. All rights reserved.
This doctoral thesis has been examined by a Committee of the Department of Chemistry as follows:

Professor Robert G. Griffin ............................................
Chairman, Thesis Committee
Professor of Chemistry

Professor Christian L. Degen...........................................
Thesis Supervisor
Assistant Professor of Physics

Professor Robert W. Field .............................................
Member, Thesis Committee
Haslam and Dewey Professor of Chemistry
Nanomechanical Systems with Small Dissipation

by

Ye Tao

Submitted to the Department of Chemistry on July 24, 2015, in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Abstract

This thesis is devoted to a systematic development of methods for controlling energy dissipation in small mechanical systems, specifically nanomechanical resonators with at least one dimension in the deep nanometer range (< 200 nm). We explored three avenues for decreasing intrinsic dissipation and one method for decreasing non-contact friction. The three routes toward lower intrinsic dissipation are surface chemical engineering, alternative materials testing, and geometric optimization through nanofabrication. Reduction in non-contact friction between a vibrating nanomechanical resonator and a surface, spaced nanometers away from the latter, was achieved by using a diamond nanowire as an integrated scanning tip. Each of the four approaches led to between one and two orders of magnitude reduction in dissipation compared to the previous state-of-the-art in the literature. Planned integration of individual successful approaches is expected to result in devices with sufficient force sensitivity and with the suitable geometry for the nanomechanical detection of a single nuclear spin by magnetic resonance force microscopy.

Thesis Supervisor: Christian L. Degen
Title: Assistant Professor
we regard the struggle to isolate one degree of freedom from all others

- i.e., the struggle for high $Q$ -

as a noble task for experimenters.

Vladimir Borisovich Braginsky
Valery Pavlovich Mitrofanov
Vladimir Ivanovich Panov

*Systems with Small Dissipation*
Acknowledgments

To My Family

I dedicate this thesis to Qian and our parents, for it is built on a foundation of their love, support, and decades of devoted sacrifice.

To the Degen Group

I sincerely thank Professor Christian Degen for a precious ticket to adventure into the nanoworld. He furnished close guidance early on and ample freedom as I grew accustomed to building and maintaining our ‘rover’-a magnetic resonance force microscope (MRFM). Together, we have sharpened its senses by upgrading the central piece of nano-gear at its core: the signal-transducing nanomechanical resonator. I will be forever grateful for the skills in instrumentation building that Christian passed onto me without reserve. I wish he and his lovely family every happiness in life and success in all future endeavors.

Special thanks go to Ben, Brad, and Kevin for their friendship and mutual support setting up the labs. Thanks to all ETH students and postdocs for such an exceptionally harmonious and amazing group environment. It was my privilege to have collaborated with Dr. Alexander Eichler, Dr. Paolo Navaretti, and Tim Holzherr.

I had the pleasure to work with an outstanding ETH undergraduate, Jens Boss, who has matured into a pillar of the Degen group as a graduate student. I look forward to seeing his great success in pushing the art of single-crystal diamond nano-structuring and sensing applications to the next levels.

To My Thesis Committee

I would like to thank Professor Robert Griffin for serving as my thesis committee chair. Despite my being nonresident half a world away, he has been extremely accessible and has encouraged me in our long-distance progress report meetings. I also want to thank Professor Keith Nelson and Professor Robert Field for serving on my committee.
To My Mentors

I would never have had enough time to become proficient in experimental physics techniques in a reasonable amount of time if it were not for a precious opportunity to receive four years of rigorous scientific training in the laboratory of Professor Eric Jacobsen, under the tutelage of Dr. Stephan Zünd.

I must also thank Professor Victoria D’Souza, Dr. Michael Durney, Professor Olof Ramström, and Professor Louis Cuccia for giving me the opportunities to participate in a variety of research areas. It was the combination of this diversity of experiences that convinced me that my current work in nanoscale magnetic resonance imaging will prove invaluable in our effort to better understand nature.

Looking back, amazing science teachers since high school and CEGEP played decisive roles in my scientific development. They are Dr. René-Yves Hervé, Dr. Aniko Lysy, and Dr. Oscar Hernandez. To this day, I admire their dedicated enthusiasm in passing down complicated scientific concepts with such clarity and efficiency that I have rarely seen since entering university. Among these rare but absolutely amazing teachers are Professor Cynthia Friend, Professor Howard Georgi, Professor Roy Gordon, and Dr. Shaw Huang.

During my time as a graduate student, I had the good luck to be mentored by amazing teachers and distinguished scientists. I thank Dr., and former Professor, Gang Liu for helping to trouble shoot the many electronic components in my experimental system and to provide fascinating conversations ranging from mass production of iron-base magnetic nanoparticles to the histories of the Three Kingdoms. I thank Dr. Roland Hauert for assisting me in the measurement and analysis of hundreds of samples by x-ray photoelectron spectroscopy. I am happy to say that due to our careful experimental planning, the vast majority of measured samples have found a useful spot on figures and tables of this thesis.
To the Cleanroom Ninjas

The art of fabrication is a craft that is most easily learned under expert guidance. I thank masters Dr. Ben Chui, Kurt Broderick, Dr. Vicky Diadiuk, Dr. Andreas Alt, David J. Webb, Donat Scheiwiller, Stephan Handschin, Dr. Yargo Bonetti, and Dr. Ute Drechsler for valuable discussions, suggestions, and assistance.

To the Technical Experts and Department Administrators

The hundreds of parts that went into my MRFM system and the various gadgets used in sample preparation were made by master machinists at the MIT Central Machine Shop and at ETH’s Zentralwerkstatt. Our group technicians and various technical experts have given me invaluable assistance in the construction and assembly of our instruments. In particular I would like to thank Andrew Gallant, Isabelle Altorfer, Cecil Barengo, Christoph Keck, Sandro Tiegermann, Martin Kloechner, Andi Stuker, Walter Bachmann, and Hansuedi Scherrer for their generous assistance and friendship. Thanks to Susan Brighton, Macall Zimmerman, Julia Tamborini, and Jennifer Weisman for helping to navigate through the various departmental procedures.

To Fellow Scientists around the World

Beside scientific knowledge communicated in papers, a type of knowledge, called ‘tacit knowledge’, can only be acquired through personal contact with experts in fields. I must thank all present and past generations of workers for providing a vast database of both theoretical knowledge and experimental tricks. In this regard, I must give special thanks to Dr. Dan Rugar, Dr. John Mamin, and Dr. Ginel Hill for hosting me at IBM for a one-month training. I have more often than not found my best efforts to fall short of your high standards in scientific rigor and creative innovation.

Colleagues around the globe have responded to my numerous and often annoyingly stupid questions with enlightening patience. I thank Dr. David Gleason-Rohrer, Dr. Bart Rijksen, and Dr. Morita Yukinori for clarifying protocols on silicon surface chemistry. I thank Dr. Chih-Hsun Hsu for a discussion about the bottom-up synthesis
of diamond nanowires. I thank Dr. John Nichol for discussions about MRFM during our one-month stay at IBM and for his friendship. I thank Professor Jens Jensen for answering my questions about his book on rare earth magnetism. I thank Dr. Zonglin Chu for assistance with water contact angle measurements.

I have also had the opportunity to collaborate with a number of scientists on various projects. I thank Dr. Marco Wolfer for performing the hydrogen-termination of diamond cantilevers discussed in Chapter 7. I thank Naveen Shamsudhin for our interesting work on the cantilever magnetometry measurements of a range of nano- and micromagnetic structures fabricated in the group of Bradley J. Nelson (Will be in Dr. Shamsudhin’s thesis). I thank Ying Pan for a collaboration on the application of surface chemical modification developed in this thesis to thermoelectric nanomaterials (Will be detailed in Dr. Pan’s thesis).

I thank scientists at ETH’s Scientific Center for Optical and Electron Microscopy for assistance with characterization and the manipulation of a family of magnetic nanowires and structures I fabricated over the years (not in this thesis). I admire their technical know-how, theoretical knowledge, and inspiring personalities. They are, in alphabetical order, Dr. Stephan Gerstl, Dr. Fabian Gramm, Dr. Joakim Reutler, and Dr. Karsten Kunze.

I thank Prof. Caroline Ross for a fascinating course on micro- and nanofabrication. I also thank her for being always available outside of class for discussions on the fabrication of nanomagnets (not presented here), and for giving me access to the instrumentation in her group. I finally thank Prof. Collin Stultz for graciously welcoming me to sit in his group seminars for a whole semester to hear about computational efforts aiming to understand the structural complexities of intrinsically disordered proteins.
## Contents

1 **Introduction** 15  
   1.1 Recent Advances in Imaging Techniques and Their Limitations . . . . 16  
   1.2 Nanomechanical Resonators in Physics and Engineering . . . . . . . 19  
      1.2.1 Ground-State Cooling of Mechanical Resonators . . . . . . . . 20  
      1.2.2 Ultrasensitive Metrology . . . . . . . . . . . . . . . . . . . . 21  
      1.2.3 Data Storage . . . . . . . . . . . . . . . . . . . . . . . . . . 21  
   1.3 Organization of the Thesis . . . . . . . . . . . . . . . . . . . . . . 24  

2 **Theory of Mechanical Dissipation** 27  
   2.1 Introduction . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 27  
   2.2 Anelastic Relaxation-  
      An Empirical Model of Internal Frictions . . . . . . . . . . . . . . . 30  
      2.2.1 Definition of an Anelastic Material . . . . . . . . . . . . . . . 30  
      2.2.2 Creep Function . . . . . . . . . . . . . . . . . . . . . . . . . . 31  
      2.2.3 Energy Dissipation Due to Quasi-Static Creep . . . . . . . . . 32  
      2.2.4 Energy Dissipation during Dynamic Operation . . . . . . . . . 34  
      2.2.5 Dissipation Term $\propto$ Velocity from Anelastic Properties . . 37  
      2.2.6 The Standard Anelastic Solid . . . . . . . . . . . . . . . . . . . 37  
      2.2.7 The Debye Peak . . . . . . . . . . . . . . . . . . . . . . . . . . 39  
   2.3 Additive Nature of Mechanical Dissipation . . . . . . . . . . . . . . 40  
   2.4 Thermoelastic Damping . . . . . . . . . . . . . . . . . . . . . . . . 42  
      2.4.1 Derivation of Thermoelastic Dissipation in the Flexural Cantilever 43  
      2.4.2 Relevance of Thermoelastic Damping for Ultrathin Si Cantilevers 48  
   2.5 Two Level Systems . . . . . . . . . . . . . . . . . . . . . . . . . . . 49
2.5.1 Dissipation in Tunneling Two-Level Systems .......................... 50
2.5.2 Importance of TLS in the Dissipation of Thin Si Cantilevers at Low Temperatures ................................................... 55
2.6 Other Types of Dissipation ...................................................... 60
  2.6.1 Clamping Loss .............................................................. 60
  2.6.2 Phonon-Electron Dissipation ........................................... 61
  2.6.3 Viscous Damping ........................................................... 61
2.7 Summary of Damping Mechanisms ........................................... 61

3 Experimental Setup and System Operating Procedures 63
  3.1 High Vacuum Generation .................................................. 65
  3.2 Mechanical Motional Detection and Signal Acquisition ............... 66
  3.3 6-Dimensional Positioning System ....................................... 69
  3.4 Radio Frequency Pulse Generation ....................................... 71
  3.5 Cryogenic System .............................................................. 71
    3.5.1 4K-300K ................................................................. 71
    3.5.2 $^3$He/$^4$He Dilution Refrigerator ................................. 74
  3.6 Labview and Labview FPGA Programs .................................... 74
  3.7 Operational Procedures ...................................................... 75
    3.7.1 Preparation of the Probe ............................................ 75

4 Exclusively Gas-Phase Passivation of Native Oxide-Free Silicon(100) and Silicon(111) Surfaces 80
  4.1 Introduction ........................................................................ 81
  4.2 Results and Discussion ....................................................... 83
    4.2.1 Gas-phase Processing Achieves Excellent Passivation Effect .. 83
    4.2.2 Surfaces Undergo Oxidative Degradation ........................... 85
    4.2.3 Oxygen-Containing Species Interact with the Organic Over-layer 86
    4.2.4 Fluorine Atoms Show Crystal Orientation-Dependent Lability 89
    4.2.5 Future Optimization Strategies and Applications ................. 93
4.3 Conclusion ................................................................. 94

5 Permanent Reduction of Dissipation in Nanomechanical Si Resonators by Chemical Surface Protection 95
5.1 Introduction ............................................................. 96
5.2 Experimental ........................................................... 97
5.3 Results and Discussion ............................................... 98
  5.3.1 Role of Native Surface Oxide ................................. 98
  5.3.2 Modification of Surface Chemistry ......................... 101
  5.3.3 Atomistic Origin of Surface Dissipation .................... 104
5.4 Conclusions ........................................................... 106

6 Facile Fabrication of Single-Crystal-Diamond Nanostructures with Ultra High Aspect Ratio 108

7 Single-Crystal Diamond Nanomechanical Resonators with Quality Factors Exceeding One Million 120
  7.1 Introduction ............................................................ 121
  7.2 Experimental .......................................................... 123
    7.2.1 Device Fabrication ............................................. 124
    7.2.2 Experimental Setup .......................................... 126
    7.2.3 Variable Temperature Measurements ...................... 127
  7.3 Temperature Dependence of $Q$ .............................. 127
    7.3.1 Quality Factors Between 4 and 300 K .................... 127
    7.3.2 Quality Factors at Millikelvin Temperatures ............ 129
  7.4 Diamond Surface Chemistry and $Q$ ......................... 130
  7.5 Discussion .......................................................... 134
  7.6 Conclusions ........................................................ 137

8 Additional Materials Exploration 139
  8.1 PECVD Silicon Nitride Torsional Oscillators .................. 139
  8.2 Commercial Wet Thermal Silicon Dioxide ...................... 142
8.3 Thermal Silicon Dioxide Produced in Air ..................................... 143
8.4 Organic Material Resonator: Polyacrylonitrile Microwire ............... 146
8.5 Conclusion .................................................................................. 147

9 Geometric Optimization ................................................................. 148
  9.1 Introduction ............................................................................... 148
  9.2 Three Inspirations ................................................................. 148
    9.2.1 First Inspiration .............................................................. 149
    9.2.2 Second Inspiration .......................................................... 150
    9.2.3 Third Inspiration ............................................................. 151
  9.3 The Nanoladder Cantilever ...................................................... 152
    9.3.1 Comsol Simulation of Nanoladder Resonators .................... 154
    9.3.2 Fabrication of Nanoladder Resonators ................................. 157
    9.3.3 Nanoladder Mechanical Characterization ............................. 159
  9.4 Conclusion and Outlook ............................................................ 162

10 Single-Crystal Diamond Nanowires and Tips for Ultrasensitive
    Force Microscopy ........................................................................ 164

11 Outlook ....................................................................................... 174
  11.1 Summary ............................................................................... 174
  11.2 Outlook .................................................................................. 175
  11.3 Applications .......................................................................... 177

A Gas-Phase Processing of Silicon Surface ........................................ 178
  A.1 Experimental Methods ............................................................ 178
    A.1.1 Substrate Preparation ....................................................... 178
    A.1.2 Preparation, Purification, and Storage of Reagent Gases ......... 178
    A.1.3 The Passivation Procedure ............................................... 182
    A.1.4 Samples Storage .............................................................. 184
  A.2 XPS Data Acquisition .............................................................. 184
  A.3 XPS Survey Spectra ................................................................. 186
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.4 XPS Fine Scan</td>
<td>187</td>
</tr>
<tr>
<td>A.5 Silicon Peak Fitting using 5-Component Model</td>
<td>190</td>
</tr>
<tr>
<td>A.6 Conversion between SiO$_2$/Si Ratio and SiO$_2$ Thickness</td>
<td>192</td>
</tr>
<tr>
<td>A.7 Atomic Concentration Evolution on Si(100)</td>
<td>195</td>
</tr>
<tr>
<td>A.8 Monolayer Reactivity</td>
<td>195</td>
</tr>
<tr>
<td>A.9 System Base Pressure and Acetylene-Propyne Comparison</td>
<td>199</td>
</tr>
<tr>
<td>A.10 Water Contact Angle Measurements</td>
<td>200</td>
</tr>
<tr>
<td>A.11 Wilcoxon Sign-Rank Test for Statistical Significance-Difference in Kinetics of Fluorine Desorption From Si(111) and Si(100)</td>
<td>203</td>
</tr>
<tr>
<td>A.12 Phosphorus Peak Background Subtraction</td>
<td>204</td>
</tr>
<tr>
<td>A.13 Comments about Future Loadlocked System</td>
<td>205</td>
</tr>
<tr>
<td>A.14 Comments about Light-Promoted Hydrosilylation</td>
<td>206</td>
</tr>
<tr>
<td>A.15 Last Comments on Si-F</td>
<td>207</td>
</tr>
<tr>
<td>B Surface Chemical Modifications of Silicon Resonators</td>
<td>208</td>
</tr>
<tr>
<td>B.1 Review of surface reactions on single-crystal silicon</td>
<td>208</td>
</tr>
<tr>
<td>B.2 Experimental Methods</td>
<td>210</td>
</tr>
<tr>
<td>B.3 Tabulation of Key Results</td>
<td>216</td>
</tr>
<tr>
<td>B.4 Quality Factor vs Temperature for Some Important Samples</td>
<td>216</td>
</tr>
<tr>
<td>B.5 X-ray photoelectron spectroscopy (XPS) Analysis of Silicon Surfaces</td>
<td>218</td>
</tr>
<tr>
<td>B.6 Frequency and Quality Factor Data from Cyclic Oxide Removal-Native Oxidation Experiments</td>
<td>222</td>
</tr>
<tr>
<td>B.7 Si and SiO$_2$ Material Properties Used in Data Analysis</td>
<td>224</td>
</tr>
<tr>
<td>B.8 Oxide Growth Underneath Polydimethylsiloxane Thin Film</td>
<td>224</td>
</tr>
<tr>
<td>B.9 Other Tested Silicon Surface Modification Strategies With Results That May be Optimized</td>
<td>227</td>
</tr>
<tr>
<td>B.9.1 Two-Step Alkylation and Amination Reactions (IIa)</td>
<td>227</td>
</tr>
<tr>
<td>B.9.2 Spontaneous Diazonium Salt Grafting (IIa)</td>
<td>227</td>
</tr>
<tr>
<td>B.9.3 Atomic Layer Deposition (ALD) of Al$_2$O$_3$ (IIc)</td>
<td>229</td>
</tr>
<tr>
<td>B.9.4 Electron Beam Evaporation of Al$_2$O$_3$ (IIc)</td>
<td>229</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

Scientific research relies increasingly on the availability of quality instrumentation and devices. In more applied fields, it is nowadays difficult for any scientist to stay productive without such tools as nuclear magnetic resonance spectrometers, a varieties of optical and electron microscopes, the many variants of scanning probe microscopes, and high-performance computation clusters. We have come to rely on these workhorse equipment for sample characterization and for monitoring physical processes. In more fundamental endeavors, the observation of new physical phenomena and the acquisition of weak signals hinge critically on the successful fabrication of devices and sensors, often nanoscale, and of high quality. In recent decades, successful experimental access to the physics at the boundary between macroscopic, classical and the atomic-scale, quantum mechanical realms have been possible only because of advances in micro- and nanofabrication technology. The engineering of better instrumentation and devices have become a rate-limiting step in the advancement of science.

A class of devices central to both applied and fundamental sciences are mechanical resonators, in particular micro- and nanomechanical resonators [1–12]. Owing to their small masses, their mechanical properties, including frequency ($f$) and quality factor ($Q$), become sensitive functions of both intrinsic processes inside the resonator material, and of their interactions with weak external disturbances (electric, magnetic, and optical fields). In other words, nanomechanical resonators can serve both as
interesting samples in their own right for the study of material properties and as signal transducers for interesting, but weak, physical interactions.

The exquisite sensitivity of nanomechanical systems has proven to be both a bliss and a curse; while miniaturization has, in general, permitted improvements in sensitivity and performance, the resulting gains have been consistently and drastically less than projections based on geometric considerations. This is due to the concurrent increase in surface-to-volume ratio that amplifies the contribution of surface defects to the overall device property [1, 13, 14]. The microscopic nature of surface defects relevant to mechanics are open scientific questions [15–21] and technologies for controlling them are yet to be developed. This thesis seeks both to gain an understanding of the defects in the most important resonator materials and to develop techniques to evade the detrimental effects on mechanical properties from intrinsic and extrinsic sources.

In the following sections, we provide the context and justification for improving nanomechanical devices for applied and fundamental research. We summarize recent advances in key imaging techniques in section 1.1 to motivate a need for better mechanical resonators for a particular technique belong to this class of instrumentation-building efforts. We then give examples of fundamental physics and engineering fields that can benefit greatly from better nanomechanical resonators in section 1.2. We finish the introductory chapter with an outline of the thesis in section 1.3.

1.1 Recent Advances in Imaging Techniques and Their Limitations

The importance of high-performance imaging instruments for science and technology can be illustrated by the many high-impact papers demonstrating ever higher spatial resolutions and measurement sensitivities. We give a few examples, most published after the start of this PhD project in 2009, in the following.

Since 2009, atomic force microscopy (AFM) has improved tremendously in resolu-
tion and speed. Using an adsorbed carbon monoxide molecule as tip, researchers have obtained atomic-resolution images of flat molecules on atomically flat substrates [22, 23]. It has also been possible to obtain high resolution images of DNA molecules in solution under conditions more relevant to biology [24].

In 2009, a pair of papers demonstrated single-atom-resolution scanning electron microscopy (SEM) [25] and scanning tunneling electron microscopy (STEM) [26]. In 2014, researchers further showed that it is possible to deduce the 3-dimensional atomic layout of thin edge regions of magnesium oxide nanocrystals by analyzing a tunneling electron micrograph [27]. These advances show that inorganic materials that are robust under electron irradiation can, in principle, be analyzed at atomic resolution under optimized conditions. The effect of single dopant atoms on the physical properties of nanoscale and molecular-scale devices may now be addressed in a meaningful way.

A 2.2 Å-resolution cryo-EM structure of β-galactosidase in complex with a cell-permeant inhibitor was demonstrated during the writing of this thesis [28]. This level of resolution makes it possible to identify atomic-scale features including hydrogen bonds, salt bridges, coordination water molecules, and alkali ions in homogenous protein samples. Such technical advances open up new opportunities for structural biology.

Beside characterizing the spatial coordinates of atoms in material, equally important is the ability to characterize collective properties that arise from the interactions among atoms due to their particular spatial arrangement. Prominent examples include the appearance of phases of magnetic and electric ordering. A variant of AFM, called magnetic exchange force microscopy, was used to image antiferromagnetic ordering in nickle(II) oxide single crystal with sub-nm periodicity [29]. Recently, yet another variant called magnetoelectric force microscopy was used to image magneto-electric domains in a multiferroic material [30].

Despite the tremendous advances summarized above, there remain important limitations to existing imaging techniques. For example, AFM can only achieve atomic resolution for a very limited class of samples lying on atomically flat substrates. Spa-
tial information is limited to top-surface topography. Electron microscopy techniques are generally destructive, often require focused ion beam processing, can induce radiation damage, and may deposit an unwanted carbonaceous contamination layer on scanned samples. Atomic resolution is also yet to be demonstrated for lighter elements.

With cryo-EM, important classes of biological materials continue to evade direct experimental characterization. These include intrinsically disordered proteins (IDP’s) [31] and heterogeneous materials composed of lighter elements that do not provide sufficient electron contrast. Despite the good resolution, cryo-EM requires averaging over a large number of identical copies of the object to achieve sufficient signal [28]. This requirement limits the range of accessible targets. All proteins, to varying degrees, display some flexibility and hence structural heterogeneity. Existing structures in the Protein Data Bank, 90 percent of which are obtained using X-ray crystallography, are biased towards proteins that have little intrinsic flexibility and are thus more amenable to crystallization [32]. It has been estimated that roughly 40 percent of all proteins or segments of proteins in the animal kingdom do not have unique 3-dimensional structures [31]. A general imaging technique for characterizing flexible proteins and protein domains is required to complete our knowledge of biological and synthetic organic materials.

A promising technique that circumvents all of the above limitations is a variant of AFM called magnetic resonance force microscopy (MRFM) [33, 34]. A genuine single-molecule technique, magnetic resonance force microscopy is ideally suited for heterogeneous samples [35–37]. Even intrinsically disordered proteins like alpha-synuclein, linked to Parkinson disease [38], could be studied by individually imaging each molecule of the structural ensemble. With no need for signal averaging over separate copies of the molecule, a continuum of conformational distributions can, in principle, be mapped out by MRFM.

A major hurdle limiting the improvement of MRFM beyond its current 4-5 nm resolution into the sub-nm resolution range is the nanomechanical signal transducer at the heart of the instrument. The signal-to-noise ratio (SNR) of a MRFM measurement
is

\[ \text{SNR} = N \frac{(\mu_N \frac{\partial B_z}{\partial z})^2 \omega_c Q}{4k k_B T \Delta f} \]  

(1.1)

where \( N \) is the number polarized nuclear spins with magnetic dipole moment \( \mu_N \), \( \frac{\partial B_z}{\partial z} \) is the magnetic field gradient experienced by the nuclear spins, \( \omega_c \) is the angular frequency of the mechanical signal transducer with spring constant \( k \) and effective mechanical quality factor \( Q \), \( k_B T \) is the thermal energy, and \( \Delta f \) is the measurement bandwidth [36]. The key parameters that can be optimized through material engineering are colored in red. From the expression of the SNR, it is clear that improving \( Q \) (without modifying other mechanical parameters) constitutes one method for improving MRFM performance. Improving the magnetic field gradient would be even more effective. One way to increase the gradient is to approach closer to the gradient source, if the closer approach did not lead to a concurrent decrease in \( Q \), as has been observed in existing studies [35, 39]. This thesis details both of these approaches. Improvement in the intrinsic magnetization of nanomagnetic field gradient source has also been achieved during this PhD work, but are omitted from presentation in the interest of space and because mechanical dissipation forms a self-contained topic.

1.2 Nanomechanical Resonators in Physics and Engineering

Micro- and nanomechanical resonators are the central players in a large number of physics experiments since the late 1990s. At least four major areas of applications have emerged, including fundamental studies of mechanics and quantum mechanics, ultra-high precision metrology, quantum signal transduction [40], and data storage. For all areas of application, achieving lower dissipation in the mechanical resonator is a common and central goal.
1.2.1 Ground-State Cooling of Mechanical Resonators

A particular active area of research in physics in the past decade has been the cooling of a macroscopic mechanical resonator via both active [41–43] and passive feedback [44–47] toward its quantum ground state. The field originated from experiments in the 1970s showing that forces from radiation pressure were sufficient to trap and levitate micro-sized objects [48, 49]. If successful, such effort would enable a large range of applications, including tests of quantum mechanics in macroscopic objects. These early efforts used a geometry in which the mechanical resonator formed one mirror of an optical cavity. Feedback force was either applied optically or mechanically. An alternative geometry in which the optical and mechanical elements are modular has also been tested [50]. Regardless of the mechanism of cooling, its efficiency always hinges on the mechanical quality factor because the thermal environment continuously counters the cooling effect by adding thermal energy back into the resonator mode at a rate proportional to $\frac{k_B T}{\hbar Q}$, where $\hbar$ is reduced Planck constant. Clearly, a higher $Q$ will shift the equilibrium towards lower temperatures for the same cooling power.

While the early experiments all succeeded in lowering the thermal occupation number in the mechanical resonator, it was not until 2009, with the publication of a set of four studies [51–54], that cooling to the ground state appeared to come within reach. These studies showed final phonon occupation numbers in the $4 - 60$ range for a variety of mechanical oscillator geometries. In two of these studies [52, 53], the cooling performances were hampered by the poor mechanical $Q$ of the resonator material, fused quartz, which is known to exhibit high levels of mechanical dissipation at liquid helium temperatures.

Success came soon afterwards in three different experiments [55–57]. In the first demonstration [55], the authors exploited a GHz mechanical mode to relax the required bath temperature for achieving ground state. Ground state was reached below 0.1 K via conventional cooling in a dilution refrigerator. Most notably, one of the three successful efforts achieved mechanical ground state from a bath temperature of 20 K [57]. A silicon nanomechanical resonator with high $Q$ was used in this study. If
the quality factor of the mechanical resonator could be improved by a factor of 10, it would be conceivable to achieve ground state cooling directly from room temperature, without conventional cryogenic pre-cooling. The current thesis shows that such improvements in $Q$ can be achieved for silicon resonators of such sizes.

Beside mechanical resonators anchored to a substrate through physical tethering, many analogous experiments using suspended micro and nanoparticles have also been demonstrated [58–64]. A major advantage of the absence of solid contact between the vibrating particle and a substrate is the nearly complete isolation from a thermal surrounding (except for occasional collision with residual gas molecules). This also means that levitated mechanical resonators can have their center-of-mass motion cooled to very low levels, directly from room temperature without cryogenic pre-cooling [61]. Recently, attonewton-force detection has also been demonstrated using such a suspended resonator [64]. Despite this branch of nanomechanics being very interesting, results from this thesis are unfortunately not applicable to suspended resonators, which do not undergo material deformation and energy dissipation in the most common sense.

1.2.2 Ultrasensitive Metrology

Nano mechanical resonators have set the records in the measurement of small charge [65], current [66, 67], forces [35, 68–71], mass [72–75], and magnetization [76, 77]. The range of applications is extremely wide, from testing of quantum mechanics to sample characterization in biology and medicine. All of these applications would achieve higher sensitivity and performance if the mechanical quality factors of the respective sensors could be improved.

1.2.3 Data Storage

The semiconductor industry is continuously driven to find new methods of data manipulation and storage. Traditionally, room-temperature orientational bi-stability of ferromagnets has enabled high-density data storage as ones and zeros. This princi-
ple underlies the functioning of long-term storage devices like the hard drive and of shorter-term storage devices exemplified by magnetoresistive random-access memory (MRAM).

One aspect of magnetic devices, however, has become increasingly inadequate as the society unremittingly quests for higher energy efficiency. While the storage of information as thermally stable magnetic bits does not cost energy, their writing by available means has required rather large inputs of energy; hard drive bits are written by nanoscale, current-driven electromagnets flying over its surface. MRAM devices are switched also by currents, albeit via a different mechanism called spin-transfer torque [78]. Evidently, an alternative strategy for controllable magnetic domain reversal that requires no dissipative current would drastically boost the value of such devices for current and future applications.

Alternative methods for writing magnetic information, including electrical control of magnetization direction, has been avidly pursued since about a decade [79–85]. For example, the reversible control of magnetization direction exclusively via electric field modulation was not achieved until very recently [85]. Kanai et al. extend the precessional switching of an in-plane-anisotropy CoFeB-MgO-CoFeB system to the corresponding perpendicular-anisotropy device [86]. Despite the success in the laboratory, major issues limit the application of this technique in industrial settings. For instance, the method currently requires a small static magnetic ‘helper’ field to counterbalance the interlayer dipole coupling. The fidelity of switching is imperfect and depends rather sensitively on the magnitude and direction of this external field. The presence of unavoidable device-to-device variation means that a uniform helper field is unlikely to be sufficient for chip-scale fidelity.

Mechanical resonators offer an alternative path to similar functionality with potentially enhanced performance. Some properties of mechanical resonators show the bi-stability required for application in data storage. These include both dynamic [87] and static properties [88]. In the dynamic example, information is stored as a phase lag between a driving signal and the response of the mechanical resonator. This requires continuous energy input, analogous to a traditional volatile RAM. The static
example shows that a doubly-clamped nano-beam under compressive stress has two stable shapes, buckled-up and buckled-down. In the demonstration study, these states are separated by a gigantic energy barrier of $10^8$ K. This situation is analogous to MRAM.

Despite the large barrier, a buckled beam could be selectively set into the up and the down states with perfect fidelity using exclusively optical control [88]. The identity of the final state was simply the wavelength of the excitation laser. In the demonstration study, large optical powers were needed for the toggling, roughly $10^7$ times that required for magnetization reversal in the CoFeB-MgO-CoFeB system [86]. Given the state of infancy of the mechanical device compared to very mature magnetic ones, drastic improvements are expected in the near future. Specifically, the current barrier of $10^8$ K between the two buckled states is much higher than what would be required for stable information storage. Optimization of optical and mechanical quality factors will also improve energy efficiency of switching. Alternative switching protocol based on electric-field-assisted or complete electrical control are avenues to be explored. Hybrid magnetic and mechanical systems can also be explored.

In summary, this section summarized three examples of important scientific and engineering areas of high importance in which nanomechanical resonators are playing the central role.
1.3 Organization of the Thesis

The thesis takes four parallel approaches to decrease both the intrinsic and the extrinsic dissipations in nanomechanical resonators. These approaches are

1. **SURFACE CHEMICAL ENGINEERING**
   Decrease surface loss in standard silicon cantilevers through chemical treatment (Chapters 4 and 5)

2. **MATERIALS ENGINEERING AND MICROFABRICATION**
   Employ materials with smaller intrinsic dissipation for resonator fabrication (Chapters 6, 7, and 8)

3. **GEOMETRY ENGINEERING AND NANOFABRICATION**
   Explore different geometric designs with less dissipation (Chapter 9)

4. **SCANNING TIP ENGINEERING**
   Fabricate nanowire tips to reduce non-contact friction between the resonator and the scanned surface under operation geometries (Chapter 10)

All four routes have proven effective, each leading to roughly an order of magnitude reduction in dissipation. We expect that combining the individual approaches in a single device would result in additive gains.

Chapter 2 provides a theoretical background to the nature of mechanical dissipation, with a particular emphasis on mechanisms most relevant to nanomechanical resonators operating at low temperatures and in high vacuum. We also show that the $Q$ in standard silicon ultrasensitive cantilevers are currently limited by the presence of a native oxide layer at both room and liquid helium temperatures.

Chapter 3 provides a summary of the construction and operation of a custom magnetic resonance force microscope capable of operating at a base temperature below 100 mK. s

Chapter 4 explores the surface chemistry of silicon. In particular, we develop exclusively gas-phase methods to remove the native oxide and to prevent its regrowth
on a time scale of days when exposed to ambient atmosphere. Due to the non-standard and cross-disciplinary techniques used, detailed processing protocols and material characterization are described in Appendix A.

Chapter 5 describes the response of the mechanical quality factors of the standard silicon devices following treatment by a number of chemical methods, including the technology developed in Chapter 4. Several useful methods emerge from the rather exhaustive screening of procedures. Again, details of the processing techniques are described in Appendix B.

Chapter 6 describes the fabrication of cantilevers from single-crystal diamond substrates. We present two independent approaches, both of which gave high yields in finished devices.

Chapter 7 contains the measurement of the mechanical properties of diamond cantilevers between room-temperature and 90 mK. The results substantiate the promise of high-purity diamond for use as next-generation ultrasensitive nanomechanical resonator material. Additional data and discussion are provided in Appendix D.

Chapter 8 discusses experiments with several common materials and oscillators fabricated from them.

Chapter 9 describes the design and the fabrication of a new type of resonator that pushes geometry to the extreme, while maintaining sufficient mechanical robustness. Measurements of its mechanical properties demonstrate significant improvement over traditional designs. We also provide other preliminary data on for several oscillators fabricated from amorphous dielectric and organic materials.

Chapter 10 explores minimization of dissipative interaction between a pendulum-style cantilever with a flat substrate by equipping the cantilever with a sharp diamond nanowire tip. We describe the fabrication of the diamond nanowires by ICP etching. Additional processing details are provided in Appendix E.

Finally, Chapter 11 summarizes the knowledge gleaned from the various approaches for producing nanomechanical resonators with small effective dissipation. We make projections about the force sensitives that should result when individual advances are combined and provide an outlook on the types of experiments and mea-
surements that are now within the capabilities of MRFM.
Chapter 2

Theory of Mechanical Dissipation

2.1 Introduction

The title of this chapter is pretentious and misleading; it seems to suggest that the loss of mechanical energy during material deformation were a well-defined phenomenon that could be satisfactorily treated with one unifying theory, and concise enough to be summarized in one chapter. The reality is that a large number of different mechanisms can lead to the loss of mechanical energy from varieties of engineering and experimental systems. Just for the common materials of silicon and silicon dioxides, many mechanisms have been proposed and volumes have been written over the last century [18, 20, 89–104]. As of 2015, a predictive microscopic theory applicable to all systems is lacking [105]. And the design of the perfect mechanical sensor from first principles is out of reach. The engineering and control of mechanical dissipation, in macro- and nanoscale devices alike, have therefore depended more or less on empirical efforts guided by a selection of understood mechanisms [99] [13–15, 17, 19, 106]. A more appropriate, though somewhat maladroit, title would have been “An Overview of Important Mechanisms behind Mechanical Dissipations in Micro- and Nanomechanical Systems”.

Despite its variety and complexity, the phenomenon of mechanical dissipation is familiar to all of us by virtue of its everyday ubiquity. Suspension and breaks on vehicles, fast deceleration of ships and swimmers after ceasing of propulsion, and the
effortless grace of skaters are instances where mechanical friction can (need) be either advantageously exploited or adroitly circumvented.

These examples offer the opportunity to illustrate a few common channels for losing mechanical energy. Vehicle suspensions are damped springs that convert kinetic energy from mechanical impulses into a time-dependent material deformation, which eventually decays into thermal energy over a time scale longer than that of the impulse. Breaks on vehicles convert kinetic energy into other forms of energy, most often as heat in the end form. This is the case for both conventional friction-based breaks and eddy-current breaks. In regenerative breaking systems, the kinetic input energy may also be converted to and stored as useful electrical, mechanical, and chemical energy [107,108]. Movement of ships in water and of the skater through air lead to efficient conversion into chaotic movement of molecules when a fluid or gas move past solid bodies in either turbulent or laminar fashions. Finally, the fact that skating works at all illustrates the relevance of surface, phase, and micro-nanoscale phenomena in certain manifestations of mechanical dissipation.

Compared to the varied everyday examples, the scope of this thesis may seem narrow and restricted; what more is there to say about a cantilever other than the fact that it is a harmonic mechanical resonator experiencing a damping force proportional to the instantaneous velocity? Well, answers to this question could start with another question: “Why do mechanical harmonic resonators experience a damping force proportional to its instantaneous velocity?” As we move through the chapter, it should become clear that a real cantilever is in fact a complex system capable of manifesting a great variety of dissipation mechanisms, including and beyond those found in the mundane examples mentioned above.

Rather than aiming for an exhaustive and up-to-date review of all accepted mechanisms and theories of mechanical dissipation, the primary goal of this chapter is to survey the intrinsic dissipation mechanisms most relevant for nano- and microfabricated cantilevers under the operating conditions of scanning probe microscopy in vacuum. The goal is to achieve a qualitative appreciation of how dissipation arises rather than to obtain quantitative models.
We will start with a general discussion of dissipation as a consequence of anelastic behavior in real materials [109]. We illustrate a classical cause of anelasticity with a detailed discussion of the thermoelastic damping effect [89, 90]. This effect has been shown to be the dominant loss channel for some silicon and silicon nitride cantilevers at room temperature [13, 101]. While the types of cantilevers important for MRFM and ultrasensitive force and mass measurements naturally avoid thermoelastic damping by their ultra-thin design, the relative simplicity and intuitive clarity of this mechanism is important as a pedagogical example. We proceed to a second, more recently elucidated cause of anelasticity having quantum mechanical origins: Tunneling of defect states with two equilibrium positions separated by a potential barrier [93–98]. Originally discovered in the study of low-temperature thermal properties of amorphous materials, we believe these tunneling, two-level systems to be the currently-limiting factor of mechanical quality factor for silicon and diamond nanocantilevers at low temperatures studied in this thesis. We end the chapter by providing a brief discussion of why other types of dissipation mechanism, such as clamping loss, viscous drag by gas molecules, and phonon-electron dissipation can be made negligible by proper design of the device and of the measurement system. They are thus irrelevant for ultrasensitive force and mass measurement applications.

From the theoretical discussion, it will become apparent that a rigorous test of any single mechanism at a quantitative level would require a series of carefully designed studies. Resonators with a wide range of geometries, material quality, surface and bulk treatments, and different experimental conditions (including, but not limited to, temperature, mode and power of excitation, and mode of displacement detection) will be needed. Such a herculean task is beyond the scope of a single PhD thesis. We have instead used existing theoretical knowledge as an intuitive guide in our engineering efforts to decrease mechanical dissipation. Our pragmatic approach has been effective and yielded several practical strategies for reducing intrinsic dissipation in state-of-the-art ultrasensitive cantilever sensors (Chapters 5, 7, and 9).
2.2 Anelastic Relaxation—

An Empirical Model of Internal Frictions

Relaxation of mechanical deformation occurs when the shape of an object (strain) is not a one-to-one function of forces (stress) acting on it. In the time domain, evolution of the shape of the object takes place when forces and pressures on it are held constant. When such time-dependent changes in deformation happen, mechanical energy is lost. One may have had the experience of walking in deep mud or snow. One would then have noticed that significantly more physical efforts are needed compared to walking on a concrete floor. One would then also have noticed that after a step is taken (constant pressure applied via weight transfer), it takes time for the foot to sink in and settle in height. We introduce concepts of an anelastic solid and derive some useful relations to guide further discussion. We follow the exposition by Nowick and Berry in this short overview [109].

2.2.1 Definition of an Anelastic Material

Before defining an anelastic material, it is useful to review equations defining the simpler, ideally elastic material in terms of Hooke’s law:

\[ \sigma = Eu \]  \hspace{1cm} (2.1)

\[ u = J\sigma \]  \hspace{1cm} (2.2)

\[ E = \frac{1}{J} \]  \hspace{1cm} (2.3)

where \( \sigma, u, E, \) and \( J \) are the stress, strain, modulus, and compliance, respectively. In this discussion, we neglect the tensorial nature of stress and strain in favor of clarity. Equations 2.1-2.2 show that stress and strain in an elastic material are linearly related, respond instantaneously to each other, and exhibit one-to-one functional relationship at equilibrium. This instantaneous settlement into the equilibrium, one-to-one relationship between stress and strain is what would impart
frictionlessness to a perfectly elastic material. The fact of the matter is that such a material does not exist in reality. All real materials require some time, no matter how short, between the onset of a stress until the attainment of an equilibrium shape. Such an anelastic material has the following properties:

1. For every stress there is a unique equilibrium value of strain, and vice versa.
2. The equilibrium response is achieved only after the passage of sufficient time.
3. The stress-strain relationship is linear.

The only difference between the perfectly elastic and anelastic materials is thus the requirement of time lapse until the attainment of equilibrium. How quickly and following what functional form that equilibrium is attained is inconsequential for the classification.

Since there are two quantities, stress and strain, an experimenter may choose to suddenly change one and monitor the evolution of the other toward a new steady-state equilibrium. Both types of experiments can be done. Both types of experiment yield the same types of information. We will, therefore, only discuss one possibility in the interest of space.

### 2.2.2 Creep Function

In one type of experiment, the experimenter abruptly applies a stress $\sigma_0$ to the sample at $t = 0$ and monitors the change of $u(t)$ as a function of time:

$$\sigma = \begin{cases} 0, & t < 0. \\ \sigma_0, & t \geq 0. \end{cases} \quad (2.4)$$

The requirement of linearity in the definition dictates that the ratio $u(t)/\sigma_0$ be a function independent of the value $\sigma_0$ chosen by the experimenter. One may thus define this ratio as the creep function:

$$J(t) \equiv \frac{u(t)}{\sigma_0}, \quad t \geq 0 \quad (2.5)$$
In realistic samples, the creep function starts at a value \( J(0) \equiv J_U \) called unrelaxed compliance to increase asymptotically toward a value \( J(\infty) \equiv J_R \) called relaxed compliance. The difference between the two extrema, \( [\delta J](t) \equiv J_R - J_U \), is called relaxation of the compliance. We therefore also have the following relation:

\[
J(t) = J_u + [\delta J](t) \tag{2.6}
\]

In case a series of stresses \( \sigma_i (i = 1, 2, ..., m) \) were applied at increasing times \( t_1, t_2, ..., t_m \), the total response of the strain can be written as a linear combination owing to the requirement of linearity in the strain response.

\[
u(t) = \sum_{i=1}^{m} \sigma_i J(t - t_i) \tag{2.7}
\]

### 2.2.3 Energy Dissipation Due to Quasi-Static Creep

The definitions and properties introduced so far are sufficient for an illustration of why mechanical energy is lost to heat when deformation lags behind the excitation force. We consider the experiment modeled in Equation 2.8 and Fig. 2-1.

\[
\sigma(t) = \begin{cases} 
0, & t \leq 0, \\
\frac{\sigma_0 t}{\delta t}, & t \in [0, \delta t], \delta t \ll \tau_\sigma, \\
\sigma_0, & t \in [\delta t, t'], \tau_\sigma \ll t', \\
-\sigma_0 \frac{t'}{\delta t} + \sigma_0 \frac{t' + \delta t}{\delta t}, & t \in [t', t' + \delta t], \\
0, & t > t' + \delta t.
\end{cases} \tag{2.8}
\]

In words, we apply stress \( \sigma_0 \) to the sample at \( t = 0 \), wait for a sufficiently longtime for the sample to reach equilibrium, and then remove the stress. Under realistic experimental setting, it always takes some time to apply and to remove the stress. We call this time \( \delta t \). We want to analyze the net work done during this sequence.

The experiment can be analyzed in four phases (Fig. 2-1). In the first phase starting at \( t = 0 \), stress increases from 0 to \( \sigma_0 \) within infinitesimal time \( \delta t \). The
strain instantaneously responds by increasing from 0 to \( J_u \sigma_0 \). During the second phase, strain relaxes via \([\delta J](t)\) while stress is held constant. In the third phase, stress decreases to 0, again within infinitesimal time \( \delta t \). The change is equivalent to having a stress \(-\sigma_0\) switched on after a sufficiently long time for the relaxation in phase 2 to reach equilibrium. At the end of the third phase, the strain has decreased to a value corresponding to the relaxation of the compliance accumulated during the second phase. In the final phase, any residual strain relaxes back toward 0 in the absence of stress.

The work, per unit volume (stress has units of pressure and strain is unitless), done on the sample in phase 1 is:
Using Equations 2.5-2.6, the work, per unit volume, done on the sample in phase 2 is:

\[
W_2 = \int_{u(\delta t)}^{u(t')} \sigma_0 du = \int_{\delta t}^{t'} \sigma_0^2 \frac{d[\delta J](t)}{dt} dt = ([\delta J](t \gg \tau_\sigma) - [\delta J](t \ll \tau_\sigma)) \sigma_0^2 \approx [\delta J](\infty) \sigma_0^2
\]  (2.10)

To find the work, per unit volume, done on the sample in phase 3, we need to invoke Equation 2.7, since there are now two instants in the history of the sample when stresses have been applied. We use the notation \(t_\infty \equiv t - t'\) to denote the length of time elapsed after the start of ramp down of the stress from \(\sigma_0\) toward 0. The strain as a function of this referenced time is therefore \(u(t_\infty) = \sigma_0 [J_U + \delta J(\infty)] + \sigma(t_\infty) [J_U + \delta J(0)]\). Argument for the \([\delta J](t)\) function in the second term is 0 because the stress has not reached the target value and the relaxation segment has not started \((\delta t \ll \tau_\sigma)\). \(\sigma(t_\infty)\) decreases from 0 to \(-\sigma_0\) between \(t_\infty = 0\) and \(t_\infty = \delta t\). Notice that relative changes of stress are used in the calculation of \(u(t)\) due to the linearity of its effect.

\[
W_3 = \int_{u(t_\infty=0)}^{u(t_\infty=\delta t)} \sigma_0 du = \int_{\sigma_0+\sigma(t_\infty=0)}^{\sigma_0+\sigma(t_\infty=\delta t)} J_U \sigma d\sigma = \int_{\sigma_0}^{0} J_U \sigma d\sigma = -\frac{1}{2} J_U \sigma_0^2
\]  (2.11)

Finally, there is no work done during the final phase when strain relaxes in the absence of net stress \((W_4=0)\). Adding work per volume from the four phases of the experiment, we obtain a net expenditure of \(W_2 = [\delta J](\infty) \sigma_0^2\), corresponding to work done during the relaxation of the sample.

### 2.2.4 Energy Dissipation during Dynamic Operation

The example in the previous subsection illustrates how energy could be lost when sample relaxes when stress is kept constant except for quasi-discrete jumps. In the
normal functioning of mechanical resonators, stress and strain are both constantly changing in time. We illustrate energy dissipation in the prototypical case when both follow sinusoidal time dependence with a relative phase lag. Let the time dependence be written as

\[ \sigma(t) = \sigma_0 e^{i\omega t} \]  \hspace{1cm} (2.12)

\[ u(t) = u_0 e^{i(\omega t - \phi)} \]  \hspace{1cm} (2.13)

In analogy with Equation 2.5, we define complex compliance as

\[ J^*(\omega) \equiv u/\sigma = |J|\omega e^{-i\phi} = J_1(\omega) - iJ_2(\omega) \]  \hspace{1cm} (2.14)

where \(|J|_{\omega} = u_0/\sigma_0\) is called the absolute dynamic compliance.

Let us now calculate the energy, per volume, that is lost from the vibrating material over a complete cycle of vibration. We analyze the problem from the perspective of the stress, as if it were an agent actively performing work on the oscillator. We will choose origin of time such that stress is real: \(\sigma(t) = \sigma_0 \cos \omega t\). The corresponding, real part of strain would be \(u(t) = -u_0 \cos(\omega t + \phi)\). Notice that the negative sign is in keeping with taking the perspective of the stress, which opposes deformation in accordance with Hooke’s law.

With this convention of perspective, the work per volume done by stress during infinitesimal deformation \(du\) is \(\sigma du\). Over a complete cycle of vibration, the stress would have performed the following work per unit volume
\[ W_{cycle} = \oint \sigma du \]
\[ = -\sigma_0 u_0 \int_{0}^{2\pi} \omega \cos \omega t [\cos \phi \sin \omega t - \sin \phi \cos \omega t] dt \]
\[ = \sigma_0 u_0 \omega \int_{0}^{2\pi} \sin \phi \cos^2 \omega t dt \]
\[ = \pi \sigma_0 u_0 \sin \phi \]
\[ = \pi J_2 \sigma_0^2 \tag{2.15} \]

where we have invoked Equation 2.14 in the last step. It is therefore clear that a net work proportional to \(J_2\) and the square of the maximum stress has to be expended every cycle in order to sustain the oscillation at the same amplitude. This work is equal to the dissipation of mechanical energy over the same period of time: \(\Delta W = W_{cycle}\).

With a similar calculation, it can be shown that the amount of stored mechanical energy in an oscillator is \(W = \frac{1}{2} J_1 \sigma_0^2\). The integration required is over quarter of a cycle, from the moment of no potential energy to the moment of maximum potential energy, for instance. We therefore have the important relation

\[ \Delta W/W = 2\pi (J_2 / J_1) = 2\pi \tan \phi \tag{2.16} \]

From the structure of the expression, it is clear that \(J_1\) corresponds to the amount of energy stored in the system and \(J_2\), the amount lost per cycle of vibration. They are thus respectively called storage compliance and loss compliance. For all cantilever material suitable for force and mass sensing applications, \(J_2 \ll J_1\), and \(\tan \phi \approx \phi\). This enables the following definition for the mechanical quality factor \(Q\) as a function of loss angle \(\phi\):

\[ Q \equiv \phi^{-1} = 2\pi \frac{W}{\Delta W} \tag{2.17} \]
2.2.5 Dissipation Term $\propto$ Velocity from Anelastic Properties

In this subsection, we return to the question posed in the chapter introduction: “Why do mechanical harmonic resonators experience a damping force proportional to its instantaneous velocity?” We show that a term proportional to the first derivative of position follows naturally from the dynamic response of an anelastic solid. We write down the equation of motion of a volume element within an anelastic material that freely oscillates at its natural frequency, determined by the complex spring constant $k^* = k_1 + i k_2 \propto \frac{J_1}{|J|^2} + i \frac{J_2}{|J|^2}$ and the effective mass $m$.

\begin{align*}
\ddot{m}x &= -F_o \\
\ddot{m}x &= -k^* x = -(k_1 + i k_2)x
\end{align*}

(2.18) 
(2.19)

Moving all terms to the same side and recognizing that $i \omega x = \dot{x}$, we obtain

\[ m\ddot{x} + \frac{k_2}{\omega} \dot{x} + k_1 x = 0 \]  

(2.20)

From the definition of $k^*$ and Equations 2.16-2.17, we recognize the coefficient of the $\dot{x}$ term to be $\frac{\sqrt{mk_1}}{Q} \equiv \Gamma$. $\Gamma$ is the mechanical dissipation in units of kg/second. It is the parameter that directly determines the sensitivity of mechanical sensors.

We have thus shown that a dissipation term proportional to oscillator velocity follows naturally from the behavior of anelastic materials. We have so far regarded the occurrence of an imaginary component in the compliance and modulus as part of the definition. In sections 2.4 and 2.5, we illustrate a couple of underlying physical mechanisms that cause this type of phase lag.

2.2.6 The Standard Anelastic Solid

Equation 2.20 is analogous to:
\[ \sigma = Au + B \dot{u} \]  

(2.21)

where \( A \) and \( B \) are constants. This asymmetric form cannot be describing an anelastic solid for all situations. Suppose that in a certain experiment, an initially unstressed material were suddenly compressed to a strain of \( u_0 \) at \( t = 0 \), and held at constant strain for \( t > 0 \). Then the derivative term would vanish and we would be left with \( \sigma(t) = Au_0 \). This result violates the second condition in the definition of an anelastic material, that a finite period of time is needed for the attainment of equilibrium between strain and stress. We are therefore missing a term proportional to \( \dot{\sigma} \) that takes stress relaxation into account. Therefore, the simplest equation that captures the definition of an anelastic solid is the following equation:

\[ \sigma + C \dot{\sigma} = Au + B \dot{u} \]  

(2.22)

that can be written in an equivalent form:

\[ J_R \sigma + \tau_\sigma J_U \dot{\sigma} = u + \tau_\sigma \dot{u} \]  

(2.23)

where \( \tau_\sigma \) was introduced in Fig. 2-1. The choices of the constants in 2.23 would become clear after solving it under the action of the stress in Equation 2.4. The result shows that strain relaxes exponentially:

\[ \frac{u(t)}{\sigma_0} = J_R - (J_R - J_U) e^{-\frac{t}{\tau_\sigma}} \]  

(2.24)

\[ = J_R - J_\delta e^{-\frac{t}{\tau_\sigma}} \]  

(2.25)

\[ = J_U + J_\delta \left[ 1 - e^{-\frac{t}{\tau_\sigma}} \right] \]  

(2.26)

The dynamic behavior of the stress-strain relationship described by Equation 2.23
is highly important. It can be derived by substituting Equations 2.12-2.14 into 2.23. Separately equating the real and the imaginary parts of the resulting equation, we have the following:

\[ J_R = J_1 + \omega \tau_\sigma J_2 \quad (2.27) \]
\[ \omega \tau_\sigma J_U = \omega \tau_\sigma J_1 - J_2 \quad (2.28) \]

\( J_1 \) and \( J_2 \) can be solved to give, as functions of frequency,

\[ J_1(\omega) = J_U + \frac{\delta J}{(1 + \omega^2 \tau_\sigma^2)} \quad (2.29) \]
\[ J_2(\omega) = \delta J \frac{\omega \tau_\sigma}{1 + \omega^2 \tau_\sigma^2} \quad (2.30) \]

When dissipation is small, \( Q^{-1} \) can now be calculated by inserting the above expressions for \( J_1 \) and \( J_2 \) into Equation 2.16.

\[ Q^{-1} \approx \tan \phi = \frac{\delta J}{J_U} \frac{\omega \tau_\sigma}{(1 + \omega^2 \tau_\sigma^2)} \]
\[ = \frac{\omega \tau_\sigma \Delta}{(1 + \Delta + \omega^2 \tau_\sigma^2)} \approx \Delta \frac{\omega \tau_\sigma}{(1 + \omega^2 \tau_\sigma^2)} \quad (2.31) \]
\[ \approx \Delta \quad (2.32) \]

where \( \Delta \equiv \frac{\delta J}{J_U} \ll 1 \) in all devices of interest for ultrasensitive measurements. The form of Equation 2.32 is important and common to all dissipation mechanisms involving relaxation processes. An example involving thermal relaxation is discussed in Section 2.4.

2.2.7 The Debye Peak

A plot of Equation 2.32 as a function of frequency would reveal a peak in dissipation centered at \( \omega = \tau_\sigma^{-1} \). Peaks of this type are known as a Debye peak. To test whether
a type of oscillator is limited by a relaxation process with time constant $\tau_\sigma$ would require the fabrication of devices that span a wide range of frequencies, at least over a couple of orders of magnitude, in order for the peak structure to be measured. This type of experiment is often difficult to conduct due to the large numbers of devices that are needed.

When the particular dissipation process is temperature activated, an alternative approach would be to measure the dissipation as a function of temperature. Assuming that new types of relaxation processes do not enter in the screened temperature range, observation of dissipation peaks as a function of temperature is an experimentally much easier way to track down a relaxation process.

The success of the temperature scan method is predicated on the assumption that the relaxation rate follows the Arrhenius equation

$$\tau^{-1} = \tau_0^{-1} e^{-E_a/k_B T}$$

(2.33)

where $E_a$ is the activation energy for the process and $k_B T$ is the thermal energy. It is important to note that relaxation processes for which the relaxation rate does not follow the Arrhenius equation are not in general suitable for analysis by scanning temperature.

### 2.3 Additive Nature of Mechanical Dissipation

As mentioned in Section 2.1, many microscopic processes may contribute to the loss of energy from a mechanical system. Under most circumstances relevant to common experimental systems, $Q > 100$ so that the loss angles of all involved dissipation channels are small. This means that from one period of oscillation to the next, the resonator does not undergo any significant change in its trajectory and the stored energy stays roughly constant over the time scale of an oscillation period. Since the common loss mechanisms are functions of the resonator motion, each of $n$ loss
mechanisms thus acts independently of the others to channel an amount of energy $\Delta W_i$ out of the mechanical mode. Together, they cause a total loss of energy in the amount of $\sum_i \Delta W_i$ during each period. Inserting this sum into Equation 2.17 and taking the reciprocal, we have

$$Q^{-1} = \frac{\sum_i \Delta W_i}{2\pi W} \tag{2.34}$$

Therefore, mechanical dissipation is additive and, in most cases, one or two mechanisms dominate the overall dissipation behavior. A key to engineering better mechanical resonators for a specific application therefore lies in identifying the dominant loss channel under the conditions of the application. In the case of micro- and nanomechanical resonators, the overall dissipation can be decomposed in the following way:

$$Q^{-1} = Q_{\text{Bulk}}^{-1} + Q_{\text{Surface}}^{-1} + Q_{\text{Design}}^{-1} + Q_{\text{Interaction}}^{-1} \tag{2.35}$$

$$Q^{-1} = \frac{\sum_i \Delta W_i}{2\pi W} \tag{2.36}$$

Here, $Q_{\text{Bulk}}^{-1}$ refers to intrinsic loss mechanisms that results from anelastic deformation of the material. $Q_{\text{Surface}}^{-1}$ results from anelastic processes in the surface layer of the mechanical resonator. $Q_{\text{Design}}^{-1}$ result from inadequate geometric design, such as clamping losses. $Q_{\text{Interaction}}^{-1}$ refer to processes involving the coupling between mechanical deformation and some field emanating from a separate piece of material or devices. This includes interactions with a probing optical, electric, or magnetic fields necessary for motional readout. Non-contact friction described in Chapter 10 is another example of energy loss due to such long-range interactions.

Which of the four pathways in Equation 2.36 dominates can be determined by analyzing the dependence of $Q$ on resonator geometry and other design parameters. A complete independence of $Q$ on geometry, for example, would point towards $Q_{\text{Bulk}}^{-1}$ and possibly $Q_{\text{Interaction}}^{-1}$ (if the expected interaction is an intensive process) as the
culprit. Each of these four categories of losses can be further divided. For example,

\[ Q_{\text{Bulk}}^{-1} = Q_{\text{TED}}^{-1} + Q_{\text{Phonon-Phonon}}^{-1} + Q_{\text{Phonon-Electron}}^{-1} + Q_{\text{Bulk-TLS}}^{-1} + Q_{\text{Bulk-Others}}^{-1} \]  \hspace{1cm} (2.37)

It is usually difficult to pin-point the exact microscopic mechanism without extensive experimentation. In the remaining sections of this chapter, we analyze a couple of common microscopic mechanisms as illustrations of the complexity of the problem.

### 2.4 Thermoelastic Damping

As a cantilever vibrates in a flexural mode, the upper and lower halves of the device separated by the central, stress-free neutral plane undergo periodic compression and dilation, respectively. Due to finite thermal expansion coefficients in real solids, such perfectly out-of-sync deformation may create a temperature gradient along the direction of flexure (usually thickness) if thermal relaxation time were significantly long compared to the oscillation period. In the presence of a temperature gradient, the system can no longer be at equilibrium and thermal relaxation can take place. This in turn leads to a change in strain, or creep. Therefore, thermal expansion couples mechanical deformation to temperature, an internal variable of the material. Together, they provide a mechanism for the onset of anelasticity.

This mechanism of the conversion of mechanical energy to thermal energy is called thermoelastic damping. The theory was developed by Zener and has been applied successfully to explain experimentally observed limits in quality factors in certain frequency ranges in silicon and silicon nitride cantilevers. We will follow Zener’s original papers [89,90], with changes in notation, in the following summary.
2.4.1 Derivation of Thermoelastic Dissipation in the Flexural Cantilever

The goal in this subsection is to derive an expression similar to Equation 2.32, where the quality factor, instead of being a function of a generic, phenomenological relaxation strength, $\Delta$, will be expressed as a function of cantilever geometry, material properties, and the bath temperature. To that end, we start by calculating the energy lost per cycle of vibration as previously done for the generic case in Equation 2.15.

We consider a cantilever with its axis lying parallel to the $x$-axis and face perpendicular to the $z$-axis. We consider flexural motion in the $x$-$z$ plane. The dominant deformation as the beam oscillates is therefore compression and extension along the $x$-axis. We consider strains and stresses acting in $y$ and $z$ directions (finite Poisson
ratio) as small linear corrections and ignore them in the following analysis. Variables are taken with respect to the equilibrium values in the absence of deformation. We write stress as a function of strain and temperature changes relative to those in the relaxed equilibrium state:

\[
\sigma_{xk} = \left( \frac{\partial \sigma_{xk}}{\partial u_{xx}} \right)_T u_{xx} + \left( \frac{\partial \sigma_{xk}}{\partial T} \right)_{u_{xx}} \Delta T \tag{2.38}
\]

To obtained the energy lost per oscillation period and per length, we substitute Equation 2.38 into the starting line of Equation 2.15 and integrate over the cross sectional area \( A \):

\[
\Delta W = \int_A \, da \oint \sigma_{xk} du_{xx} 
\]

\[
= \int_A \, da \oint \left[ \left( \frac{\partial \sigma_{xk}}{\partial u_{xx}} \right)_T u_{xx} + \left( \frac{\partial \sigma_{xk}}{\partial T} \right)_{u_{xx}} \Delta T \right] du_{xx} \tag{2.39}
\]

\[
= \int_A \, da \oint \left( \frac{\partial \sigma_{xk}}{\partial T} \right)_{u_{xx}} \Delta T du_{xx} \tag{2.40}
\]

\[
= \left( \frac{\partial \sigma_{xk}}{\partial T} \right)_{u_{xx}} \int_A \, da \oint \Delta T du_{xx} \tag{2.41}
\]

\[
= \left( \frac{\partial \sigma_{xk}}{\partial T} \right)_{u_{xx}} \int_A \, da \int_0^{\frac{2\pi}{\omega}} \Delta T \frac{\partial u_{xx}}{\partial t} dt \tag{2.42}
\]

Between the second and third lines, we dropped the first term using the fact that \( u_{xx} \) is periodic. To proceed further, we need to determine the time and spatial dependences of the integrand. The types of cantilevers we are interested in are harmonic resonators. Strain therefore varies sinusoidally with time. In the steady state of oscillation, temperature must also follow the same functional form with a phase lag. We express strain and temperature change as products of spatially-dependent and time-dependent parts. We choose the spatial part of \( u_{xx} \) to be real and absorb the phase
lag in $\Delta T$ into its, thus complex, spatial component: $\Delta T^*(r) = \Delta T_1(r) + i\Delta T_2(r)$.

$$u_{xx}(r, t) = \text{Re}\{u(r)e^{i\omega t}\} \quad (2.44)$$

$$\Delta T(r, t) = \text{Re}\{\Delta T^*(r)e^{i\omega t}\} \quad (2.45)$$

Using these expressions, we calculate the time integral over one period of oscillation.

$$\int_0^{2\pi \over \omega} dt \frac{\partial u_{xx}}{\partial t} \Delta T = \int_0^{2\pi \over \omega} dt \text{Re}\{i\omega u(r)e^{i\omega t}\} \text{Re}\{\Delta T^*(r)e^{i\omega t}\}$$

$$= \int_0^{2\pi \over \omega} dt [-\omega u(r) \sin \omega t] [\Delta T_1(r) \cos \omega t - \Delta T_2(r) \sin \omega t] \quad (2.46)$$

$$= \pi \Delta T_2(r) u(r)$$

This result allows the simplification of $\Delta W$ into an integral over spatial coordinates.

$$\Delta W = \pi \left( \frac{\partial \sigma_{xk}}{\partial T} \right)_{u_{xx}} \int_A da \Delta T_2(r) u(r) \quad (2.47)$$

$u(r)$ is set by the cantilever oscillation mode shape. We will see that the exact form of the mode shape is inconsequential for the form of the dissipation; it only amounts to minor changes of a multiplicative constant. The complex component of the temperature change can be determined if we can find an expression for $\Delta T^*(r)$. Temperature at any point in the material changes via two mechanisms. It can equilibrate with its surrounding as a result of thermal diffusion (with diffusion constant $D$) and it can change as a result of adiabatic strain oscillations (at constant heat). The analysis therefore requires considering the time-dependent transport of heat. We have

$$\frac{\partial \Delta T(r, t)}{\partial t} = D\nabla^2 \Delta T(r, t) + \left( \frac{\partial T}{\partial u_{xx}} \right)_Q \frac{\partial u_{xx}(r, t)}{\partial t} \quad (2.48)$$

Substituting in Equations 2.44-2.45 to again eliminate the time dependence, we have
\[ [D \nabla^2 - i\omega] \Delta T^*(r) + i\omega \left( \frac{\partial T}{\partial u_{xx}} \right)_Q u(r) = 0 \] \hspace{1cm} (2.49)

Temperature as a function of position inside the cantilever can be expanded in any orthonormal basis in which every vector satisfies the same boundary condition as \( \Delta T^*(r) \), namely that gradients of \( T^*(r) \) at the top and bottom cantilever surfaces are zero. Such a basis exists. An example is the basis \( \{ \sin \left( \frac{2n+1}{t} \pi t z \right) : n \in \mathbb{N} \} \), where \( t \) is the thickness of the cantilever and \( z \) is the vertical distance along flexural direction of the volume element measured from the neutral plane. Any other complete basis can also be used, and we choose the set \( \{ v_k : n \in \mathbb{N} \} \) that satisfies the following condition to simplify further calculations.

\[ [D \nabla^2 + \omega_k] v_k = 0 \] \hspace{1cm} (2.50)

where \( \omega_k \) are values to be determined. \( \Delta T^*(r) \) is now expanded as

\[ \Delta T^*(r) = \sum_i b_i v_i \] \hspace{1cm} (2.51)

Substituting this expression into Equation 2.49, multiplying from the left by \( v_k \) and integrating over the cross sectional area, we have, after simplification using Equation 2.50 and rearrangement,

\[ b_k = \left( \frac{\partial T}{\partial u_{xx}} \right)_Q \frac{i\omega \int_A v_k u(r) da}{\omega_k + i\omega} \equiv \left( \frac{\partial T}{\partial u_{xx}} \right)_Q \frac{i\omega}{\omega_k + i\omega} U_k \] \hspace{1cm} (2.52)

Remember from Equation 2.47 that we need the imaginary component \( \Delta T_2(r) \) of \( \Delta T^*(r) \). We arrive at an important intermediate result.
\[
\Delta W = \pi \left( \frac{\partial \sigma_{xk}}{\partial T} \right)_{u_{xx}} \left( \frac{\partial T}{\partial u_{xx}} \right) Q \int_A da \sum_k \left( \frac{\omega_k \omega}{\omega_k^2 + \omega^2} \right) U_k v_k(r)
\]

\[
= \pi \left( \frac{\partial \sigma_{xk}}{\partial T} \right)_{u_{xx}} \left( \frac{\partial T}{\partial u_{xx}} \right) Q \sum_k \left( \frac{\omega_k \omega}{\omega_k^2 + \omega^2} \right) U_k^2
\]

(2.53)

\(Q^{-1}\) of the vibrating beam, in case thermoelastic damping were dominant, can now be calculated according to Equation 2.17 and 2.53. We also use the fact that the total mechanical energy per length stored in the beam is

\[
W = \frac{1}{2} E \int_A u(r)^2 da \equiv \frac{1}{2} EU^2.
\]

\[
Q^{-1} = \frac{1}{E} \left( \frac{\partial \sigma_{xk}}{\partial T} \right)_{u_{xx}} \left( \frac{\partial T}{\partial u_{xx}} \right) Q \sum_k \frac{U_k^2}{U^2} \left( \frac{\omega_k \omega}{\omega_k^2 + \omega^2} \right)
\]

(2.54)

The modulus \(E\) here depends on the frequency of vibration relative to thermal relaxation. For slow vibrations, it is the isothermal modulus. For fast vibrations, it is adiabatic. Since the two values are very close to each other in most materials, errors less than the order of a percent is made in using either [90]. We simplify the coefficients in front of the summation by using the adiabatic modulus:

\[
\frac{1}{E} \left( \frac{\partial \sigma_{xk}}{\partial T} \right)_{u_{xx}} \left( \frac{\partial T}{\partial u_{xx}} \right) Q \left( \frac{\partial u_{xx}}{\partial \sigma_{xk}} \right) Q \left( \frac{\partial \sigma_{xk}}{\partial T} \right)_{u_{xx}} \left( \frac{\partial T}{\partial u_{xx}} \right) Q \left( \frac{\partial \sigma_{xk}}{\partial S} \right)_{\sigma_{xk}} \left( \frac{\partial S}{\partial T} \right)_{\sigma_{xk}} \left( \frac{\partial u_{xx}}{\partial T} \right)_{\sigma_{xk}} \left( \frac{\partial \sigma_{xk}}{\partial u_{xx}} \right) T
\]

(2.55)

\[
= T \alpha^2 \frac{E T}{C_p}
\]

where \(\alpha\) is the thermal expansion coefficient, \(T\) is the temperature, and \(C_p\) is the heat capacity at constant pressure. Zener showed that for simple cross-sectional areas like a rectangle and a circle, \(U_0\) accounts for greater than 98% of the weights of coefficients.
$U_k$ in Equation 2.54. To a very good approximation, we have

$$Q^{-1} = \frac{T \alpha^2 E_T}{C_p} \left( \frac{\omega_0 \omega}{\omega_0^2 + \omega^2} \right)$$

(2.56)

The functional form of this last result is the same as that derived for the standard anelastic solid (Equation 2.32), as it should be for a dissipation process involving a relaxation process. The characteristic frequency $\omega_0$ can be expressed as a function of material properties and cantilever thickness, $t$, as \[90,101\]

$$\omega_0 = \frac{\pi^2 K}{\rho C_p t^2}$$

(2.57)

where $K$ is the thermal conductivity and $\rho$ is the density.

A similar mechanism involving the relaxation of phonon population distribution during oscillation of materials has been analyzed by Boemmel and Dransfeld [92].

### 2.4.2 Relevance of Thermoelastic Damping for Ultrathin Si Cantilevers

The preceding section provided a detailed discussion of a model that has found quantitative agreement with experiments using microcantilevers [13,101]. That the $Q$’s in some microcantilevers are limited by this mechanism is due to the matching (or cross over) between the cantilever mechanical frequency and the inverse of the characteristic thermal relaxation time. The former increases with cantilever thickness ($\propto t$) whereas the latter decreases with cantilever thickness ($\propto t^{-2}$). When devices with lengths in the tens to hundreds of microns have their thicknesses decreased to the 100 nm range and below, mismatch between the mechanical frequency and the inverse thermal relaxation time means that a temperature gradient between the two sides of the cantilever beam can no longer be sustained and that the device operates under isothermal conditions. Using material constants for silicon [13] and Equation 2.57,
one can verify that for a silicon device with thickness below 300 nm, the frequency of oscillation need to be in the GHz range and above in order to match the thermal relaxation frequency. We can therefore safely conclude that this mechanism is not the dominant source of dissipation for kHz devices with thicknesses around 100 nm. Thermoelastic damping is therefore negligible for ultra-sensitive force detection using low-spring constant nanomechanical resonators [35, 69] operating at cryogenic temperatures (Equation 2.56).

In thin devices useful for MRFM operating at low temperatures, other intrinsic dissipation pathways can arise. These dissipation channels are likely mediated by structural defects in the cantilever materials. Possible candidates include lattice impurities, vacancies, and surface transition layers. Regardless of the identity of the defect mediating dissipation, a common denominator between these defect-mediated dissipation channels is the fact that a varying strain field disrupts the original equilibrium distribution of atomic positions. The process of phase-lagged return back to equilibrium gives rise to anelasticity and relaxation. In Chapter 7, data suggest that diamond devices are limited by substitutional impurities like nitrogen dopants. After an exposition of the theory of the so-call two-level systems (TLS), we discuss the relevance of these defects for thin silicon devices with the aid of variable-temperature data collected on silicon cantilevers with chemically defined surfaces. A more thorough exposition of silicon surface chemistry, device processing, and measurements are given in Chapters 4, 5 and Appendices A and B.

### 2.5 Two Level Systems

In the following subsection, we provide a derivation of the quantum tunneling mechanism. Specifically, we show how relaxation via tunneling of TLS can lead to energy dissipation. We follow a derivation provided in a review by Hunklinger and Arnold [98].
2.5.1 Dissipation in Tunneling Two-Level Systems

A tunneling defect in an amorphous material consists of a single or a group of atoms that can move collectively to access two configurational local minima in energy. In the case of native oxide on silicon surface, this could be, for example, the rotation of a silanol group to hydrogen bond with either one of two sets of hydrogen bond donors/acceptors in its vicinity. In the stress-free crystal in the motional ground state, we call the energy splitting between these minima $\Delta$. In addition, due to the finite barrier height, the defect continuously tunnels between the localized states of the two energy minima. This mixing is phenomenologically described by an off-diagonal term $\delta$. The magnitude of $\delta$ decreases exponentially with the height of the barrier and with the physical distance between the two configurational minima. In the real-space basis (RSB) corresponding to the defect existing in one or the other local minimum, we have the following Hamiltonian:

$$
\hat{H}_{0_{\text{RSB}}} = \frac{1}{2} \begin{pmatrix}
\Delta & -\delta \\
-\delta & -\Delta
\end{pmatrix}
$$

(2.58)

The localized states are clearly not the eigenstates of this unperturbed Hamiltonian. The eigenstates in the absence of disturbance by phonons have energies $U_{\pm} = \pm \sqrt{\Delta^2 + \delta^2}$, where $U_{\pm} - U_{\mp} = U$ is the energy splitting. Moving forward, we will work in the basis spanned by the eigenstates of Hamiltonian 2.58. We therefore have

$$
\hat{H}_0 = \begin{pmatrix}
U_+ & 0 \\
0 & U_-
\end{pmatrix} = \frac{1}{2} \begin{pmatrix}
U & 0 \\
0 & -U
\end{pmatrix}
$$

(2.59)

When the mechanical oscillator vibrates, the motion sets up periodic strain waves through the material. The strain modulates the energy splitting $U$ via its intermediate effect on $\Delta$ and $\delta$. We assume that for small oscillation amplitudes, such modulations occur proportionally to the strain. When this is satisfied, the energies of
the eigenstates of the unperturbed Hamiltonian are changed with a proportionality constant called \textit{deformation potential}: \( D \equiv \frac{2\Delta}{U} \frac{\partial \Delta}{\partial u} + \frac{2\delta \partial \delta}{U \partial u} \). Generally, the strain field is unlikely to preserve the original eigenstates. We therefore also have terms off-diagonal in the perturbation:

\[
\hat{H}' = \frac{1}{2} \begin{pmatrix} D & 2M \\ 2M & -D \end{pmatrix} u
\] (2.60)

It was realized that the form of the Hamiltonian for this two-level system problem can be mapped onto that for the spin-$\frac{1}{2}$ particle in a static magnetic field with a small sinusoidal perturbation. The same techniques can therefore be used for its analysis. The equivalent magnetic fields are

\[
\vec{B}_0 = \left( 0, 0, \frac{-U}{\hbar \gamma} \right)
\]

\[
\vec{B}'(t) = \left( -\frac{2M}{\hbar \gamma}, 0, -\frac{D}{\hbar \gamma} \right) u(t)
\] (2.61)

To find how TLS dynamics contribute to the imaginary part of the elastic constant, we first would like to express the contribution of TLS’s to the elastic constant, \( \delta E \). From Equation 2.3, we have

\[
\delta E = \frac{\delta \sigma}{u} = \frac{1}{u} \frac{\partial U_{\text{TLS}}}{\partial u}
\] (2.62)

where \( U_{\text{TLS}} \) is the energy content of the the ensemble of TLS’s per unit volume. Within the spin analogy, this quantity can be calculated as
\[ U_{\text{TLS}} = -\bar{\mu}_v \cdot \vec{B}' \]
\[ = -N_v \langle \mu \rangle \cdot \vec{B}' \]
\[ = -N_v \gamma h \langle \vec{S} \rangle \cdot \vec{B}' \]
\[ = N_v [2M \langle S_x \rangle + D \langle S_z \rangle] u(t) \] (2.63)

where subscript \( v \) denotes density of TLS’s per volume. To get an expression without spin-related quantities, we express angular momentum as the product between a susceptibility and the field energy.

\[ S_i(t) = \mathcal{X}_i(\omega) h \gamma B'_i(t) \] (2.64)

Substituting Equations 2.63 and 2.64 into Equation 2.62, we have

\[ \delta E(\omega) = -2N_v [4M^2 \mathcal{X}_x(\omega) + D^2 \mathcal{X}_z(\omega)] \] (2.65)

We know from previous sections that the mechanical dissipation will be proportional to the imaginary components of the susceptibilities above. We proceed to calculate the susceptibilities in the following. We will only calculate in detail the susceptibility for \( z \)-polarization, corresponding to loss by relaxation rather than by resonance.

We denote longitudinal and transverse relaxation times by \( \tau_1 \) and \( \tau_2 \). The Bloch equations read

\[
\begin{align*}
\frac{d}{dt} \langle S_x(t) \rangle - \gamma [\langle S_y \rangle B_z - \langle S_z \rangle B_y] + \tau_2^{-1} \langle S_x \rangle &= 0 \\
\frac{d}{dt} \langle S_y(t) \rangle - \gamma [\langle S_z \rangle B_z - \langle S_x \rangle B_z] + \tau_2^{-1} \langle S_y \rangle &= 0 \\
\frac{d}{dt} \langle S_z(t) \rangle - \gamma [\langle S_x \rangle B_y - \langle S_y \rangle B_x] + \tau_1^{-1} \langle S_y \rangle &= \frac{S^\text{Eq}_z[B_z(t)]}{\tau_1}
\end{align*}
\] (2.66)
where $S^\text{Eq}_z[B_z(t)]$ denotes the equilibrium $z$ polarization toward which the actual polarization would decay if $B'_z(t)$ were suddenly set to zero at time $t$. From the Boltzmann distribution, the equilibrium polarization for the instantaneous field strength $B_z(t)$ can be written as

$$S^\text{Eq}_z[B_z(t)] = \frac{1}{2} \tanh \left[ \frac{\hbar \gamma B_z(t)}{2 k_B T} \right] \approx S^0_z(B_0) + B'_z \frac{dS^0_z}{dB_0} \quad (2.67)$$

where $S^0_z(B_0)$ is the equilibrium polarization of the TLS’s in the absence of strain in the crystal.

We model the perturbing field in the usual way as

$$\vec{B}'(t) = 2 \vec{B}' \cos \omega t = \vec{B}' (e^{i\omega t} + e^{-i\omega t}) \quad (2.68)$$

where we have chosen to use the half-amplitude, $\vec{B}'$, in order to simplify notation in subsequent calculations involving multiplications of the complex exponential functions.

We assume that at steady state, the responses of the polarization vectors consist only of the DC component along $z$ and a component at the same frequency as the perturbation field. We therefore ignore higher-frequency components and use the following ansatz:

$$\langle \vec{S}(t) \rangle = S^0_z + \vec{S}_1 (e^{i\omega t} + e^{-i\omega t}) \quad (2.69)$$

To facilitate further calculation, however, it is useful to include all frequency multiples in the expansion

$$\langle \vec{S}(t) \rangle = S^0_z + \sum_{m=-\infty}^{m=+\infty} \vec{S}_m e^{-i m \omega t} \quad (2.70)$$
We use $S_{\pm} = S_{x} \pm iS_{y}$ to combine the $x$ and $y$ components of the Block equation into one equation to simplify writing. We substitute Equations 2.68 and 2.70 into the simplified Block equation to obtain, after singling out frequency components $m\omega$,

\[(m\omega \pm \omega_0 + \tau_2 m^{-1})S_{\pm,m} = \pm \gamma B'_{z}(S_{\pm,m} + 1 + S_{\pm,m-1}) \mp \gamma B'_{x}s_{z}^{0} \delta_{m,\pm 1} + (S_{z,m+1} + S_{z,m-1})\]

\[(-i m \omega + \tau_1^{-1})S_{z,m} = \frac{i \gamma}{2}B'_{x}[S_{z,m+1} + S_{z,m-1} - S_{z,m+1} - S_{z,m-1}] + B'_{z}\tau_1^{-1} \frac{dS_{z}^{0}}{dB_{0}} \delta_{m,\pm 1}\] (2.71)

Notice that the $m \pm 1$ terms are due to multiplication between the perturbing field (2.68) and the polarization response (2.70).

To find the susceptibility of the $z$ component, we substitute $m = 1$ into the corresponding Equation of 2.71 and refer to 2.70.

\[\mathcal{X}_{z}(\omega) = \frac{S_{z,1}/\hbar \gamma\tau_1}{B'_{z}} = \frac{1}{\hbar \gamma(1 - i \omega \tau_1)} \frac{dS_{z}^{0}}{dB_{0}}\] (2.72)

Dissipation due to relaxation of TLS’s is proportional to the imaginary component of $\mathcal{X}_{z}(\omega)$. We finally use Equations 2.65 and 2.67 to obtain

\[Q_{\text{TLS}}^{-1}(\omega) \propto N_{v}D^{2}\frac{e^{-U/k_BT}}{k_BT[1 + e^{-U/k_BT}]^{2}} \frac{\omega \tau_1}{1 + \omega^{2}\tau_1^2}\] (2.73)

The form of this expression is as expected from a relaxation process. The value of $\tau_1$ in silica is estimated to be in the $10^{-1} - 10^{1}\mu\text{sec}$ range around 1 K [98]. This means that within the temperature ranges of interest for MRFM, cantilevers in the low kHz range are located at a tail of the dissipation Debye peak. It also would suggest that higher frequency Si cantilevers in the 100 kHz to 10 MHz ranges may be particularly susceptible to TLS-mediated dissipation from the native oxide layer.

We have omitted a discussion of the resonant process in which the cantilever oscillation frequency is matched with the energy splitting of the TLS, since low kHz cantilevers correspond to TLS’s with energy splittings below the $\mu K$ range that are
Figure 2-3: SEM Micrographs of Ultrasensitive Silicon Cantilevers Used for MRFM (A) An overview of an entire cantilever chip bearing six devices. (B) The tip region of one of the devices. (C) High-resolution image of the top surface and edge of the cantilever shaft. Significant surface roughness is visible. Scale bars are 100 µm (A), 10 µm (B), and 100 nm (C).

too low to overlap with any significant fraction of the TLS population.

2.5.2 Importance of TLS in the Dissipation of Thin Si Cantilevers at Low Temperatures

A surface damage layer and structural imperfections resulting from machining and polishing procedures can increase dissipation in macroscopic ($10^{-2} - 10^{-1}$ m) sapphire resonators by up to two orders of magnitude between room and liquid helium temperatures [99]. In the case of nanomechanical resonators ($10^{-8} - 10^{-6}$ m), surface-to-volume ratio is increased by 4-7 orders of magnitude. One would therefore expect that any surface roughness or defect layer is more likely to constitute the dominant source of mechanical dissipation in NEMS devices compared to micromechanical and macroscopic resonators.

Fig. 2-3 shows SEM images of standard ultrasensitive silicon cantilevers used for
magnetic resonance force microscopy and nanomagnetometry [35,69,76,77]. One goal of this thesis is to improve the performance of such devices by reducing their intrinsic mechanical friction. A first step of such effort consists of identifying the limiting sources of dissipation. The critical dimension of these devices is a thickness of about 100 nm (Fig. 2-3B-C). Due to this diminutive thickness, structural imperfection, even on the atomic scale, may already constitute a significant portion of the device’s volume and mass.

Fig. 2-3C shows a high-magnification image of the surface and edge of a cantilever. These surfaces exhibit significant roughness and structural imperfections on the 1-50 nm length scale. These are due to the wet and dry etching steps used to machine the devices. In addition to a defect layer that is attached to the Si crystal via covalent bonds, there is also a layer of adventitious organic adsorbates (invisible in the SEM images) with thicknesses of roughly 1 nm [35] (Fig. 4-2). The adsorbate layer is unavoidable and is present on virtually any surface that has been exposed to the atmosphere. Therefore, both the covalently attached imperfection layer and the physisorbed layer may participate in energy dissipation. In this subsection, we illustrate the importance of the TLS theoretically discussed in the previous subsection. We further discuss data that demonstrate the preponderance of surface loss in the total mechanical friction in ultrasensitive silicon cantilevers.

To obtain a lower-bound estimate of surface layer contributions to the total friction, we removed both the organic adsorbate layer and the native oxide (SiO$_2$) layer by UV-ozone oxidation followed by vapor HF etching (Fig. 2-4A, black data points). The $Q^{-1}$ vs. temperature curve of such a surface-cleaned device lies significantly below that of a default device from the same wafer, throughout the measured temperature range (dark-red data points). Between liquid helium- and room temperatures, the average ratio between the dissipations of the default device and the surface-cleaned device was $4.5 \pm 2.0$. The ratio is highest (10:1) at both 4K and 295K and is lowest (2:1) around 100 K. Since most important applications of nanomechanical resonators take place at either room- or liquid-helium temperatures, we conclude that surface losses constitute the dominant source of mechanical dissipation under experimentally-
Figure 2-4: Surface layers are the primary source of mechanical dissipation in Si cantilevers (Fig. 2-3). (A) \(Q^{-1}\)-vs-T curves of cantilevers with three well-defined types of surfaces: 1) default state with both native oxide and organic physisorbate layers; 2) device without native oxide but with a monolayer of octoxyl groups covalently attached to the crystal. A physisorbate layer should also be present; 3) a Si-H device without native oxide and with a decreased level of physisorbate. (B) Net mechanical dissipation due to surface layers. Curves are obtained by subtracting the \(Q^{-1}\) values of the hydrogen-terminated Si-H device from the other two devices in (A). (C) Net surface mechanical dissipation in 3 types of organic monolayer-covered devices. The octyl and octadecyl devices were prepared via liquid-phase procedures and are expected to have higher levels of surface adsorbates. The octoxyl device was prepared via a cleaner gas-phase process.

We are thus justified to consider the data from the cleaned Si-H device as an upper-bound background due to non-surface-related dissipation pathways. We subtract this background from other datasets to facilitate further analysis of surface loss channels (Fig. 2-4B-C). The contributions from the native oxide and surface organic adsorbates can be differentiated experimentally. To this end, a device without native oxide but with a monolayer of octoxyl groups covalently attached to the silicon surface was prepared by methods of Chapters 4 and 5 and measured (Fig. 2-4, blue data points). Two other devices with octyl and octadecyl monolayers were also prepared (Fig. 2-4C). Comparison of the results show that the data can be roughly divided into three 100 K-wide regions: 4-100 K, 100-200 K, and 200-300 K. In the following, we discuss each region separately.

Below 100 K, a high level of dissipation is unique in the default device; the strength of this dissipation is approximately at a constant level. Those of the other devices decrease sharply with cooling. The only common difference is the presence or the
absence of the native oxide layer. We therefore conclude that dissipation below 100 K is due to processes occurring in the native SiO$_2$ layer.

In the 100-200 K region, a common peak centered between 130-150 K occurs on every type of surface, including the cleaned Si-H device. The intensity of this peak is lowest for Si-H, higher for the default native oxide surface (note the high background below 100 K), still higher for the octoxyl and octyl samples, and highest for the octadecyl surface. Fig. 7-2 and B-2 show that diamond and silicon nitride cantilevers also show display peaks in this region. Together, the data suggest that this peak is likely due to both physisorbed and chemisorbed organic molecules. Microscopically, hydrocarbon chains are the likely source of this peak.

Above 200 K, the default device with native oxide also shows higher dissipation. The dissipation is also higher for monolayer samples prepared in the liquid-phase than samples prepared in the gas-phase (Fig. 2-4C). These trends suggests that both the oxide and additional surface contaminants due to the wet processing are contributing in this region.

The goal of the thesis is to improve mechanical performance at liquid-helium temperatures and below. The above analysis therefore shows that understanding and controlling the dissipation mechanism associated with the native oxide becomes crucial.

Native oxide on silicon has the structure of fused-quartz. Extensive study of the ultrasonic properties of SiO$_2$, many other types of glasses, and amorphous organic solids were conducted since the 1970s [93–98]. These investigations revealed that thermal and sound absorption behaviors of amorphous material showed common behaviors that deviated from Debye’s theory for crystalline solids.

Two examples of the behaviors, which we reproduce in our devices, are shown in Fig. 2-5. Unlike crystals, in which sound velocities decrease with increasing temperature, amorphous materials show first a decrease, then an increase (Fig. 2-4A). The frequency data are for three of the devices discussed in Fig. 2-4 and a fused quartz cantilever produced by the thermal oxidation of a default device (Fig. 8-3). The frequency change patterns for both the silicon crystals and the fused quartz agree
Figure 2-5: Native oxide on silicon is the dominant source of dissipation below 50 K. (A) Fractional frequency changes as a function of temperature for several types of cantilevers with identical geometry (B) Mechanical dissipation ratios (over a surface-cleaned Si-H silicon cantilever) of surface-modified and of a fused silica cantilever.

Another behavior is the occurrence of significant dissipation between 1K and 100 K, with the peak generally centered around 50 K. This dissipation peak is observed in our fused quartz cantilever (Fig. 2-4B). In this figure, we have normalized the dissipation data against the surface-cleaned Si-H device. The normalization procedure is useful for analyzing similarities and differences between the thin native oxide and fused quartz. In the low-temperature region, we observe between 1-2 orders of magnitude higher total dissipation in the fused quartz cantilever compared to the native oxide-covered default. A more detailed calculation using the frequency, spring constant, and $Q$ of these devices show that the fused quartz exhibited roughly 50 times the mechanical dissipation compared to the native oxide layers on the silicon device. Considering that the total native oxide thickness is about 2-3 nm for the two sides of the device, this difference is in good qualitative agreement with a thickness of 280 nm for the fused quartz cantilever. The native oxide shows higher, per thickness, dissipation. This is likely due to a higher defect density at the interfaces compared to the bulk.
The analysis in this section showed that understanding and controlling surface loss is important for the advancement of nanomechanical resonators fabrication and engineering. In the case of silicon resonators, we have shown that the native oxide layer is the dominant source of friction at liquid helium temperatures. The tunneling, two-level systems model has been invoked to explain both the sound velocity and dissipation anomalies in glass like SiO$_2$, which has roughly the same structure as the native oxide [110]. The model assumes that the amorphous nature of glass means that a large concentration of atomic groups could exist in alternative configurations separated by shallow energy barriers. These barriers are so low that thermal activation around 50 K was sufficient for significant flux between the two states. At still lower temperatures below the single-digit Kelvin range, thermal activation is forbidden, but quantum mechanical tunneling underneath the barrier is still possible.

2.6 Other Types of Dissipation

Previous sections provided theoretical and experimental evidence that the dominant source of mechanical dissipation relevant for low-spring constant nanomechanical resonators used in force and mass sensing experiments is the surface. In the particular case of silicon cantilevers, TLS’s in its native oxide are the primary culprit. Until this source of dissipation is fully understood and eliminated, it will be difficult to experimentally determine the next limiting mechanism. In this last section, we discuss, for completeness, several other commonly invoked loss mechanisms in the mechanical resonator literature and explain why they are, for the moment, negligible from an experimental point of view.

2.6.1 Clamping Loss

Most mechanical resonators are physically attached to a substrate. Exceptions include optically trapped ions, nano- and microparticles [58–64]. When the resonator is attached to a substrate, mechanical deformation of the resonator inevitably induces deformation of the substrate near the clamping point. Phonons may thus leak out
of the resonator into the substrate [102]. The process is most efficient when the resonator and substrate are mechanically impedance-matched. Analytical calculations have predicted that solid and massive clamping are useful to suppress this mechanism. Practical wisdom also suggests that long and slender cantilevers are relatively immune to this type of loss.

In both the silicon and diamond cantilevers studied in this thesis, we have not observed a length dependence of clamping loss (Chapter D). These observations are diagnostic that the large aspect ratio devices investigated in this thesis are not limited by clamping loss so this mechanism will not be considered further.

### 2.6.2 Phonon-Electron Dissipation

Phonon-electron dissipation is a form of intrinsic dissipation that exists in electrical conductors. Since the materials we use in this thesis: Low-doping Si and high-purity diamond are both insulating at low temperatures, this pathway is not relevant.

### 2.6.3 Viscous Damping

The measurements reported in this thesis were undertaken at pressures below $10^{-6}$ mbar. At these pressures, collisions with gas molecule cause no measurable dissipation in similar cantilevers reported in the literature [13]. At liquid helium temperatures and below, additional cryo/pumping reduce pressure below $10^{-8}$ mbar where this mechanism is completely negligible.

### 2.7 Summary of Damping Mechanisms

This chapter has provided a basic yet hopefully clear perspective on how energy dissipation arises during the shape deformation of a mechanical resonator. The complexity of the solid state and of material interfaces mean that complete microscopic understanding of energy dissipation phenomenon in micron- and nanoscale mechanical devices is a difficult goal that will require the accumulation of knowledge over
many years and generations of scientists. Continued advances in both experimental and computational methods bode well for an eventual understanding at the atomic level [16].

The rest of the thesis details a pragmatic approach to empirically decrease the intrinsic dissipation and non-contact frictions in nanoresonators used for ultrasensitive force measurements. A substantial amount of empirical data accumulated in the process has allowed a clear picture of the identity of the limiting dissipation pathway to emerge. For high-purity silicon and diamond devices with low defect concentrations in the bulk, processes happening at the interface between the crystalline bulk and vacuum are most relevant from a practical point of view.

We finish the chapter with a table summarizing several key loss processes. The perspective is for ultra-soft nanomechanical resonators designed for the detection of small forces, masses, and fields.

<table>
<thead>
<tr>
<th>Dissipation Mechanism</th>
<th>Characteristic Time Geometry Dependent?</th>
<th>Avoidable Via Engineering/Design?</th>
<th>Diagnostic Test (Measure Q vs.)</th>
<th>Relevance for Ultrasensitive Force Sensors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermoelastic</td>
<td>Yes</td>
<td>Yes (↓ thickness)</td>
<td>Frequency</td>
<td>Medium</td>
</tr>
<tr>
<td>Two Level Systems</td>
<td>No</td>
<td>Difficult</td>
<td>Temperature</td>
<td>High</td>
</tr>
<tr>
<td>Clamping Loss</td>
<td>No</td>
<td>Yes (↑ length)</td>
<td>Cantilever Length</td>
<td>Low</td>
</tr>
<tr>
<td>Viscous Damping</td>
<td>N.A.</td>
<td>Yes (↓ pressure)</td>
<td>Pressure</td>
<td>Low</td>
</tr>
<tr>
<td>Detector-Induced</td>
<td>Maybe</td>
<td>Maybe (Change detection mode)</td>
<td>Detector Power</td>
<td>Medium</td>
</tr>
</tbody>
</table>

Table 2.1: Summary of Key Dissipation Mechanisms and Their Characteristics
Chapter 3

Experimental Setup and
System Operating Procedures

Figure 3-1: Picture of the mK Magnetic Resonance Force Microscope System
Constructed during This PhD Thesis Project The cryostat (blue) rests on an air table
suspended from the ceiling for maximizing work space underneath. The reddish-brown tower
on the left is the $^3$He/$^4$He gas handling system. The electronics and controller instruments
are housed in the tower on the right side, next to the computer.
The magnetic resonance force microscope (MRFM) built during the course of this thesis research (Fig. 3-1 and 3-2) is a slightly modified version based on the design developed at IBM Almaden in the group of Dr. Daniel Rugar. The sample positioning stage was redesigned by Professor Christian Degen for improved stability. The same modified design has been implemented in both low-temperature systems currently operating in the Degen group and has been found to be stable and robust.

An MRFM instrument consists of six major components:

1. High vacuum system for eliminating viscous damping of resonator motion

2. Mechanical resonator motional detection and readout system (using a Fiber-optic interferometer)

3. Piezo-based coarse and fine positioning system for relative motion between mechanical resonator and the sample surface

4. Hardware and software for mechanical resonator feedback control, signal acquisition, scanning control, and data analysis
5. Radio frequency pulse generation and application system.

6. Dilution refrigerator system for variable-temperature (80 mK-399 K) operation

In the following sections, we briefly describe each component. Similar systems have been described in much more detail in theses dedicated to hardware construction by other groups [111–114]. We only provide an overview description since the construction of an instrument as complex as a MRFM is most efficiently learned on site. To be able to reproduce such a system, we suggest that interested researchers to get in touch with groups with such expertise for the nitty-gritty details essential for a successful effort.

3.1 High Vacuum Generation

The MRFM probe head sits inside a vacuum chamber that is evacuated using a turbo-molecular pump to a pressure of $p < 10^{-6}$ mbar during operation. The vacuum is necessary for eliminating gas-damping dissipation of the resonator. Operation under vacuum has the additional benefit in that improvement in $Q$ achieved by many methods in this thesis are permanent when the cantilever is kept in high vacuum (Chapter 5) but degrades slowly if stored in air (Fig. 5-4).

Instead of the usual indium metal seal, we have used a Kapton disc to seal the sample chamber (Fig. 3-3). This approach was found to be sufficient for high vacuum and has the important advantage of operational simplicity. Each Kapton disc was found to have a life-time of roughly a couple of years, with on average weekly opening and closing events.

Due to the long and narrow path from the top of the cryostat all the way down to the probe head at the bottom of the cryostat, vacuum generation takes a relatively long time. Base pressure in the $10^{-6}$ mbar range is usually reached only after 24 hours of pumping.
3.2 Mechanical Motional Detection and Signal Acquisition

MRFM detects the effect of weak magnetic dipole-gradient force on the motion of a nanomechanical resonator, most often in the geometry of a pendulum-style scanning cantilever or nanowire. Various methods for detecting their mechanical motion have been demonstrated. Successful methods include, from order of appearance in the literature, fiber-optic interferometry using unpolarized and polarized laser light \cite{115,116}, coupling between the mechanical motion and conduction in a quantum-point contact \cite{117}, and coupling between a magnetized mechanical resonator and a superconducting quantum interference device \cite{118}. For our instruments, we have implemented the classical fiber-optic interferometry due to its relatively easy construction and sufficient performance to support advancing MRFM to the next levels of resolution and sensitivity, which is currently limited by mechanical dissipations and non-contact frictions. These limiting factors are the optimization targets addressed by this thesis research.

Optical interferometry functions as a result of light interference, giving rise to
Figure 3-4: Simplified Block Diagram of the MRFM Control and Signal Acquisition Systems

intensity variation that can be measured. One of the two branches of light that interfere comes from a directly reflected portion of the laser light as it hits the end of the cleaved optical fiber. Let us call this branch the reference branch. The second branch exits the fiber, is focused onto the mechanical resonator, gets partially reflected and re-coupled back into the fiber along the same optical path. To increase the intensity of the reference branch, the end of the cleaved fiber was coated with 70 nm of evaporated amorphous silicon. This layer increased the reflectivity at the end of the fiber to roughly 60% of the impinging light.

In our system, we have implemented two laser wavelengths. We chose 1550 nm laser standard for optical communication systems for the low absorbance of silicon cantilevers in this wavelength range. We have also implemented a 830 nm laser to provide complementarity to the 1550 nm in cases where insufficient reflection from the mechanical resonator, due to its thickness value, prevents sufficient reflection at
To make the laser source, commercially available butterfly-style 12-pin 1550 nm laser diodes with built-in TEC were purchased. The + and - termini of the laser diodes were connected in parallel with protective Zener diodes with break-down voltages that would limit the maximum currents through the laser diode to within about 50% of the maximum allowable value of 200 mA. Connections to the TEC and the DC current supply were made through BNC connectors. The whole assembly was housed in a die-cast aluminum alloy Pomona box with dimensions 4.25 in x 2.64 in x 1.71 in. A total of three 1550 nm laser boxes and one 830 nm laser box were constructed, all showing comparable behaviors. Fig. 3-5A shows the power output characteristics of one of the resulting laser boxes as a function of driving current. I-V curve in Fig. 3-5B suggests that the protective zener diodes should have breakdown voltages below 3 volts in order for the maximum current passed through the laser diode to be below about 100 mA. Fig. 3-5C demonstrates that the protective diode wired in parallel with the laser diode has the desired property.

Photodiodes sensitive to IR light connected to either single-stage or two-stage inverting operational amplifiers were wired and housed inside the same type of Pomona boxes as for the laser boxes described above. With the resulting IR-sensitive photodetectors, we determined the linear response range of the photodiodes-amplifier
assembly. Fig. 3-6 together with Fig. 3-5A suggest that the photodiode box 2 (PDB2), which has a I-V converter gain of $10^5$, is linear only at very low laser illuminations in the microwatt range. This level of linear response range is sufficient for monitoring MRFM laser signal in the nanowatt range that are necessary for avoiding heating of the sample.

### 3.3 6-Dimensional Positioning System

The complete MRFM probe boasts 6-axis coarse positioning and 3-axis fine positioning capability (Fig. 3-2). Coarse positioning of sample surface with respect to the mechanical resonator is enabled by attocube x-y steppers (model ANPx51) and z stepper-scanner (ANPz51). The fine positioning capability was achieved using an xy-scanner (model ANSxy100). Three of the six coarse positioning degrees of freedom was assigned to the sample stage for enabling relative motion between the cantilever and the attached sample surface. The remaining three steppers were mounted as a stack, at the back of the probe, to enable movement of the laser and lens system. This is an important capability that permit the characterization of multiple resonators during the same cooldown run.

As a simultaneous illustration of the positioning system and of the signal detection electronics, we performed the calibration experiment shown in Fig. 3-7. A mirror was mounted on the Attocube positioning stage, perpendicular to the laser, and moved
in directions approximately parallel (x) or orthogonal (y) to the laser beam. As the mirror moves through 1/2 of the wavelength, a full cycle of signal maximum to minimum is observed that result from the interference between the light reflected at the end of the fiber with the light that exits the fiber, reflects at the cantilever surface, and reenters the fiber.

Fig. 3-7B and 3-7C show the resulting interference fringes as the mirror is moved with respect to the laser light in the y and x directions using the high-resolution x-y scanner, respectively. These interference fringes can be converted to linear displacement of the positioning system, taking into account the fact that each cycle of the fringe corresponds to $\lambda/2$ in terms of actual spatial movement. The resulting displacements of the positioning system as a function of applied control voltages to the scanners are plotted in Fig. 3-7A. The results suggest that the Attocube scanner,
model ANSxy100, has good linear response to control voltage within a 20 $\mu$m $\times$ 20 $\mu$m scanning area at room temperature.

### 3.4 Radio Frequency Pulse Generation

This system was not used in the work described in this thesis. For completion, we provide a brief description. A National Instrument dual channel waveform generator (PXIe-5451) housed in an external PXIe-1073 chassis was used for RF signal generation. The instrument is capable of 400 MS/s output with 16-Bit resolution and a maximum output values of 2.5V and 50 mA. The signal generated by PXIe-5451 usually need to be amplified before passing into the cryostat for use in, for instance, nuclear spin manipulation. The waveform is generated in Labview and programmat-ically uploaded onto the waveform generator prior to pulse generation.

### 3.5 Cryogenic System

The MRFM system built during this thesis research is integrated into a cryogen-free dilution refrigerator, Model CF250, manufactured by Leiden Cryogenics BV. In the absence of thermal load, the system was shown to reach a base temperature of about 60 mK. During actual experimental runs, we have been able to achieve a minimum of 80 mK.

#### 3.5.1 4K-300K

Operation between liquid helium and room temperatures is achieved using a pulse tube refrigerator powered by a Cryomech compressor. The operation of a pulse tube refrigerator is based on the cyclic compression and expansion of helium gas across fixed, porous boundaries. Over each cycle of compression and expansion, net heat absorption, at a heat exchanger in contact with cryostat, or net heat release, at a heat exchanger in contact with the surrounding, occur.
An important point for MRFM operation is that the cyclic compression and expansion of gas at frequency $f_{\text{comp}}$, powered by the compressor (picture), creates periodic vibrations of the system at multiple frequencies, for instance at a frequency close to 1 Hz (and its multiples) due to cyclic compression and expansion of the working fluid. There are also higher frequencies from the vibrations of the working compressor. These disturbances creates significant and visible vibration in the entire cryostat. The mechanical transducing cantilever is severely agitated by this vibrational disturbance and the effective mode temperature, as judged by measuring its thermal peak amplitude, can be in the hundreds to thousands of Kelvins even when the bath was at liquid helium temperature.

The vibration problem was partially alleviated by mechanically decoupling the heat exchanger from the cryostat. This has been achieved by lifting the cold head
up by a couple of centimeters, and remaking thermal contact using flexible copper braids (Fig. 3-9). To provide mechanical support for the heat exchanger, a custom vibration-damping clamp was constructed and mounted on top of the floating table to hold the heat exchanging cold head in place (Fig. 3-9). An example of thermal cantilever spectrum is shown in Fig. D-8. The result shows that the vibration damping was sufficiently effective to maintain thermal vibration amplitude below 10 K. The mechanical decoupling also caused a deterioration of system cooling performance, from the original base temperature slightly below 4 K, the current system base temperature is around 5 K, with minor fluctuation from run to run.

Practically speaking, a pulse-tube-cooled system has both advantages and disadvantages. The advantage is that during extended operations, on the order of a month or longer, minimal maintenance is required. For example, cryogen-cooled system need roughly weekly refills of liquid helium and nitrogen, which is not the case
for a pulse-tube cooled system.

The major disadvantages include slow experiment cycle time; each cooldown from room temperature to the base temperature requires between 40 to 55 hours, depending on whether a superconducting magnet is also attached. Another major disadvantage specific to MRFM is the presence of residual mechanical excitation, which will make effective cooling of resonator mode temperature into the mK range problematic.

3.5.2 $^3$He/$^4$He Dilution Refrigerator

The operation of a dilution refrigerator has been described in detail in numerous online resources and will not be reproduced here. Briefly the method exploits a negative enthalpy of mixing between liquid $^3$He and liquid $^4$He to achieve cooling. The working fluid is $^3$He, which is circulated in a closed loop through liquid $^4$He by turbo-molecular pumping.

3.6 Labview and Labview FPGA Programs

NI Labview provides a convenient programming platform for MRFM research, where programs need to be constantly modified and improved. For this thesis research, a range of hardware control and signal processing programs were written. They are too numerous to describe in full glory, and only a coarse outline of the most important control routines is given.

Two important low-level programs included FPGA-based control loops. A laser fringe PID controller finds the mid-point between the maximum and the minimum of the fringe by scanning the laser wavelength and locks the DC value of reflected power to the mid-point where the slope of signal intensity over mechanical sensor displacement is maximum.

Another program, also written for FPGA, was used for controlling the resonator motion. This program contains digital filters to phase-shift and amplitude-modulate, in real time, the measured signal before feeding the result back onto the cantilever via piezo actuation. An all-pass filter and a low-pass filter were implemented. This
enabled simultaneous and separate self-oscillation and feedback damping of the mechanical sensor.

Higher-level programs such as 2D frequency scanners, topography scanner by cantilever touch-down mapping, and signal acquisition programs were written based on the key FPGA-based control loops.

3.7 Operational Procedures

For future generations of students operating the mK-MRFM system, we list the following step-by-step procedure for assembling the probe, pre-position the sample with respect to the cantilever, close the cryostat and perform a the cooldown.

3.7.1 Preparation of the Probe

When not being used, the probe chamber is kept under vacuum to minimize water adsorption onto the larger inner surface area of the central insert. To change the sample, perform the following steps:

1. Opening the sample vacuum can.
   
   (a) Make sure that the sample stage is retracted from the cantilever.
   
   (b) Turn off the turbo pump and wait for 5 minutes until chamber is vented.
   
   (c) Unscrew and remove all but two opposing M5 screws. Temporarily keep the screws on top of the probe chamber.
   
   (d) Holding the vacuum can in place with one hand, remove the two last screws.
   
   (e) **Very slowly and carefully lower the vacuum can to avoid lateral movements that may break a fiber or wire.** Set the vacuum can aside after wrapping a glove over it to minimize dust accumulation.
   
   (f) Install the aluminum bar to fix the suspended lower stage relative to the upper stage.
(g) Visually inspect the probe to make sure everything is ok and that no wire or fiber is trapped in a fragile position.

(h) Fully retract the sample attocube z-axis.

2. Unmounting the cantilever holder

(a) Find a good pair of tweezers and the dedicated Allen key for mounting cantilever holder.

(b) Hold the tweezers in the right hand and grab the cantilever holder from the right side when facing the probe.

(c) Loosen the screw by half a turn or so. Make sure that the tweezers have a good grip on the cantilever holder. Unscrew completely. Gently remove the cantilever holder by retracting towards oneself, without lateral or up/down movements. Do not loose the screw and washer by tilting the holder.

(d) Put the cantilever holder back into a sample box and fix well. Remove the screw and washer and store in dedicated glass dish.

3. Removing the attocube and unmount the surface sample.

(a) This procedure can be done independently of whether a cantilever is mounted. For precious cantilever sample, it is recommended to remove it first for maximum safety.

(b) Unplug the 3 attocube connecters controlling the $xy$ scanners and the $z$-walker/scanner.

(c) Slightly loosen the screws fixing the clamping spring.

(d) Gingerly remove the scanner tower. **This procedure should only be attempted after training!**

(e) Remove the surface sample or the stripline sample. **This procedure should only be attempted after training!**

(f) Store scanner in dedicated drawer space.
To switch in new surface sample and cantilever sample, simply follow the above procedure in reverse. Once both the attocube and cantilever samples have been reinstalled, one can proceed to the following procedure for pre-aligning the cantilever with respect to the sample surface.

1. Locate the probe in the alignment microscope, find the focus and zoom in.

2. Set the attocube stepping voltage to 30V.

3. Step +100 steps in $Z$. Check in the microscope to confirm that little has changed.

4. Step 1000 steps in $Z$ and watch through the microscope at the same time.

5. It is usually ok to step a total of 3000 steps from the fully retracted position.

6. The cantilever should be sufficiently close to the surface now to enable $xy$ alignment.

7. Perform $y$ axis alignment until the cantilever is roughly aligned with the desired touch down location

8. Rotate the microscope 90 degrees (Demonstrated during training) and align $x$ axis.

9. Rotate back to default viewing angle and slowly approach in $z$ until just before touching.

10. Fine tune $xy$ alignment.

The samples are now pre-aligned. After static charge removal, the vacuum can can be closed and pumped down. Once the desired surface feature has been located in frequency scan, the system can be closed for cooldown following this procedure:

1. Retract the $z$ stepper by 200 steps.

2. Close the inner shield. Be very careful not to deform the rim.
3. Close the magnet. Make sure that the rotational orientation is properly chosen. Connect the leads and heater. Make sure that current can be passed into the switch heater.

4. Close the inner vacuum chamber (IVC). **Careful not to destroy the Kapton ring by clamping down on it in case it moves accidentally out of alignment.**

5. Pump the inner vacuum chamber and watch to make sure that pumpdown rate is normal.

6. Close the 50K shield.

7. Close the outer vacuum chamber (OVC). Make sure that the O-rings are properly cleaned and positioned nicely.

8. Pump the OVC if the pressure of the IVC is below 1 mbar.


10. Start pulse tube refrigerator (and consider taking a 2-day vacation!).
Various thermal shields and vacuum dewar cans in the system are necessary for efficient thermal isolation of the cryostat.
Chapter 4

Exclusively Gas-Phase Passivation of Native Oxide-Free Silicon(100) and Silicon(111) Surfaces

This chapter is submitted for publication as:

Y. Tao, R. Hauert, and C. L. Degen, Exclusively Gas-Phase Passivation of Native Oxide-Free Silicon(100) and Silicon(111) Surfaces, submitted (2015).

Abstract

Reactions in the gas-phase are of primary technological importance for applications in nano- and microfabrication technology and in the semiconductor industry. We present exclusively gas-phase protocols to chemically passivate oxide-free Si(111) and Si(100) surfaces with short-chain alkynes. The resulting surfaces showed equal or better oxidation resistance than most existing liquid-phase-derived surfaces and rivaled the outstanding stability of a full-coverage Si(111)-propenyl surface [119, 120]. The most stable surface (Si(111)-ethenyl) grew one fifth of a monolayer of oxide (0.04 nm) after 1 month of air exposure. We monitored the regrowth of oxides on passivated Si(111) and Si(100) surfaces by X-ray photoelectron spectroscopy (XPS) and observed a significant crystal-orientation dependence of initial rates when total oxide thickness was below approximately one monolayer (0.2 nm). This difference was correlated with the desorption kinetics of residual surface Si-F bonds formed during HF treatment. We discuss applications of the technology and suggest future directions for process optimization.
4.1 Introduction

The chemical passivation of oxide-free silicon surfaces by Si-C monolayers [119–135] improves both the electrical and the mechanical properties of a variety of silicon-based devices. Si-C monolayers can, for example, enhance the performance of silicon-based photovoltaic devices [136, 137], increase the sensitivity of silicon field-effect sensors and devices [138, 139], act as a dielectric layer with tunable tunneling barrier [140, 141], provide a path to precision surface doping [142], and reduce electromechanical dissipations in nanoelectromechanical systems (NEMS) ([15, 143] and Chapter 5). Due to its often easy integration into wafer-scale processes, the technology provides an important opportunity for industrial applications.

While working to improve the mechanical properties of silicon-based NEMS and MEMS devices (Chapter 5), we discovered that the vast majority of Si-C formation reactions rely on liquid-phase chemistry. Liquid-phase processes are incompatible with delicate NEMS that are susceptible to mechanical failure by sonication, agitation, or surface tension, and that are extremely sensitive to surface contamination by insoluble residues and metallic impurities [144–146]. This is especially true in the final stages of fabrication [14, 147, 148]. Besides such structural issues, the liquid-phase fluoride etching step (HF, NH₄F, or buffered HF), necessary for removing the native oxide, also attacks other common structural and functional materials in nanofabricated devices, including dielectric spacers and metallic contacts [149, 150]. Finally, existing Si-C surfaces, with the exception of the Si(111)-propenyl surface, suffer from finite air-stability with oxide regrowth time constants typically on the order of days to weeks [119, 120, 151].

Complications arising from liquid-phase chemistry are conveniently circumvented via gas-phase reactions. Initial attempts included gas-phase hydrosilylation reactions aiming for high surface coverage. These pioneering efforts employed standard liquid-phase hydrofluoric acid etching for native-oxide removal [152, 153] and a specialized, in situ-synthesized H-terminated nanoparticle substrate [154]. On a longer run, gas-phase reactions could provide many additional advantages, including reagent-solvent...
economy, cleanliness [155], better etching selectivity resulting in wider material com-
patibility [156,157], as well as procedural simplicity. These are expected to facilitate
integration into automated, vacuum processing sequences that are standard in the
semiconductor industry.

With the goal of a generally applicable method in mind, we developed a set of
exclusively gas-phase reaction sequences to prepare native oxide-free, C-terminated
silicon(100) and silicon(111) surfaces. We found that the resulting surfaces exhib-
ited similar or better air stabilities than liquid-phase-prepared, fully covered alkyl-
and alkynyl-Si(111) surfaces. The best protocols led to stabilities approaching that
of the fully alkylated Si(111)-propenyl surface [119]. We used X-ray photoelectron
spectroscopy (XPS) to study the mechanism of native-oxide regrowth and monolayer
aging in air. We found that passivated Si(111) surfaces were significantly more sta-
ble than identically-treated Si(100) surfaces in the initial stages of oxide regrowth.
We discuss possible mechanisms behind the oxidative degradation and suggest future
avenues for further optimizing the surface stability.

Details of the processing can be found in Appendix A. Briefly, we removed car-onaceous adsorbates from as-purchased wafers by a UV-ozone treatment or an oxy-
gen plasma ashing step. The surface oxide was then removed via gas-phase hy-
drofluoric acid etching [156,157]. The Si-C bond was finally formed by thermal or
photochemical hydrosilylation with gaseous terminal alkynes at a pressure of 1 atm
inside a custom-built high-vacuum reaction chamber (Fig. A-1). After hydrosilyla-
tion, samples were put inside waffle-pack boxes, wrapped in aluminum foil, and stored
in ambient atmosphere (23±2°C, 50±10% humidity). We chose octene and propyne
as our model reagents as their hydrosilylation products respectively represent a pro-
totypical alkyl monolayer and the ultra-stable Si-propenyl benchmark surface. We
also used acetylene, 3,3,3-trifluoropropyne, cyanoacetylene, and trivinylphosphine to
probe the effects of reactant geometry, electronic properties, and to test applicability
in doping applications.
4.2 Results and Discussion

4.2.1 Gas-phase Processing Achieves Excellent Passivation Effect

We first assessed whether gas-phase processing is a potentially useful approach capable of producing films with good air-stability. Fig. 4-1A compares the native oxide regrowth kinetics of exclusively gas-phase-processed Si(111) samples with those of comparable Si(111) samples prepared by the standard liquid-phase two-step chlorination-Grignard alkylation sequence. The data showed that gas-phase H-terminated and octyl-terminated surfaces had comparable stabilities as liquid-phase H-terminated and alkyl-terminated surfaces. Gas-phase propenyl samples showed stabilities that were intermediate between those of solution-phase alkynyl and propenyl samples. A possible explanation of the difference in stabilities between liquid-phase and gas-phase Si(111)-propenyl surfaces is the presence of residual Si-F bonds on the latter. This point will be discussed in detail.

We note that during the course of this study, we used the same 1 atm (in reactor volume) of each alkyne gas for more than 100 reaction runs by recondensing the gases back into their respective reservoirs. We have not noticed a visible decrease in the amount (1-2 ml) of recollected compounds. This observation clearly highlights the reagent economy, cleanliness, and procedural simplicity of gas-phase processes.

Fig. 4-1B plots analogous oxide regrowth data for Si(100) surfaces, with a qualitatively similar result to that of Si(111). Fig. 4-1C further shows that the optimal reaction temperature for propyne hydrosilylation was between 100-120°C. The existence of an optimal temperature can be expected: monolayer formation on a surface requires adsorption as a first step, which would become unfavorable at high temperatures due to entropic penalty. Similar results for acetylene are provided in Fig. A-19. The data also suggested that Si(111) surfaces are slightly more stable than identically treated Si(100) samples.
Figure 4-1: Oxide Regrowth Kinetics (A) Kinetics of native oxide regrowth on representative gas-phase- and liquid-phase-processed Si(111) samples. Data were taken by X-ray photoelectron spectroscopy (XPS) and plotted in thickness units for intuitive clarity (Section A.6). Gas-phase data (filled symbols and solid lines) are from this study. Liquid-phase data (open symbols and dashed lines) are literature values [119,151]. Dashed line for liquid-phase octyl samples is omitted. Error bars for gas-phase data are standard errors from multiple experimental runs, some at different temperatures. Error bars for liquid-phase data [119] are from uncertainties in a unit conversion procedure (Section A.6). (B) Kinetics of native oxide regrowth on gas-phase-processed Si(100) samples. (C) Thickness of regrown oxide on identically treated pairs of Si(111) and Si(100) plotted as a function of hydrosilylation temperature. Solid and dashed lines are guides to the eye.
Figure 4-2: Temporal Evolution of Elemental Composition on Passivated Surfaces

Changes in the atomic percentage of surface carbon (A), silicon (B), and oxygen (C) as samples were exposed to air for up to three months. Data are for Si(111) samples. Si(100) samples showed similar trends (Fig. A-14). Solid lines are guides to the eye.

4.2.2 Surfaces Undergo Oxidative Degradation

In order to better understand the air-aging mechanism, we monitored the evolution of the surface atomic composition by XPS for up to 90 days. Survey scans demonstrated that the chemisorbed and physisorbed molecular population on the surface contained carbon, oxygen, silicon, and fluorine, but no other elements (Fig. A-2). We first focus our attention on the atomic fractions of the majority elements: carbon, oxygen, and silicon. Fluorine was also monitored and is discussed separately in Fig. 4-4.

Fig. 4-2A shows that the hydrogen-terminated surface had about 15 atomic percent of carbon. This value represents a typical level of unavoidable adventitious organic carbon physisorption [158]. The ratios of C1s peak area to Si2p peak area on these samples are between 0.19 and 0.27, agreeing quantitatively with literature data [158]. Exposures to gaseous octene and propyne increased the surface density of carbon-containing species above the background physisorption level. The magnitude of the increase is consistent with the addition of roughly another monolayer of carbonaceous adsorbate. Due to the dramatic reduction in oxide regrowth rates, this additional monolayer was most likely covalently bound.

Figs. 4-2B and C respectively plot the evolution of silicon and oxygen concentrations. While the silicon concentration decreased, the oxygen concentration increased,
and the sum of Si and O contributions was roughly constant with time. This observation suggests that oxygen-containing species were added above the silicon crystal. The oxygen concentration can increase in two ways: A first pathway is native oxide regrowth when $O_2$ and $H_2O$ molecules chemically react with the underlying silicon lattice. Alternatively, oxygen-containing molecules may accumulate via physisorption and/or chemical reaction with the organic monolayer.

### 4.2.3 Oxygen-Containing Species Interact with the Organic Over-layer

To identify the dominant pathway for oxygen accretion, we divided the oxygen population into forms of silicon oxides ($SiO_x$) and in all other forms. This distinction was possible because the amount and type of silicon oxides can be determined by analyzing the Si 2p region of the XPS spectra (Fig. A-12 and Section A.5). Fig. 4-3A plots the atomic percentage of silicon-bound oxygen versus that of all oxygen species on the octyl samples. The axes are on the same scale as both percentages are referenced to the total surface atomic population (all elements) probed by the spectrometer. The plot indicates that all oxygen beyond a threshold concentration of about 7% was added in the form of $SiO_x$ (straight line fit with slope $1.10 \pm 0.16$). Oxygen therefore added to the Si-octyl surfaces predominantly via native oxide regrowth.

Fig. 4-3B plots the corresponding data for Si-H (slope: $0.65 \pm 0.10$), Si-propenyl ($0.58 \pm 0.14$), Si-ethenyl ($0.81 \pm 0.15$), and Si-3,3,3-trifluoropropenyl ($0.48 \pm 0.08$) samples. The last two types of surfaces were fabricated to probe the mechanism of film aging. The data are qualitatively similar to those for octyl surfaces, but slope values are significantly less than unity. This suggests that for these films, oxygen was only partially incorporated in the form of native oxide.

We speculate that the significant differences between surfaces are due to physisorption and chemical reactions, depending on the surfaces under study. Between Si-octyl and Si-H, the different oxygen incorporation may be due to differences in incremental water adsorption, and possibly a changing composition in the physisorption layer.
Figure 4-3: Different surface organic coatings exhibit different affinities for oxygen. (A) Amount of oxygen atoms in the form of SiO\textsubscript{x} as a function of the total amount of oxygen on Si-octyl surfaces. (B) Equivalent data for Si-H, Si-propenyl, Si-3,3,3-trifluoropropenyl, and Si-ethenyl surfaces. (C-F) Air aging-induced carbon 1s spectral change for Si-octyl, Si-propenyl, Si-H and Si-3,3,3-trifluoropropenyl surfaces. Arrows indicate the direction and magnitude of the observed spectral shift. (G) The amount of carbon 1s spectral change can be quantified and correlated with oxygen incorporation in forms other than SiO\textsubscript{x}. The y-axis is integrated spectral difference between fresh and aged samples (See Section A.8). Data in (A-B) and (G) are combined Si(111) and Si(100) data sets. For clarity, only one crystal orientation is shown in (C)-(F). Data for both crystal orientations are consistent (Section A.8). Solid lines are linear fits to the data. Point (1,0) in (G), representing neither oxygen net incorporation into nor loss from the carbon film, is marked with a star.
In octyl samples, the growing hydrophilic oxide is buried underneath a hydrophobic monolayer. On bare Si-H surfaces, the growing oxide layer is directly exposed to the atmosphere. Therefore, physical processes alone are sufficient to account for the observations.

Differences between the Si-octyl and the Si-alkenyl samples, in contrast, may entail an additional chemical component. Oxidation of the covalently attached, unsaturated organic moiety is conceivable. After all, Si-alkenyl surface groups are vinylsilanes that are known to undergo dihydroxylation under rather gentle conditions [159]. Such reactions would increase the hydrophilicity of the covalent monolayer, which could in turn lead to a dynamic increase of the oxygen content of the physisorption layer.

In the following, we propose two mechanisms for the oxidation of alkenyl carbon chains. While we describe each as a step-wise mechanism for narrative clarity, we note that their concerted analogues may also be operative.

In a first possible mechanism, a radical cation (radical on \(\alpha\)-carbon and charge on the \(\beta\)-carbon) stabilized by hyperconjugation with the Si-C bond forms by the injection of a \(\pi\) electron and its recombination with a hole in the bulk. Molecular oxygen is another possible electron acceptor in this process. The cation would then be susceptible to a nucleophilic attack by oxygen-centered nucleophiles like water. The higher slope value of the Si-ethenyl samples compared to that of the Si-propenyl samples may be due to the reduced stability of the primary carbocation intermediate (Fig. 4-3B).

A second possible mechanism is the direct nucleophilic attack by water on the \(\beta\)-carbon, with the resulting excess negative charge on the \(\alpha\)-carbon stabilized by the neighboring silicon atom. A fast proton-shuffling step would subsequently quench the negative charge. Since the trifluoromethyl group inductively increases the electrophilicity of the \(\beta\)-carbon, the lower slope value of the trifluoropropenyl surfaces is in favor of this pathway (Fig. 4-3B).

To check for indications of chemical changes in the carbon over-layer, we examined the time-evolution in the C1s spectra. We observed significant spectral shifts to higher chemical-shift in the Si-H, Si-propenyl, and 3,3,3-trifluoropropenyl samples
with time (Fig. 4-3D-F and Section A.8). In contrast, hardly any change was visible in the octyl samples (Fig. 4-3C). (We have not obtained sufficient time-dependent data on Si-ethenyl for an equivalent analysis). A quantitative analysis of the spectral evolution revealed a linear correlation between the C1s spectral change and the oxygen incorporation or accumulation at the surface monolayer (Fig. 4-3G, see Section A.8 for details of the quantification and error analysis). The data are therefore consistent with a scenario where oxygen-rich species interact with the unsaturated organic monolayers, and with an exposed native oxide surface.

4.2.4 Fluorine Atoms Show Crystal Orientation-Dependent Lability

The XPS analysis also revealed a low concentration of fluorine on all surfaces. The chemical shift of the fluorine peak was 686.4(2) eV, indicating covalently bonded Si-F that was a remnant from the oxide removal step by hydrofluoric acid vapor [158,160].

The evolution of the fluorine atom surface concentration was highly interesting, as it displayed a significant difference between (100) and (111) crystal orientations. Fig. 4-4A shows that the surface had an initial fluorine content of 2-3% that decreased to below 1% during the three-months aging period. The two datasets in Fig. 4-4A are averaged over samples where time-dependent data were available.

The decrease in fluorine atomic % was much faster for (100) surfaces compared to (111) surfaces. The Si(100) data showed a monoexponential decay where the fast-desorbing portion accounted for roughly two thirds of the fluorine population. By contrast, the Si(111) showed a biexponential decay with a similar fast-desorbing portion but an additional slow-desorbing portion. Here, the fast-desorbing component accounted for roughly one third of the total population. We further performed a pair-wise Wilcoxon signed-rank test on a data set of 74 samples (Fig. A-22). This statistical test confirmed that the crystal-orientation difference was significant with a Z-value of 3.52 ($p < 0.0005$).

Interestingly, the ratios of labile-to-stable fluorine types coincided with the ra-
Figure 4-4: Si(100) surfaces show faster fluorine desorption and oxide growth than Si(111). (A) Surface fluorine concentration as a function of air exposure. Desorption from Si(100) occurs in a single, fast step. Desorption from Si(111) shows a fast and a slow component. Solid lines are mono- and biexponential fits, respectively. Data are from Si-propenyl and Si-octyl samples. (B) Corresponding regrowth of oxide. Solid lines are monoexponential fits that assume a final native oxide thickness of 0.8 nm (see main text for discussion). (C) Pair-wise ratio of oxide thicknesses for identically-treated Si(100) and Si(111) surfaces. Data are from 40 pairs. The decay length of 0.06(3) nm indicates that Si(111) and Si(111) mainly differ in the formation of the initial monolayer, while subsequent oxide growth is similar. (D-E) Schematic illustrations of the transition states for Si-F hydrolysis by a pair of water molecules on Si(100)-propenyl and Si(111)-propenyl surfaces, respectively. Green dotted lines are incipient bonds and red dotted lines are breaking bonds.
tios of dihydrides-to-monohydrides on HF-etched Si(111) and Si(100) surfaces [161]. Si(100) is predominantly dihydride-terminated whereas Si(111) is predominantly monohydride-terminated. If residual Si-F had no positional preference during formation, its distribution in micro-environments, either in a pseudo-dihydride (Si$_2$SiHF) or in a pseudo-monohydride (Si$_3$SiF), would be determined by the natural abundances of dihydrides and monohydrides.

The most likely candidate process behind the fluorine decrease is the chemical hydrolysis of Si-F polar bonds. This process has been studied theoretically and experimentally for small organosilanes [162,163] and for the Si(111) surface [164]. We see two prominent reasons why hydrolysis of Si-F on Si(100) should be more efficient than on Si(111).

First, DFT calculations showed that the energetically most favorable transition-state structure is a 6-membered ring involving 2 water molecules [162] (Fig. 4-4D-E). One of the water molecules plays the role of a dual-activation catalyst: It increases the nucleophilicity of the other water molecule, and facilitates the leaving of the fluoride. This occurs in a concerted, proton-shuffling step. For Si-F in a pseudo-dihydride microenvironment (Fig. 4-4D), the catalytic 6-membered transition state can easily form. The scissile bond is oriented at an angle from the surface normal, leaving room for both the nucleophilic and the catalytic water molecules to approach along the surface normal. In contrast, the catalytic 6-membered transition state cannot easily form within the pseudo-monohydride microenvironment predominant on the Si(111) surface (Fig. 4-4E), because it would entail the collision between the nucleophilic water molecule (specifically its spectator proton and lone pair) with the silicon crystal plane. As a result, a catalyzed pathway is not accessible to the pseudo-monohydride Si-F.

Second, steric hindrance around the silicon center was found to often determine the kinetics of hydrolysis [163]. The pseudo-monohydride Si-F center is obviously more sterically hindered by three ‘bulky silyl groups’. In addition, three rigid backbonds limit the freedom of the silicon atom for structural rearrangement when going to the pentavalent transition state. By contrast, strain can relax more efficiently in the case
Figure 4-5: Gas-phase processing could be optimized and extended in several directions. (A) Surface concentration of Si-F is tunable and can be reduced by changing HF vapor composition during initial oxide removal. (B) Better vacuum quality can improve the effectiveness of protection. Si(111)-ethynyl samples prepared at a better base pressure showed less regrown oxides after 1 month of air exposure. (C) Demonstration of phosphorus surface doping in the gas-phase using trivinylphosphine. The chemical shift of the phosphine corresponds to a phosphine oxide.

of a pseudo-dihydride Si-F with only two bonds constrained by the crystal. Therefore, the kinetics of fluorine desorption is consistent with the partitioning into monohydride and dihydride microenvironments on HF-etched Si(111) and Si(100).

The hydrolysis of Si-F may act as the starting points for surface reoxidation. The formation of Si-OH is the initial and rate-limiting step in sub-oxide formation on Si-H surfaces [165,166]. This step is followed by insertion of oxygen atoms into the adjacent Si-Si back-bonds. Fig. 4-4B-C indeed confirms that the formation of the first monolayer of oxides proceeds faster on Si(100) samples. Fig. 4-4C provides conclusive verification of generality (Z-score of 3.88, \( p < 0.00005 \)) for the trend observed in the propenyl samples (Fig. 4-4B). Returning to Fig. 4-3B, we note that propenyl samples showed an increase of up to 7 atomic % in SiO\(_x\) oxygen, roughly 4 times the fluorine loss. This number makes a lot of chemical sense since hydrolytic substitution, followed by 3 additional insertions into surrounding back-bonds predicts incorporation of roughly 4 oxygen atoms for each leaving fluorine atom.
4.2.5 Future Optimization Strategies and Applications

During the course of this study, a few avenues for future optimization of the gas-phase processing became apparent that are briefly discussed in the following. The most important parameters for improvement appear to be the saturation coverage, and pristine monolayer growth conditions with no fluorine or oxygen present.

Firstly, we found that the amount of residual fluorine following native oxide removal seems tunable. This is important, given that the residual fluorine appears to play an important role in oxide formation. In a test run, we subjected UV-ozone cleaned samples to a vapor of 1% HF in methanol inside an enclosed vial. Si-H surfaces thus obtained showed more than 50% reduction in residual Si-F concentration (Fig. 4-5A). A more detailed investigation using samples with variable residual Si-F concentrations will be the subject of a future study.

Second, vacuum quality during monolayer formation was found to be important. While all reactions are conducted at 1 atm alkyne pressure, the base pressure before gas introduction is an indication of the cleanliness of the chamber and of its residual oxygen and moisture content. Samples prepared with an elevated base pressure of $3 \times 10^{-6}$ mbar showed more than twice the amount of oxide regrowth after one month (0.04 nm vs 0.11 nm) as compared to samples prepared at a lower base pressure of $2 \times 10^{-7}$ (Fig. 4-5B). Even lower pressures could be easily achieved using a loadlocked system.

Thirdly, while we employed thermal activation in this study, photochemical assistance might help improving saturation coverage. UV illumination in the gas phase was found to promote film growth by polymerization and protection of the underlying silicon against air oxidation (Section A.14).

We finally explored the potential of our gas-phase processes for surface doping of silicon, which is an important technological capability [142,167]. For this purpose we exposed Si-H samples to trivinylphosphine at a vapor pressure of a few percent of an atmosphere. An XPS analysis revealed that 4 atomic percent of phosphorus were attached to the surface, corresponding to about a quarter of a silicon monolayer and
roughly one monolayer of the dopant precursor molecule (Fig. 4-5C). The binding energy of the phosphorus was consistent with that of phosphine oxides [167], as expected for a sample that was exposed to air for several hours before the measurement. We envision that for future applications, alkynyl phosphines [168] in mixtures with acetylene or propyne could impart concentration tunability and air stability.

4.3 Conclusion

In conclusion, we have demonstrated that stable oxide-free Si(111) and Si(100) surfaces can be produced using exclusive gas-phase processing. The demonstrated air stability is comparable to that by solution-phase methods. Significant mechanistic understanding of native oxide regrowth and organic monolayer degradation has been obtained to guide further optimization of the process. We expect that the presented procedures can be extended with only minor modifications to other important materials, including germanium [169], silicon carbide [170], and diamond [171]. The procedural simplicity, cleanliness, gentleness, reagent economy, and full compatibility with standard cleanroom technology of gas-phase processes are advantages that we believe will be of great benefit to silicon NEMS in research and industry.
Chapter 5

Permanent Reduction of Dissipation in Nanomechanical Si Resonators by Chemical Surface Protection

This chapter is submitted for publication as:

Y. Tao, P. Navaretti, R. Hauert, U. Grob, M. Poggio, and C. L. Degen,

Abstract

We report on mechanical dissipation measurements carried out on thin (∼100 nm), single-crystal silicon cantilevers with varying chemical surface termination. We find that the 1-2 nm thick native oxide layer of silicon contributes up to 90% of the friction of the mechanical resonance. We show that the mechanical friction is proportional to the thickness of the oxide layer, and that it crucially depends on oxide formation conditions. We further demonstrate that chemical surface protection by nitridation, liquid-phase hydrosilylation or gas-phase hydrosilylation can inhibit the rapid oxide formation in air, and result in a permanent improvement of the mechanical quality factor between 3- and 5-fold. This improvement extends to cryogenic temperatures. Presented recipes can be directly integrated with standard cleanroom processes and may be especially beneficial for ultrasensitive nanomechanical force- and mass sensors including silicon cantilevers, membranes or nanowires.
5.1 Introduction

Single-crystal silicon has played an important role in the evolution of micro- and nanomechanical devices. For example, nanomechanical silicon beams and membranes have been successfully used as sensors of record small forces [68] and masses [72], and led to pioneering advances in ultrasensitive scanning force microscopy [36], chemical screening [172] and biomolecular recognition [173]. Despite their small active volumes, nanomechanical devices can have very high quality factors of the mechanical resonance in the range of $Q \sim 10^3 - 10^7$ [147, 174]. The high quality factor compared to electrical resonant circuits makes nanomechanical devices especially attractive for high-frequency signal transduction [175] and as ultrasensitive, narrowband mechanical sensors [36]. Low-loss nanomechanical resonators are furthermore promising device elements for parallel data storage [176] or classical and quantum transducer architectures [177].

A potential drawback of silicon as a low-loss mechanical resonator material is the presence of a $\sim 1 - 2$ nm native oxide layer on its surface [178]. The oxide layer or associated defects are believed to play a pivotal role in the mechanical friction. Even for devices as thick as several $\mu$m, surface-related loss has been shown to dominate mechanical friction and to lead to a linear decrease of the mechanical $Q$ with decreasing thickness [13, 14]. The reduction in $Q$ is particularly severe as dimensions of devices start approaching length scales in the deep nanometer range, such as for ultrathin silicon cantilevers [68], membranes [179], or nanowires [116, 174]. The native oxide is a complex and heterogeneous amorphous solid, with a number of silicon suboxides at the bulk silicon interface and fully oxidized silicon dioxide in upper layers [110]. Oxide formation strongly depends on environmental factors, such as humidity, and the precise morphology and thickness of the oxide is variable [178]. Although it is possible to remove the oxide layer by annealing to $800^\circ$C in ultra high vacuum (UHV) [180, 181] or using chemical etching, the oxide-free silicon surface is unstable in air and the oxide layer regrows within minutes under ambient atmosphere [178]. In a series of investigations, Henry, Hines and coworkers found that some permanent improvement
in the mechanical quality factor is possible by monolayer coating of the surface with alkanes \([15,17,21]\). It is, however, unknown whether these improvements extend to low temperatures where many of the most sensitive measurements are carried out. Moreover, the liquid-phase chemistry is difficult to carry over to ultrasoft and fragile mechanical structures.

Here, we present a detailed study of the mechanical dissipation of ultrasensitive silicon cantilevers as a function of surface termination. We show that the dissipation is proportional to the thickness of the native oxide, and that it subtly depends on oxide formation conditions. We further investigate several approaches for chemical passivation of the surface, including thermal nitridation and organic monolayer deposition by liquid-phase or gas-phase hydrosilylation of medium-sized terminal alkenes, alkynes, and aldehydes. All strategies are found to achieve long term \((>1\) day\) protection against air oxidation and quality factor improvements between 3- to 5-fold compared to default devices. In most cases, these improvements extend to and are even more pronounced at cryogenic temperatures. The passivation steps are procedurally simple and can be easily integrated into existing lithographic recipes and carried out with standard cleanroom equipment.

### 5.2 Experimental

The demonstration devices used in this study were \((1,0,0)\)-oriented cantilever beams of ~120 nm thickness, 4 \(\mu\)m width, and lengths between 90-120 \(\mu\)m fabricated from an insulating single-crystal-silicon substrate (see Fig. 5-1) \([3]\). Similar cantilevers have been extensively characterized in the context of ultrasensitive force microscopy, where they are established as some of the most sensitive nanomechanical force sensors in use \([36,68,69,180]\). Since these cantilevers are long and thin, thermomechanical and clamping losses are negligible \([13]\), making them an ideal testbed to assess surface friction. Moreover, potential advances towards lower surface friction achieved in this study will directly impact pertinent force sensing applications.

We analyzed surface friction through measurements of the mechanical quality fac-
tor $Q$. The mechanical quality factor describes the energy loss per oscillation cycle, and the inverse quality factor $Q^{-1}$ is directly proportional to the mechanical dissipation parameter, $\Gamma \propto Q^{-1}$ [13]. The quality factor $Q$ and mechanical dissipation $\Gamma$ are important parameters that directly determine the force sensitivity of a mechanical sensor [147]. For our silicon test devices, mechanical friction is composed of two different sources of friction, including the material’s intrinsic (or “bulk”) dissipation $\Gamma_0$ and a surface-specific dissipation $\Gamma_s$ [13,147]. Since friction is additive, the total dissipation is given by $\Gamma = \Gamma_0 + \Gamma_s$. For most NEMS with a crystalline core, including the present silicon devices, the dominant contribution comes from the surface and $Q^{-1} \propto \Gamma_s$ [13,14].

We measured the mechanical $Q$ using the ring-down method [13,182]. For this purpose, cantilevers were mounted in a custom-built atomic force microscope that allowed for mechanical excitation of devices by a small piezoelectric element. The cantilevers were briefly driven at the mechanical resonance ($f_c \sim 10$ kHz), and the ring-down of the mechanical oscillation monitored by a low-power fiber-optic interferometer [182]. The mechanical $Q$ is then given as $Q = f_c/(2\tau)$, where $\tau$ is the 1/e ring-down time. Measurements were carried out in a variable-temperature cryostat ($4 - 300$ K) and in high vacuum ($p < 10^{-6}$ mbar).

5.3 Results and Discussion

5.3.1 Role of Native Surface Oxide

We initiated the study by assessing the contribution of the $1 - 2$ nm native oxide to the total mechanical dissipation of the devices. For this purpose, we stripped the oxide by hydrofluoric acid (HF/H$_2$O) vapor, resulting in an oxygen-free (hydrogen-terminated) surface. Fig. 5-2(a) shows that the mechanical quality factor right after oxide stripping increased by almost an order of magnitude, in agreement with earlier studies on UHV-annealed silicon cantilevers [181]. We found a similar ten-fold increase in $Q$ also at 4 K (see Appendix B). Bulk dissipation thus only amounts at most
Figure 5-1: Cantilever Devices Used in This Study for Dissipation Minimization

(a) Schematic build-up of silicon cantilever devices, showing the trimorph-like SiO$_2$(1nm)–Si(120nm)–SiO$_2$(1nm) cross-section and the atomistic make-up of the native surface oxide layer. Si atomic labels are omitted for clarity. (b) Scanning electron micrographs of one of the 120-nm-thick cantilever.

to about 10% of the total dissipation in these devices, and the remaining 90% are contributed by surface friction, both at room and cryogenic temperatures.

Fig. 5-2(a) further shows that the mechanical quality factor rapidly decreases (within minutes) following air exposure due to regrowth of the native oxide. We compared the reduction in the $Q$ to the thickness of the oxide layer measured by X-ray photoelectron spectroscopy (XPS). The data showed a roughly linear dependence of dissipation on the thickness of regrown oxide (Fig. 5-2(b)). We conclude that the dissipation is therefore mainly generated within the oxide film, and not by interfacial defects, adsorbates or crystal termination defects [16, 93–96, 98].

We carried out several additional experiments to better understand the mechanism of oxide formation. Fig. 5-2(c) shows repeated cycles of hydrofluoric acid vapor cleaning followed by air exposure under different conditions. We found that the reduction in $Q$ is reversible to within experimental error, confirming the oxide layer as the origin of dissipation and not, e.g., residual contamination during device lithography or by adsorbates. The rate of $Q$ degradation was reduced in the dark,
Figure 5-2: Role of Native Oxide in Room-Temperature Dissipation

(a) Mechanical quality factor $Q$ (black, left scale) and thickness of native oxide layer $t_{\text{SiO}_2}$ (red, right-scale) plotted as a function of ambient air exposure. Dashed lines are guides to the eye and dotted line is the baseline (default device with no surface oxide stripping). (b) Inverse mechanical quality factor $Q^{-1}$ plotted against $t_{\text{SiO}_2}$, showing that friction increases with oxide layer thickness. Dashed line is a guide to the eye. (c) Cyclic removal and regrowth of the native oxide layer shows reversible changes in $Q$. Light is found to promote oxidation while surface deuteration by DF does not influence oxide growth. The trend to lower $Q$ with the number of removal/regrowth cycles is due to the decreasing thickness of the device. (d) The fractional change in mechanical resonance frequency $\Delta f_c/f_c$ with oxide thickness $t_{\text{SiO}_2}$ allows one to determine the Young’s modulus and mass density of the surface oxide. All measurements were carried out at room temperature.

a result consistent with visible light-driven reactivity of hydrogen-terminated silicon surfaces [130]. We further measured no significant difference between the effects of HF and DF (deuterium fluoride) treatments, as expected from the oxide growth mechanism [166]. Finally, we observed differences in oxide growth under different atmospheres; these results are presented further below.
As an interesting side note, we found that the cyclic removal and regrowth of the native oxide layer allows us to investigate the elastic modulus (Young’s modulus) and the mass density of the native SiO$_2$ layer. The oxide-covered silicon cantilever can be modeled as a bimorph consisting of a thick silicon layer and a thin silicon dioxide layer of twice the native oxide thickness (as both sides of the cantilever are oxide-covered). The difference $\Delta f_c$ between the mechanical resonance frequencies of the bimorph $(f_c + \Delta f_c)$ and the bare silicon cantilever $(f_c)$ depends on the elastic properties of both materials as well as their thicknesses. For thin surface films ($t_{\text{SiO}_2} \ll t_{\text{Si}}$) the frequency difference is [183]

$$\frac{\Delta f_c}{f_c} = \left( \frac{3E_{\text{SiO}_2}}{2E_{\text{Si}}} - \frac{\rho_{\text{SiO}_2}}{2\rho_{\text{Si}}} \right) \frac{t_{\text{SiO}_2}}{t_{\text{Si}}} . \quad (5.1)$$

Here, $E_{\text{SiO}_2}$ and $E_{\text{Si}}$ are the Young’s moduli, $\rho_{\text{SiO}_2}$ and $\rho_{\text{Si}}$ the densities, and $t_{\text{SiO}_2}$ and $t_{\text{Si}}$ the thicknesses of the SiO$_2$ and Si layers. Using known parameters for bulk silicon ($E_{\text{Si}} = 171$ GPa, $\rho_{\text{Si}} = 2.329$ g/cm$^3$, $t_{\text{Si}} = 120$ nm), we can fit the linear dependence of $\Delta f_c/f_c$ on the oxide thickness $t_{\text{SiO}_2}$ using Eq. (5.1) and obtain an estimate for either $E_{\text{SiO}_2}$ or $\rho_{\text{SiO}_2}$ (see Fig. 5-2(d)). Inserting the bulk value $\rho_{\text{SiO}_2} = 2.20$ g/cm$^3$ [184] for the density of fused quartz, we obtain $E_{\text{SiO}_2} = 97.1 \pm 1.7$ GPa by fitting the linear dependence of $\Delta f_c/f_c$ on the oxide thickness $t_{\text{SiO}_2}$ (see Fig. 5-2(d)). This value is larger than the commonly accepted elastic modulus of fused quartz ($E_{\text{SiO}_2, \text{bulk}} = 72$ GPa) [184,185], which could be due to the presence of suboxides, interfacial stress, or hardening of the material by defects. The deviation could also be explained by a lower density of the native oxide; inserting $E_{\text{SiO}_2, \text{bulk}} = 72$ GPa, we obtain a native oxide density of $\rho_{\text{SiO}_2} = 1.18 \pm 0.07$ g/cm$^3$ from the fit. This density appears unrealistically low. The Young’s modulus of the native oxide on silicon surface is therefore most likely significantly higher than that of fused quartz.

### 5.3.2 Modification of Surface Chemistry

In order to stabilize the oxide-free surface and to maintain the low mechanical dissipation for extended periods of time, we screened various chemical surface modifications
oxide removal by HF vapor
hydrosilylation
thermal
nitridation
organic 
monolayer
Si
native
oxide
H-termination
ultrathin
oxynitride

Figure 5-3: Schematic and Atomistic Pictures for Chemical Surface Modification and Passivation

In a first step, the native oxide layer (red) is removed by HF, and in a second step a surface protection reaction is carried out. Two different surface modifications are depicted, including thermal nitridation (blue) and hydrosilylation (yellow).

both in liquid and gas phases. The three most successful approaches are presented in Fig. 5-3, and include thermal nitridation [186] and organic monolayer deposition by liquid-phase [17] and gas-phase hydrosilylation (Chapter 4).

Additional reactions tested include spontaneous grafting of diazonium salt, coating of diffusion barrier layers by atomic-layer deposition and by electron beam evaporation, simultaneous exposure to HF vapor and alkenes, and exposure of Si-H surface to a few gas-phase carbenes (CF$_2$ and CCl$_2$). These results are provided in Appendix B.

Nitridation – In a first approach, we explored thermal nitridation as a way to passivate the surface against oxidation [186]. Although thermal nitride merely replaces one surface layer against another, one could expect that the low bulk dissipation of silicon nitride (another favorite NEMS material) will be less detrimental than lossy amorphous SiO$_2$ (Fig. B-2). The thermal nitride was grown in ammonia at 700-1000 °C using a rapid-thermal processing (RTP) system. Fig. 5-4 shows that thermal nitridation has a beneficial effect, resulting in a slight (1.5×) improvement in mechanical $Q$ at room temperature and a 2× improvement at 4 K. We found the film thickness and nitrogen content to increase significantly with reaction temperature (Fig. B-5, Table B.3), and an optimal $Q$ was observed at 800 °C. We observed no degradation
in $Q$ after the nitride-passivated sample had been stored in ambient atmosphere for 24 h, confirming the expected long-term stability against oxidation. Overall, the silicon nitridation approach has the advantages of good air stability and operational simplicity. On the other hand, improvements in $Q$ are modest ($1.5 - 2\times$) and the high processing temperatures ($> 700{}^\circ\text{C}$) may not be compatible with some devices.

**Liquid-phase alkylation/amination** – A second approach is the formation of a self-assembled organic monolayer that blocks the access of reactive O$_2$ molecules. Such an approach by-passes the high temperatures required for thermal nitridation, and has been successfully employed for stabilizing high $Q$ in doubly-clamped, ⟨1,1,1⟩-oriented torsional oscillators [17]. We explored three recipes for monolayer formation, including (i) thermal hydrosilylation of terminal alkenes and alkynes [121], (ii) a two-step bromination/alkylation reaction [124,187], and (iii) a two-step bromination/amination process [188,189]. The recipes had mixed success. Fig. 5-4 shows that standard liquid-phase hydrosilylation, (i), enhanced the low temperature $Q$ by $2 - 3\times$ above the native-oxide default, but we found little to no improvement at room temperature. We found minimal degradation of mechanical $Q$ with time, confirming the good air stability of organic monolayers [17]. The two-step procedures (ii) and (iii), on the other hand, did not lead to improved $Q$ factors (Table B.1). In the alkylation case, (ii), we attribute the failure to surface contamination. For all three liquid phase processes we found that the use of an ultraclean critical-point drying system was essential. In our study, only a brand-new instrument yielded unpolluted devices while all other driers from shared user facilities led to devices with abysmal $Q$ values due to severe cross-contamination.

**Gas-phase hydrosilylation** – In a third approach we applied a simple vapor-phase thermal hydrosilylation recipe that avoids both liquid-phase and high-temperature process steps. Gas-phase hydrosilylations are not well developed in the literature and the presented reactions were conceived to extend the hydrosilylation process to the gas phase (Chapter 4). We demonstrated the process using both octene and octanal. In contrast to the analogous liquid-phase hydrosilylation recipe, we found the gas phase reaction to provide a significant improvement in mechanical $Q$, with $2.7\times$
Figure 5-4: Long-Term Improvement of the Mechanical Quality Factor $Q$ for Presented Surface Modifications. The data were obtained at (a) room temperature and (b) cryogenic (4 K) temperature. The first bar shows the quality factor of an untreated device. The remaining bars show quality factors of protected devices after they were exposed to air for 24 h. The right scales shows the improvement of the quality factors relative to an untreated device. Improvements of up to $2.7 \times$ (room temperature) and $4.4 \times$ (4 K) are found for devices with an octene monolayer deposited by gas-phase hydrosilylation. (c) Quality factor of propyne-protected devices prepared by gas-phase hydrosilylation for up to one month of air exposure. A drop in quality factor is observed during day 1, possibly due to conversion of residual Si-F to Si-OH termination (Fig. 4-4). No further deterioration occurs thereafter. Solid line is an exponential with decay time of 1.3 days. Error bars reflect the standard deviations of between 5 and 46 measured devices and are omitted if smaller than the symbol.

higher values at room temperature and $4.3 \times$ higher values at cryogenic temperatures. The improved performance is likely due to cleaner device surfaces in the absence of any liquid contact. Consistent with Ref. [19], chain length-matched alkene and aldehyde gave similar $Q$ at room temperature. At low temperature, we found the alkyl monolayer to be slightly superior to the alkoxide monolayer.

5.3.3 Atomistic Origin of Surface Dissipation

In the last part of this study we investigated surface oxide formation under different chemical atmospheres. For this purpose, we immersed freshly HF-cleaned devices in vapors of mono-, di- and trichloroalkylsilane under a N$_2$ atmosphere for a duration of
Figure 5-5: The structure-property relationship between surface layers formed under different conditions and the resulting dissipation behavior is complex. (a) Behavior of cantilevers that have a purposely grown oxide layer by silanization. Shown is the $Q$ factor of devices that underwent silanization by mono-, di- and trichloroalkylsilane, and are then exposed to air. Almost no oxide is grown under monochloroalkylsilane atmosphere, resulting in a high initial $Q$ that rapidly drops with air exposure (blue). Significant oxide is grown under dichloroalkylsilane (red) or trichloroalkylsilane (green) atmospheres, resulting in lower initial $Q$ that are stable against air exposure. Curve of default device (black) is the same as in Fig. 5-2(a). (b) Native oxide continues to grow after dichloroalkylsilanization. The plot shows the mechanical $Q$ as a function of the additional oxide grown (measured by XPS). Surprisingly, the $Q$ factor does not change as the native oxide is formed.

30 minutes (Section B.2). The silane vapors led to the formation of an oxide beneath a thin alkyl layer. These oxides could then be compared to the native oxide formed in air. Not all silanes were equally efficient in promoting oxide growth, and additional oxide could still grow in air after the procedure. Reactivity increased with the number of chlorines in the silane.

As shown in Fig. 5-5(a), the oxides grown in different silanes had very different impacts on the mechanical $Q$. Monochlorodimethylsilane ($\text{Me}_2\text{ClSiH}$) reacted very little with the silicon surface, and the rate of $Q$ deterioration was very similar to that of untreated devices. Trichloro(1H,1H,2H,2H-perfluoroctyl)silane (CF$_3$(CF$_2$)$_2$(CH$_2$)$_2$Cl$_3$Si), on the other hand, led to the formation of $\sim$ 2 nm of oxide beneath a fluoroalkyl monolayer (Fig. B-7, Table B.6); the amount of oxide thus formed was thicker than the native oxide grown in air. $Q$ values were slightly below those of native-oxide devices.
The most interesting case is dichlorodimethylsilane (\( \text{Me}_2\text{Cl}_2\text{Si} \)), which led to an air-stable \( Q \) that was roughly 2\( \times \) better than that of native devices. XPS measurements revealed a thin layer of oxide beneath a polydimethylsiloxane film that continued to grow in air until the native oxide thickness (1 -- 2 nm) was reached (Section B.8). Despite the growth of additional oxide in air, no degradation in \( Q \) occurred. (A similar beneficial effect was found for dichlorodiethylsilane vapor, and no improvement in \( Q \) was observed if silanization occurred after the native oxide had already formed). We hypothesize that the concurrent silanization/oxidation had a “templatinf effect” that lead to a more ordered atomic arrangement and reduced the dissipative properties of the oxide film. We more recently found that post-exposure of native-oxide-bearing devices to oxygen plasma can also raise the \( Q \) factor by 2\( \times \) at room temperature, which may be explained by a similar (partial) re-arrangement of atoms. Together, all observations support the conclusion that the amorphous nature of the native oxide, and not the simple presence of Si-O-Si bonds, is crucial to explain surface dissipation at room temperature [105].

5.4 Conclusions

To summarize, we have performed a detailed study of the role of the \( \sim 1 -- 2 \text{ nm} \) native oxide in the mechanical friction of thin (\( \sim 100 \text{ nm} \)) silicon cantilever beams. The data presented show that, for our test devices, the surface oxide contributes up to 90\% to the total dissipation, both at room and cryogenic temperatures. We find the friction to be proportional to the oxide thickness and to subtly depend on formation conditions, indicating that dissipation is intricately related to the atomic arrangements of the amorphous oxide. We have further developed three different chemical surface modifications, including thermal nitridation, hydrosilylation, and gas-phase silanization, that inhibit oxide formation and partially preserve the low dissipation of the oxide-free devices. The improvements in mechanical quality factor compared to default (native-oxide-bearing) cantilevers are up to 3\( \times \) at room-temperature and extend to 5\( \times \) at cryogenic temperatures. We suspect that even higher improvements
will be seen as dimensions of nanomechanical devices continue to shrink.

We finally note that the facile surface passivation reactions may be beneficial to several technological efforts beyond the fields of micro- and nanoelectromechanical systems. The presented gas phase reactions have several advantages over their commonly-used liquid-phase counterparts, including gentle mechanical handling, scalability, and absence of cross-contamination. For instance, the surface modification of silicon nanowires may further improve the thermoelectric figure of merit ($zT$) of this mass-produced thermoelectric material [190, 191]. Given the easy integration of presented surface modification reactions into standard cleanroom processes the advances described may offer a simple and straightforward way to enhance a broad range of silicon nanotechnologies.
Chapter 6

Facile Fabrication of
Single-Crystal-Diamond
Nanostructures with Ultra High Aspect Ratio

This chapter is published in:

Abstract
We present details of two robust and facile methods for making MEMS and NEMS devices from single-crystal diamond material. The methods rely entirely on standard cleanroom and micromachining techniques and do not make use of ion bombardment, thus avoiding defects in substrate and device layers. The methods are exemplified through fabrication of singly-clamped cantilever beams with thicknesses as thin as 45 nm, lateral dimensions up to 240 μm, and aspect ratios up to 2,600 using quartz and silicon handling substrates. We expect that the presented methods will make micro- and nanofabrication of high-quality single-crystal diamond devices readily accessible to a large number of researchers.
Compatibility with batch fabrication is a technological challenge facing many promising materials for NEMS applications, including carbon nanotubes [4], graphene nanoribbons [192, 193], nanowires of various material compositions [194, 195], and single-crystal diamond. Often times, multiple reasons prevent a promising material system from ‘going batch’, such as low yield during material synthesis, difficulty in controlling geometry, placement, and orientation during growth and processing, as well as poor consistency in the quality of finished devices. Single-crystal diamond is one of such promising materials, the unparalleled material properties of which have not yet been fully unlocked due to difficulties associated with its growth and processing [196–199].

These difficulties are unfortunate because diamond holds fascinating promise for many cutting-edge fields of research. Its exceptional mechanical properties are poised to boost efforts in force sensing and optomechanics by a simple exchange of device material [35, 69, 200]. The wide optical transparency window and high refractive index are ideal for plasmonic and photonic structures that may be integrated in optical networks [201]. Purposely created lattice impurities and defects, such as the nitrogen-vacancy (NV) center, hold promise for single photon generators and ultrasensitive detectors for magnetic fields under ambient conditions [202–205]. Progress toward
such integrated and high-quality diamond devices would be greatly accelerated by the availability of methods for batch-fabrication of single-crystal diamond.

The central reason that makes diamond nanofabrication difficult is the fact that single-crystal diamond cannot be grown heteroepitaxially. In other words, no wafers with a single-crystal diamond device layer are currently available. As a result, obtaining high-quality starting material that facilitates subsequent device elaboration becomes the central challenge. Chemical-vapor-deposited (CVD) diamond, the highest quality material currently grown in industrial processes, is limited in size to $< 10 \times 10$ mm (more typically $< 4 \times 4$ mm) plates at a thickness of several hundred microns. This starting material must subsequently be micromachined and lithographically processed to arrive at the desired MEMS or NEMS device.

Existing strategies for making single-crystal diamond nanostructures can be roughly divided into three categories based on the nature of the starting material. In no particular order, category A is the fabrication of devices directly on the top surface of a thick, polished single crystal. Methods employed so-far include direct FIB machining [198], creation of a suspended surface layer from bulk diamond via implantation damage to an underlying sacrificial layer followed by its selective removal [10,196,199,206], and transferring of ebeam-defined resist structures to the bulk diamond by angled anisotropic plasma etching [207]. Category B relies on heteroepitaxial polycrystalline diamond films with large grain size. Although polycrystalline, this material can still exhibit single-crystal quality if the relevant device dimensions are substantially smaller than the grain size [208]. Here, suitable substrate layers, specialized nucleation techniques, and sufficient growth time lead to a thick polycrystalline film ($> 10$ μm) with characteristics of a dislocation-rich single-crystal at the top surface [209]. Following diamond growth and mechanical polishing of the top surface, the supporting substrate and the bulk part of the epitaxial film need to be removed from the backside via plasma etching steps to provide a suspended device layer. The advantage of this method is the possibility of growing wafers up to several inches in diameter, while the disadvantage is that single-crystal areas are restricted to the grain size and may not be suitable for larger devices. Category C,
finally, employs commercially-available single-crystal plates that are laser-sliced and polished down to 10-40 \( \mu m \) thickness by manufacturers. These diamond sheets are then further thinned by extensive plasma etching to the desired device layer thickness and structures, defined by standard lithographic methods [210,211].

Category C holds several key advantages for enabling batch processing and general usage and is the route of choice in this paper. It currently is the only approach for making large-area (mm-sized) structures that avoids ion bombardment (category A) and grain boundaries (category B). Furthermore, fabrication can be done using no specialized equipment or processes other than those available in standard cleanrooms. Given the large initial thickness of the diamond plates used in this approach (tens of microns) compared to the typical device layer thickness with common wafers (hundreds of nanometers), several technical hurdles will still need to be overcome to advance diamond nanofabrication to a level similar to, say, that of silicon. The first hurdle is a method for producing uniformly-thick plates with sub-micron wedge over mm lateral dimensions. The second hurdle is finding simple and robust methods for forming a strong and stable bond between the single-crystal diamond plate and an arbitrary handling substrate. Finally, for very thin devices (\( \lesssim 100 \) nm), etch processes must be very uniform and methods need to be developed to precisely monitor thicknesses of such samples.

Here, we present a protocol to easily shape commercially available single-crystal diamond plates into diamond NEMS with thickness down to below 100 nm and lateral dimensions up to several hundred microns, thus achieving aspect ratios over 2,000. The protocol features a template-assisted precision repolishing step for achieving high thickness uniformity, two independent wafer-bonding strategies, and final device elaboration using standard lithography and plasma etching. We demonstrate these processes by fabricating single-crystal diamond nanocantilevers with thicknesses between 50-800 nm and lengths up to 240 \( \mu m \). These cantilevers exhibit exceptional mechanical quality factors exceeding one million at room temperature (Chapter 7). We conclude with a discussion of the prospects and the limitations of the presented methods for making even thinner, higher-aspect-ratio structures and for extending
fabrication toward integrated, three-dimensional structures.

Our starting point for fabricating MEMS and NEMS devices are commercially-available single-crystal diamond plates grown by chemical vapor deposition (CVD). These plates can be grown at extraordinarily high purity and with low internal strain, which is important for many applications. Plates are typically laser-cut and polished to a lateral size of several mm$^2$, thickness 10-50 μm, and a surface roughness ≈ 1 nm-rms. As the polishing step is difficult to control precisely, plates usually exhibit large wedges, with thickness variations often exceeding 10 μm across a plate. This thickness variation is a major hurdle when fabricating sub-micron structures, as it is directly transferred onto the device layer when the material is further thinned by uniform plasma etching.

To overcome this hurdle we devised a template-based polishing strategy that allowed us to consistently reduce the wedge across plates to below 0.5μm per mm. Our approach is explained in Fig. 6-1A: The original diamond plate is fixed by glue in the central pit of a larger polycrystalline diamond support wafer. This pit was created by plasma-etching, with the depth less than the diamond plate thickness (typ. 10-20 μm) and lateral dimensions slightly larger than (but similar to) those of the diamond plate. The diamond plate thus protrudes beyond the polycrystalline diamond wafer. Upon polishing the material from the single crystal plate is thus removed first. Moreover, owing to the better mechanical wear resistance of polycrystalline diamond compared to $<1,0,0>$ single-crystals [212], material removal essentially comes to a halt as the polycrystalline surface is reached. The released diamond plate then has a thickness set by the depth of the polycrystalline mold, and a thickness uniformity given by the initial uniformity of the pit. Since the pit is created by plasma etching, which can be made very uniform, very flat plates result. Representative profilometer scan images are shown in Fig. 6-1B, with additional data given in Appendix C. These measurements showed an average improvement in thickness uniformity from 6.6±2.5μm (1.5±0.5μm/mm) for as-received material to 1.4±1.0μm (0.3±0.2μm/mm) for re-polished plates. Complementary measurements of the etched pit showed a depth variation of about 1 μm, suggesting that the final
Figure 6-2: Outline of the “Sandwich” and “DOI” (diamond-on-insulator) Methods for Single-Crystal Diamond (SCD) NEMS Fabrication (A) In the “sandwich method”, diamond sample is patterned with cantilevers on the front side and a 5μm-deep pit on the backside to serve as mechanical support for released cantilevers. (B) The quartz handle is prepared for diamond sandwiching by ICP etching a square receptacle to accommodate the diamond plate and to allow direct contact of the two mating quartz slides. A macor frame is used to align glass masks to the quartz slide during ICP etching. (C) After placing the diamond plate within the receptacle pit, quartz slides are brought into contact and subjected thermo-pressure wafer bonding, resulting in a “sandwich” structure. (D) Devices are released by a long ICP etch from the back side by removing excess diamond material. (E) In the “DOI method”, diamond sheet is wafer-bonded to a handling substrate, in this example a silicon wafer bearing a SiO₂ layer, via spin-coated HSQ interlayer. (F) Diamond device layer is thinned down to desired cantilever thickness by ICP etching while masked by glass mask, positioned over the sample with the aid of a macor alignment frame. (G) Fully released diamond cantilevers are fabricated following standard procedures as known for DOI and SOI wafers [3].
crystalline diamond template during the etch process; for this study, the template wafer was simply placed in the ICP etcher without any sample rotation. It should thus be possible to directly improve thickness uniformity compared to the present $\sim 0.3\mu m/mm$.

In the next step, we describe two facile wafer-bonding processes to bond the diamond sheet on arbitrary substrates, most notably silicon and quartz. A bonded diamond plate can then be handled and further processed like any conventional device layer on a carrier wafer. In a first, more specialized approach, we explored clamping of the repolished diamond sheet between two thermally-fused quartz slides, resulting in a quartz-diamond-quartz sandwich structure (Fig. 6-2). In this way, the diamond plate remains accessible from both sides, which facilitates fabrication of membrane-like MEMS or NEMS structures. Moreover, quartz can be used both as a convenient handling and mask material. (We note that while quartz was used as the substrate here, many other materials, such as sapphire, would be equally suited or even superior substrates.) Moreover, the dual use of the quartz substrates saves several mask deposition and patterning steps and provides a few further advantages that are discussed in more detail later.

The second approach explored involved direct bonding of diamond sheets to an oxide-bearing silicon carrier wafer using hydrogen silsesquioxane (HSQ) resist as the bonding agent. HSQ is a flowable oxide that converts into silicon dioxide under heat development, resulting in a generic diamond-on-insulator (DOI) substrate. The basic bonding steps are shown in Fig. 6-2: We first cleaned the diamond film in a boiling piranha solution, followed by DI water rinsing, air drying, and a 5-minute dehydration bake at 200 °C. We spin coated the oxide wafer chip (thermal or PECVD) with HSQ for 10 seconds at 2000 RPM. The diamond film was deposited onto the HSQ-coated surface at the desired location. Sturdy bonding developed after 30 minutes under pressures $>10^8$ kPa and at 500 °Celsius. We emphasize that hydrophilic surfaces are essential for bonding.

While we also tested several existing methods for producing DOI substrates [210, 211, 213], we found HSQ-mediated bonding to be particularly robust and to show
Figure 6-3: Representative Optical, SEM, and Profilometry Images of Devices
(A-F) are optical and SEM images of diamond cantilevers fabricated using the sandwich method. Scale bars are 100 μm. (G-H) are profilometry, (I) is an SEM, and (J-L) are optical images of a DOI sample during device elaboration and after wafer bonding. (G) and (J): After Device Layer Thinning step (as in Fig. 6-2F). (H) and (K): Before backside patterning and etching. In this sample, the diamond has been covered with a layer of PECVD oxide and nitride for protection during backside processing. (I) and (L): After device release step (as in Fig. 6-2G). Scale bars are 200 μm ((G), (H), (J)) and 50 μm ((I), (K), (L)).
a high tolerance towards surface roughness and undulations. The fluid and slightly moldable nature of the HSQ interlayer has given essentially 100% success rate for mating surfaces having up to 10 nm-rms roughness. Secondly, we found it possible to bond diamond sheets that are buckled, wrinkled, or that have kinks on the surface. For the latter it is essential to use a soft interlayer between the bonding platen, such as graphite wafers, that can elastically deform. Lastly, we found the resulting bond to be extremely stable. Extended soaking in 49% HF, sometimes overnight for large samples (>4mm²), were necessary to dislodge a bonded diamond sheet.

In a last fabrication step, the bonded diamond sheet is either fully etched away to release pre-patterned devices (Sandwich Method, Fig. 6-2D) or thinned to sub-micron thickness using Ar/Cl-based ICP etching [214,215] (DOI Method, Fig. 6-2F). The thinning process uses glass or quartz mask to shield the outer portions of the DOI substrate and is held in place by a Macor alignment frame. Thickness of the bonded diamond sheet was monitored after each cycle of ICP etching by profilometer scans across the sample. Once the film was thinned down to the desired sub-micron thickness, standard lithographic fabrication procedures [3] were used to yield, after front- and backside patterning and etching steps, fully released cantilever test devices (Fig. 6-2G).

Fig. 6-3 collects a series of optical, scanning electron microscope, and profilometer images of intermediate steps and finished devices. Four batches were prepared during the course of this study, with an overall yield of released cantilevers after ICP etching of >98% (over 100 devices were fabricated).

Fig. 6-4 illustrates that device thickness < 100 nm can be achieved and that thickness can be precisely controlled. We employed three independent methods for monitoring thickness of devices during thinning: Optical thin-film interferometry, scanning electron microscopy (SEM), and measurements of mechanical resonance frequencies combined with theoretical modeling. Fig. 6-4A-C shows optical micrographs of a diamond sheet before, during, and after device release by ICP etching. We notice that an interference pattern becomes visible as the membrane thickness is reduced to below around 1 μm, with a thickness difference of 110(8) nm between two green fringe
Figure 6-4: Methods for Determining Thickness of Diamond Membrane and Cantilever Devices (A-C) show optical micrographs of the initial diamond plate (A, thickness ~ 10 𝜇m), with the thickness of the membrane reduced by ICP etching to ~ 1 𝜇m (B), and with an additional thickness reduction of ~ 0.8 𝜇m (B). Successive green fringes are marked by fringe order and are separated in thickness by 110(8)nm. (D-F) show examples of SEM images used to measure thicknesses of diamond cantilevers.

maxima. We found the diamond etch rate to be well reproduced using fringe-based thickness estimation. For example, fringes receded by about 7 orders between Fig. 6-4B and 6-4C, corresponding to a thickness reduction by 770±56nm using 20 min of etching. This is in good agreement with the calibrated etch rate of 840±60nm per 20 min (see Table C.1). To confirm the interference measurements, we also determined the thicknesses of several cantilevers at the tip and at the base using SEM images (Fig. 6-4). We found good agreement for thicker devices, but found SEM measurements to systematically yield smaller thickness values for thin (≲ 200nm) devices. Moreover, we compared thickness data to measured values of mechanical resonance frequencies combined with numerical calculations (Comsol), and found those data to be in excellent agreement with the optical interference measurements. We thus believe that the optical data are the most precise, and suspect the systematic errors in SEM thickness measurements to come from charging effects and limited imaging.
resolution. Overall, we estimate the error in fringe-based thickness estimation to be < 30 nm.

In an attempt to further reduce the thickness of devices, we subjected fully released, free-standing nanocantilevers to additional ICP etching. While not all devices survived this ICP and the following cleaning process, some of the resultant cantilevers showed thicknesses between 40-50 nm (see Fig. 6-5). As can be seen from the figures, smallest dimensions occurred near the base of the devices. The thickness variation may be both due to the residual wedge from the polycrystalline diamond polishing mold, or due to non-uniform etching in the ICP. We note that most cantilevers in this additional thinning process were actually lost while drying them from the post-etching IPA rinse; we did not have access to a critical-point dryer (CPD) at the time of the experiment and just pulled the cantilever sample out from liquid IPA. Thus, we expect that ICP etching would support even thinner structures.

![Figure 6-5: Thinnest Devices Fabricated in this Study using a Second ICP Etching Step](image)

(A) Optical image of two sub-100-nm thick cantilever devices. The longer cantilever is 240-μm in length and has a thickness of 47(8) nm at the base and 125(8) nm at the tip, respectively. (B) Scanning electron micrograph of the same cantilever, measuring a base thickness of about 50 nm. (C) Optical image of two other cantilever devices exhibiting a sub-100nm thickness at the base. Scale bars are 20 μm.

In summary, we have presented two robust and facile methods for fabricating single-crystal diamond NEMS and MEMS devices. Two key technical innovations were presented: Firstly, a novel polishing approach based on a polycrystalline diamond mold template was introduced that allowed for achieving sub-micron thickness uniformity in bulk diamond plates. Secondly, two wafer bonding methods were presented including quartz-diamond-quartz sandwich structures and HSQ-mediated
diamond-on-insulator substrates with a silicon carrier wafer. Both methods could be easily extended to other substrate materials, such as sapphire. Furthermore, both methods are versatile starting points for further refinement of diamond device fabrication: The sandwich method, for example, is ideally suited for fabricating more complex, three-dimensional structures due to the dual-side access to the diamond layer. One could envisage making sharp AFM tips [216], mass-loading, [3] or optical micro-lenses [217] on one side of the diamond sheet before patterning and releasing the cantilever by etching from the opposite side. The DOI method, on the other hand, could be easily combined with ion implantation and homoepitaxial regrowth [199,218] as an alternative to laser-cut, re-polished, and etch-thinned diamond plates. We have exemplified the capabilities of the methods presented in this study by lithographically fabricating nanocantilevers with extreme aspect ratios (over 2,000), including device thicknesses down to 50 nm and lengths up to 240 um. Given the extreme mechanical strength of the material, which is reflected in an almost 100% yield of finished devices, there is considerable scope that single-crystal diamond structures with even more extreme aspect ratios may be feasible. In the absence of a method for heteroepitaxially growing single-crystal diamond, we believe that methods reported herein provide a promising platform for enabling single-crystal diamond NEMS and MEMS fabrication for high-end research and industrial applications.
Chapter 7

Single-Crystal Diamond
Nanomechanical Resonators with
Quality Factors Exceeding One Million

This chapter is published in:

Abstract
Diamond has gained a reputation as a uniquely versatile material, yet one that is intricate to grow and process. Resonating nanostructures made of single-crystal diamond are expected to possess excellent mechanical properties, including high quality factors and low dissipation. Here we demonstrate batch fabrication and mechanical measurements of single-crystal diamond cantilevers with thickness down to 85 nm, thickness uniformity better than 20 nm, and lateral dimensions up to 240 μm. Quality factors exceeding one million are found at room temperature, surpassing those of state-of-the-art single-crystal silicon cantilevers of similar dimensions by roughly an order of magnitude. The corresponding thermal force noise for the best cantilevers is \( \sim 5 \cdot 10^{-19} \text{N} \cdot \text{Hz}^{-1/2} \) at millikelvin temperatures. Single-crystal diamond could thus directly improve existing force and mass sensors by a simple substitution of resonator
material. Presented methods are easily adapted for fabrication of nanoelectromechanical systems, optomechanical resonators, or nanophotonic devices that may lead to new applications in classical and quantum science.

### 7.1 Introduction

Nanomechanical resonators have led to pioneering advances in ultrasensitive sensing and precision measurements. Applications range from nanoscale detection of forces in the context of scanning probe microscopy [219] to molecular-recognition-based mass screening in the medical sciences [220]. The sensitivity of submicron-thick devices has progressed to a point where the attonewton force of single spins [69] or the mass of single molecules and proteins [74,75] can be measured in real time. Singly-clamped cantilever beams have been pivotal in several fundamental physical discoveries, including the detection of persistent currents in normal metal rings [67] and the observation of half-height magnetization steps in Sr$_2$RuO$_4$ [66]. Resonators coupled to optical cavities [177] or spins [221] are furthermore intensively explored as quantum mechanical device elements in quantum science and technology.

A key figure of merit for a sensitive mechanical resonator is the rate at which it gains or looses mechanical energy, described by the mechanical quality factor $Q$. In the quantum mechanical regime, for example, the life time of an oscillator’s vibrational ground state is

$$\tau = \frac{\hbar Q}{k_B T} \quad (7.1)$$

where $\omega_c$ is the resonator frequency and $k_B T$ is the thermal energy. Thermomechanical noise also limits the sensitivity toward measurement of small forces, with a minimum detectable force (per unit bandwidth) given by

$$F_{th} = \sqrt{\frac{4k_B T k_c}{\omega_c Q}}, \quad (7.2)$$

where $k_c$ is the spring constant. State-of-the-art silicon cantilevers can achieve force
sensitivities of typically $10^{-16} \text{N} \cdot \text{Hz}^{-1/2}$ at room temperature and $10^{-18} \text{N} \cdot \text{Hz}^{-1/2}$ at millikelvin temperatures [182, 222]. Despite considerable effort, attempts to improve this sensitivity well into the zeptonewton-range ($1 \text{zN} = 10^{-21} \text{N}$) have not been particularly successful. One strategy has been the development of thinner, more compliant resonators with lower spring constant $k_c$ ($\mu \text{N} \cdot \text{m}^{-1} - \text{mN} \cdot \text{m}^{-1}$). The projected gain in sensitivity, however, was found to be counteracted by a decrease in the mechanical $Q$ with decreasing thickness due to surface friction [13, 14]. Several other routes have been explored, including, for example, surface cleaning under UHV conditions [181] or the use of doubly-clamped beams at high spring tension [223]. Exciting recent progress has further been made with bottom-up devices such as suspended carbon nanotube [71], silicon nanowire [116] or trapped ion [224] oscillators. All of these approaches have their drawbacks, however; for example, ultra high vacuum (UHV) conditions are often not sustainable, high spring tensions lead to no net gains in force sensitivity (due to increased stiffness), and the geometry of bottom-up devices may not be compatible with many applications.

The goal of the current effort is to explore whether single crystal diamond may serve as a low dissipation material for sensitive NEMS and MEMS applications. Since diamond excels in many properties such as mechanical strength, optical transparency, thermal conductivity, and chemical resistance, the material is an interesting platform for integrated nanoscale devices. Diamond is, for example, a promising choice for low-loss photonic devices [209, 211] and ultra-high-frequency mechanics [225]. In addition, diamond hosts interesting intrinsic dopants – most prominently the nitrogen-vacancy center – that have been recognized as a rich resource for single photon generation [201], quantum engineering [226], and nanoscale magnetic sensing [227]. A particularly interesting avenue is the combination of diamond resonators in opto-mechanical transducers that exploit all the mechanical, optical, and dopant properties offered by the material. Unfortunately, however, fabrication of single-crystal diamond into high-quality MEMS and NEMS is notoriously difficult, and only over the last few years has material amenable to nanofabrication become available [228].

To illustrate the challenges in fabricating single-crystal diamond nanostructures,
one may note that the material cannot be grown on any other substrate than single-crystal diamond itself [228], precluding wafer-scale processing. Early diamond NEMS have therefore focused on polycrystalline diamond that can be readily grown as a thin film on various substrates, including silicon. In 2004, researchers demonstrated fabrication of 40 nm-thin devices (grain size 10-100 nm) exhibiting Q-factors up to 10,000 at cryogenic temperatures [2, 229]. Only recently have researchers tackled fabrication of single-crystal diamond MEMS and NEMS. In the absence of wafer material, the main route to producing thin films has relied on ion bombardment. In this approach, a flat diamond surface is exposed to a large dose of high energy (MeV) ion irradiation, resulting in a damage layer typically a few hundred nanometers below the surface that can be selectively etched to peel off thin membranes [230]. Impinging ions, however, have to travel through the device layer, leaving a large number of defects in their track, thus degrading the material. While the issue might be circumvented by re-growth of pristine material [199], quality factors of ion-irradiation-fabricated membranes have so far been limited to $Q \lesssim 20,000$ [10].

7.2 Experimental

In this contribution, we report on two significant advances made towards ultrasensitive diamond nanomechanical resonators. In a first part, we present two strategies to fabricate high-quality and high-aspect ratio ($> 2'000 : 1$) nanocantilevers from ultrapure, single-crystalline diamond starting material, achieving a processing level comparable to silicon. In a second part we show that these procedures lead to nanomechanical resonators with exceptional quality factors ($Q > 10^6$) and low intrinsic dissipation. Finally, we gain significant insight into the underlying physical dissipation mechanisms that provide rational basis and strategies for further improvement of diamond MEMS and NEMS.
Figure 7-1: Batch Fabrication of Single-Crystal Diamond Nanocantilevers

a. A roughly $3 \times 3 \times 0.03 \, \text{mm}^3$ single-crystal diamond plate is template-polished to a thickness uniformity $< 1 \, \mu\text{m}$ over the entire plate. b. In the diamond-on-insulator (DOI) approach, plate is first wafer-bonded using hydrogen silsesquioxane (HSQ) to form a DOI substrate. c. Plate is thinned to $0.1 - 1 \, \mu\text{m}$ thickness by reactive ion etching, and cantilevers are patterned using optical lithography. d. Cantilevers are released using conventional back-side etching. e. In the “quartz sandwich” approach, cantilevers are first patterned using optical lithography. f. Diamond plate is clamped between two fused quartz slides with a $\sim 2 \times 2 \, \text{mm}^2$ central aperture. g. Exposed diamond plate is etched down until cantilevers become released. h, i, j. Scanning electron micrographs of finished “quartz sandwich” devices. Scale bars are 20 $\mu\text{m}$.

7.2.1 Device Fabrication

The basic fabrication pathway is shown in Fig. 7-1. Our route taken starts with mm-sized single-crystal diamond plates of $20 - 40 \, \mu\text{m}$ thickness and $< 100 >$ surface orientation grown by chemical vapor deposition [228]. The advantage of these plates is the high material quality (single crystal, low doping) and the fact that they are commercially available. The large thickness variation (up to $10 \, \mu\text{m}$ over the entire
plate) and the delicate handling, however, are significant obstacles if large-area, sub-micron-structures are to be made. We have therefore developed a template-assisted re-polishing procedure to improve thickness uniformity to < 1 μm based on a polycrystalline diamond mold. To facilitate handling, we have implemented two different bonding strategies: In a first approach, we achieved direct wafer bonding to a thermal oxide-bearing silicon substrate using hydrogen silsesquioxane (HSQ) resist as intermediary. The advantage of this approach is a generic diamond-on-insulator (DOI) substrate amenable to any type of follow-up lithography. In a second strategy, we have clamped diamond plates between two SiO$_2$ substrates resulting in a fused “quartz sandwich” structure. The advantage of this method is the simpler and faster processing exploiting quartz as both the handling substrate and mask material. In a next step, the diamond device layer was thinned to <500 nm using reactive ion etching based on an argon-chlorine (Ar/Cl) plasma [217]. This procedure is known to produce very uniform and smooth etches with resulting surface roughness well below 1 nm-rms. Cantilevers were then defined by standard optical lithography before they were fully released by backside etching steps. For samples made with the quartz sandwich method, a thick diamond ledge (∼ 5 μm) was conserved at the base of the cantilevers to reduce clamping losses, while for DOI devices, the SiO$_2$ layer served as the clamping structure. Despite these precautions, clamping loss was observed in overetched DOI and some of the short sandwich devices (see Fig. D-1 and D-2). Micrographs of several devices are shown in Fig. 7-1(h-j). More details on device fabrication are given in the Methods section.

For the present study we have fabricated four single-crystal diamond chips bearing roughly ∼ 25 cantilevers each. Three devices were made using the quartz sandwich method and one using the DOI method. We found both methods to be highly robust, achieving an overall 106 out 108 cantilever yield. Of the four devices, three were fabricated from “optical-grade” starting material (Delaware Diamond Knives Inc.) with a doping concentration [N] < 1 ppm, and a fourth chip was made from “electronic-grade” material (ElementSix) with a much lower doping of [N] < 5 ppb, [B] < 1 ppb. Cantilevers were between 20 and 240 μm long, between 8 and 16 μm wide, and be-
between 80 and 800 nm thick. Thickness variation along the entire length was found to be less than 100 nm, even for the longest 240-μm-cantilevers. Corresponding resonance frequencies were between \( \omega_c/(2\pi) = 2 \text{kHz} - 6 \text{MHz} \) and spring constants were between \( k_c = 60 \mu\text{N} \cdot \text{m}^{-1} - 300 \text{N} \cdot \text{m}^{-1} \). In the following study we concentrated on the thinnest and longest (highest aspect ratio) devices, as they are the most interesting for force sensing. Moreover, thermoelastic damping and clamping losses are negligible for these structures \([13, 105]\).

The large number of finished devices allowed us to obtain a detailed picture of the mechanical dissipation in these structures. In particular, we have assessed the dependence of the quality factor on geometry, surface termination, temperature, and doping concentration. For these measurements we used a custom-built force microscope apparatus operated under high vacuum (< 10^{-6} mbar) mounted at the bottom of a dilution refrigerator (80 mK – 300 K). The high vacuum eliminated viscous (air) damping and the refrigerator both served for temperature-dependence studies and for minimizing thermomechanical noise. Quality factors \( Q \) were measured by the ring-down method using a low-power (≤ 10 nW) fiber-optic interferometer for motion detection \([13, 182]\). More details on the experimental setup are provided in Chapter 3.

### 7.2.2 Experimental Setup

Mechanical properties of diamond nanoresonators were measured in a custom-built scanning force microscope designed for magnetic resonance force microscopy \([69]\). Cantilevers were prepared under ambient conditions and then mounted in a high-vacuum chamber (< 10^{-6} mbar) at the bottom of a dilution refrigerator (~ 80 mK – 300 K). Resonator frequency \( \omega_c \) and quality factor \( Q \) were measured using the ring-down method \([13]\), and the spring constant \( k_c \) calibrated via a thermomechanical noise measurement at room temperature \([182]\). As a consistency check \( \omega_c \) and \( k_c \) were independently calculated from the geometry using a finite element software (COMSOL). Resonator motion was detected using a low-power fiber-optic interferometer operating at a wavelength of 830 nm and producing less than 10 nW of laser light.
incident at the cantilever. To exclude cavity effects, it was verified that the same $Q$ factor was obtained whether the measurement was done on the positive or negative (red- or blue-shifted) side of the interferometer fringe.

### 7.2.3 Variable Temperature Measurements

To measure temperature dependence of quality factors, two complementary measurement techniques were employed. For temperatures between $0.4 - 300$ K, $Q(T)$ was measured the usual way by slowly ($\lesssim 0.2$ K $\cdot$ min$^{-1}$) sweeping refrigerator temperature and assuming thermal equilibrium between resonator and bath. For very low temperatures ($T < 2$ K) the refrigerator was operated at base temperature (80 mK) and resonator temperature was adjusted by varying interferometer laser power through absorptive heating (see Appendix D Note 3). The advantage of the latter method is that resonator temperature can be directly estimated via the low-temperature thermal conductivity of diamond. (Cantilever mode temperature could also be inferred from a thermomechanical noise measurement [182], but this method was inaccurate < 10 K due to slight mechanical vibrations introduced by the refrigerator circuit.) Further details are given in Appendix D Notes 3 and 4.

### 7.3 Temperature Dependence of $Q$

#### 7.3.1 Quality Factors Between 4 and 300 K

In a first set of experiments we have measured the temperature-dependent quality factors between 3-300 K of nine diamond resonators total. Two representative measurements, one of an electronic grade (low doping) and one of an optical grade (high doping) device, are shown in Fig. 7-2a. A third and fourth curve of a polycrystalline diamond cantilever and an ultrasensitive single-crystal silicon cantilever are added for reference. The polycrystalline cantilever was produced from 3-5 nm grain size material (Advanced Diamond Technology), while the silicon cantilever was identical to those used in single-spin detection experiments [69, 182] and served as a "best-of-
Figure 7-2: Quality Factors of Single-Crystal Diamond Nanoresonators between 0.1-300 K

a. Two representative diamond devices (out of 9 measured) are compared to reference devices made from polycrystalline diamond and single-crystal silicon of similar thickness (100 – 300 nm). $Q$ factors between 100’000-1’000’000 are observed for diamond devices at room temperature, roughly 10-100× higher than the reference devices. Cooling to 3 K leads to an increase in $Q$ for the electronic grade (low doping) as well as the two reference resonators that are dominated by surface friction (solid arrows). Conversely, a reduction is seen in $Q$ for the optical-grade (high doping) diamond resonator that has a strong contribution of bulk friction (dashed arrow). Single-crystal diamond devices were made by “quartz sandwich” method and all diamond cantilevers were oxygen terminated. Silicon cantilever was according to Ref. [182].

b. Quality factor of a 660-nm-thick electronic-grade resonator in the millikelvin regime. Red dot data are obtained by sweeping refrigerator temperature, and red square data (with error bars) are obtained by varying the laser power incident at the resonator (see Methods). Solid black line is a power-law fit with $Q^{-1} \propto T^{1.6\pm0.2}$. Inset shows the 0.1 – 1 K data in a log-log plot against the standard tunneling model (solid line) and a model of thermally-activated two level systems (TLS, dashed line). Additional parameters for all cantilevers can be found in Table 7.1.
tors. For instance, the room-temperature $Q$ values of the two diamond resonators shown are 150,000 and 380,000 with a device thickness of only 100 nm and 280 nm, respectively (see Table 7.1. Other resonators showed room-temperature $Q$ factors up to 1.2 million at a thickness of 800 nm (see below). These values are between one and two orders of magnitude higher than similar polycrystalline [229] and single-crystal silicon resonators [13,14].

Second, Fig. 7-2a shows a clear difference between the electronic-grade (low-doping) and optical-grade (high-doping) single-crystal diamond resonators. Most prominently, we observe that the $Q$ factor of the electronic-grade resonator (and the two reference devices) increases towards cryogenic temperatures while that of the optical-grade resonator decreases. Our understanding of this difference is as follows (more evidence will be given below): at room temperature, mechanical dissipation of all resonators is limited by surface friction. Surface friction is the most common dissipation mechanism for sub-micron-thick cantilevers [13,14] and commonly attributed to surface passivation layers or adsorbate molecules. Since all devices show a similar behavior as they are cooled from 300 K, the surface dissipation mechanism appears generic, such as related to common adsorbates. As temperatures approach 3 K, surface friction is markedly reduced (reflected in higher $Q$ values) but it remains the dominating dissipation mechanism. The only exception is the optical-grade resonator: Here, a second friction mechanism begins to dominate at 3 K, reflected in lower $Q$ values. Since the only nominal difference between the electronic- and optical-grade diamond resonators is their doping concentration, it would be natural to assume that bulk impurities are related to the increase in friction.

7.3.2 Quality Factors at Millikelvin Temperatures.

To explore the potential of diamond nanomechanical resonators for millikelvin applications [69,177], we have investigated dissipation in the best electronic-grade resonator down to about 0.1 K. These data are shown in Fig. 7-2b. We find that below about one Kelvin, the $Q$ factor further increases and for this particular device attains a value of almost six million at base temperature ($\sim 93$ mK). This is the highest $Q$
factor we have observed in this study. We have assessed four additional electronic-grade resonators at refrigerator base temperature (∼ 400 mK resonator temperature, see Methods), and found that while some devices do show an increase in $Q$ compared to 4 K, others do not (see Appendix D Table 1). We have seen a similar variability already with the (large dataset) of optical-grade devices in the 4 – 300 K-range, and attribute it to the fact that single crystal diamond often has growth sectors of different quality even in the same crystal [231] and to variability in device fabrication. The manifestation of high $Q$ factors at millikelvin temperatures, even if not observed in all devices, underlines that diamond as a material – if of high quality – has very low intrinsic dissipation.

We have attempted to explain the low-temperature increase in $Q$ based on the standard tunneling model [18, 105]. For this purpose, we have fit the millikelvin data to a power law as $Q^{-1} = Q_0^{-1}[1 + (T/T_0)^\epsilon]$, yielding a baseline quality factor of $Q_0 = 6.8 \cdot 10^6$ and $T_0 = 0.3$ K. The exponent $\epsilon = 1.6 \pm 0.2$ is, however, considerably larger than the $\epsilon = 0.5$ predicted by the standard tunneling model, indicating that the model does not fully describe the dissipation in our nanoresonators at low temperatures. We have found that the data fits reasonably well to a thermally-activated model that assumes an ensemble of identical two-level systems (TLS) non-resonantly coupled to the resonator mode (see Appendix D Note 1). In the TLS model, the baseline quality factor is $Q_0 = 5.9 \cdot 10^6$ and the thermal activation barrier is $\Delta E/h \sim 13$ GHz. Both the power law and TLS models are plotted in the inset to Fig. 7-2b.

### 7.4 Diamond Surface Chemistry and $Q$

To further investigate the dissipation mechanism we have surveyed between 15 and 40 optical-grade resonators under four different chemical surface terminations. We have in addition surveyed 20 electronic-grade resonators under two different chemical surface termination. This second set of measurements served to explore whether surface chemistry affects dissipation, and to find out whether diamond resonators can be improved by proper choice of surface termination. In a first round, optical-grade
Figure 7-3: Impact of Surface Chemistry on Dissipation  Three different chemical surface terminations (sketched) are investigated on 15-40 devices of an optical-grade chip. Red dots are 300 K values and blue triangle are 3 K values, and dashed lines serve as guides to the eye. Large variation of $Q$ factors is seen as surface chemistry and thickness are changed, underlining the critical role of surface friction. Very high $Q$ factors, exceeding one million at room temperature, are found for oxygen-terminated devices.

cantilevers were measured “as-released” right after the final Ar/Cl plasma reactive ion etch. In this state, the surface has a mixture of covalently attached elements, including H, O and Cl (see atomistic sketch in Fig. 7-3). In a second round, the surface was oxygen-terminated using low-temperature ($450 \, ^\circ C$) annealing in air [232]. O-termination represents the standard hydrophilic surface termination of diamond [233]. In a third round, the oxygen termination was converted to fluorine termination using CF$_4$ plasma [234]. F-termination is known to produce a simple monolayer coverage that is both hydrophobic and oleophobic with little molecular adsorption. We found O-terminated cantilevers to be very stable with no measurable degradation in $Q$ after a two-months exposure to ambient atmosphere (F-terminated cantilevers were not re-measured).

The data of these measurements are shown in Fig. 7-3 and are grouped by surface termination. We immediately see that the particular surface chemistry has a strong impact on dissipation, with a more than tenfold variation between “as-released” and O-terminated devices. While the improvement with O- and F-termination compared to the “as-released” state can be understood in terms of cleaner surfaces with better-defined surface chemistries (see Methods), the superior performance of O-terminated
compared to F-terminated devices poses more challenges to interpretation. One hypothesis is that the terminating atoms are directly responsible for dissipation with little influence of adsorbates, and that F-atoms more efficiently engage in energy relaxation. Another hypothesis is that the inductive withdrawing effect of the polar C-F chemical bonds stabilizes a layer of electronic defects right below the surface that enhances energy relaxation [235]. If the second interpretation were true, it would be interesting to examine less polar termination groups including chlorine, sulfur, amine, hydrogen, and alkyl groups [236].

Using an electronic-grade sample, we investigated the effect of hydrogen-termination on 20 previously O-terminated cantilevers. Based on knowledge acquired in Chapter 5, hydrogen-termination of diamond is unlikely to cause strong dissipation; C-H bond lack the alternative conformation needed to engage in anelastic relaxation. Also, no charge transfer doping layer is expected to form when the sample is kept in a chamber pumped to high vacuum. [237]. Fig. 7-4A shows a scatter plot of quality factor in the H-terminated state vs the previous quality factor in the starting O-terminated state. Interesting, while both terminations exhibited high quality factors, there are distinctly three regions. On the upper left part of the graph, devices exhibited an improvement in quality factor after hydrogen plasma treatment; a reduction in dissipative defect has resulted. On the lower right part of the graph, the opposite has happened; hydrogen plasma exposure caused an increase in dissipative defects. Around straight line \( Q_H = Q_O \), the plasma treatment led to negligible net change in dissipation. That different devices show opposite trend may be an indication that only a small number of highly dissipative defects actually contribute to the bulk of the dissipation. When the number of most detrimental defects is small, it is conceivable that stochastic chance could cause such random swings.

We believe that the observed randomness is a result of both surface and bulk defects. It is known that hydrogen plasma treatment can quench defect centers such as the nitrogen-vacancy color center buried tens of micrometers deep [238]. Due to the small density of nitrogen in these electronic-grade cantilevers, it is expected that only very few NV can be found in each device. It would be interesting in future
Figure 7-4: Impact of Surface Chemistry on Dissipation Two different chemical surface terminations (sketched) are investigated on 20 devices of an electronic-grade chip. **a.** Correlation between the 4K quality factors measured in an oxygen-terminated state vs in a hydrogen-terminated state. Very high $Q$ factors above 1 million are found for both oxygen-terminated and hydrogen-terminated devices. Each data point refers to the same device. A weak correlation is observed. **b.** Correlation between the room-temperature quality factors measured in an oxygen-terminated state vs. in a hydrogen-terminated state. Hydrogen terminations induced substantial dissipation at room temperature. **c.** The fractional contribution of surface dissipation following C-H formation procedure is thickness-dependent, as expected.
experiments to correlate the appearance and disappearance of optically-active defects with changes in $Q$.

At room temperature, H-terminated samples displayed substantial dissipation (Fig. 7-4B). This is attributed to the presence of about 1 nm-thick of carbonaceous material produced during the H-termination procedure. For the moment, there is no experimental method to selectively remove this carbonaceous material from these cantilevers in a controllable way without affecting the underlying C-H termination.

Besides the variation with surface chemistry, we also observe that most plots in Fig. 7-3(a-c) show a roughly linear relationship between $Q$ and thickness (shown by dashed lines). A thickness dependence of $Q$ indicates a surface-related dissipation mechanism, whereas no thickness dependence would be characteristic of a bulk friction mechanism. The linear relationship between $Q$ and thickness is most pronounced at 300 K (red data); at 3 K (blue data), the linear dependence is much weaker and $Q$ values between O-terminated and F-terminated resonators converge. These observations confirm the picture from the temperature-dependence study in Fig. 7-2a: at room temperature, all resonators are limited by surface friction independent of surface chemistry, while at 3 K, bulk friction is strongly contributing and mostly dominating for F-terminated devices.

7.5 Discussion

In an attempt to compare presented diamond resonators to existing devices made from silicon or polycrystalline diamond, we have compiled a number of $Q$ values from the literature and plotted them alongside the single-crystal diamond data from Fig. 7-3. The comparison is shown in Fig. 7-5(a). We find that for the same device thickness, single-crystal diamond may offer between one and two orders of magnitude higher $Q$ factors compared to silicon or polycrystalline diamond. To make a similar comparison representative for force sensing applications we must also take material stiffness and density into account, which affect sensitivity through $k_c$ and $f_c$ (see Eq.
Assuming that $Q$ is limited by surface dissipation and thus scales linearly with thickness, Eq. (7.2) can be rewritten as $F_{th} \propto \sqrt{\alpha(wt/l)}$, where $w$ is a cantilever’s width, $t$ its thickness, and $l$ its length (see Appendix D Note 2):

$$\alpha = \frac{\sqrt{E\rho}}{Q/t}$$  \hspace{1cm} (7.3)

is a specific mechanical dissipation parameter that is now independent of geometry, yet contains all material properties. We note that $\alpha$ is related to the (geometry-dependent) “loss parameter” $\gamma = k_c/(Q \omega_c)$ \cite{13} as $\gamma \propto \alpha(wt^2/l)$. Values for $\alpha$ are plotted in Fig. 7-5(b). The plot confirms that diamond shows consistent low dissipation, although the improvement compared to silicon is somewhat less than with the mechanical $Q$ due to the increased stiffness and density of diamond.

It is furthermore instructive to evaluate the mechanical dissipation levels of diamond in the light of applications in quantum nanomechanics or ultrasensitive force sensing. Although our low-frequency resonators have a mean quantum-mechanical occupation number $\bar{n}$ that is far from the quantum mechanical ground state, we notice that their thermal decoherence time is quite long. For the device shown in Fig. 7-2(b), for example, we find $\bar{n} \approx k_B T/\hbar \omega_c \approx 6 \cdot 10^4$ and $\tau \approx 0.5$ ms at $T = 93$ mK. This thermal decoherence time is long and well exceeds the oscillation period of $T_c = 1/f_c \approx 30$ $\mu$s. $\bar{n}$ could be reduced, for example, by going to lower temperatures \cite{118} or by active feedback cooling \cite{43}. $\bar{n}$ could also be reduced by going to higher-frequency geometries \cite{213}, although it remains to be seen if the high $Q$ factors are maintained at much higher frequencies. The exciting prospect of presented resonators is that the low mechanical dissipation may be combined with other virtues of the diamond host material, such as optical transparency and high-quality nitrogen-vacancy impurities. Current resonators may be especially suitable for hybrid quantum architectures that do not a priori need ground state cooling, such as quantum spin transducers based on nanoelectromechanical resonator arrays \cite{241}.

We have also assessed the sensitivity of these resonators toward the measurement of small forces. The force sensitivity achievable by a freely vibrating resonator is
Figure 7-5: Comparison of $Q$ Factors between Nanomechanical Resonators Made from Different Materials

**a.** Comparison of $Q$ factors highlighting that for similar device dimensions, quality factors of single-crystal diamond are consistently higher by about an order of magnitude over single-crystal silicon devices. **b.** Comparison of the geometry-independent dissipation parameter $\alpha$ (see Eq. 7.3)). Open symbols are 300 K values and filled symbols are $\sim 4$ K values. Dashed lines indicate linear thickness dependence of $Q$. Diamond data are from this study, silicon 4-K data are taken from a compilation in Ref. [13], silicon 300-K data are from our earlier measurements. Polycrystalline diamond data are shown for comparison only, and those resonators may be limited by bulk rather than surface dissipation. Data sources: Single crystal diamond data are from this study. Silicon $\sim 4$ K data are from Ref. [13] and references therein. Silicon 300 K data are from a $\sim 1.3$ $\mu$m-thick cantilever with $Q \sim 380'000$ (Nanoworld, Arrow TL1Au), a $\sim 70$ nm-thick cantilever with $Q \sim 8'200$ (custom-made), and the 135 nm-thick silicon reference cantilever with $Q \sim 11'000$ (Table 7.1). Polycrystalline diamond cantilever data are from Refs. [105,229,239,240].

Ultimately limited by its thermal motion, equivalent to a thermal force noise $F_{th}$ given through Eq. (7.2). According to the equipartition theorem, a mechanical force sensor is thermally limited if its noise temperature equals $T = k_c x_{rms}^2/k_B$, where $x_{rms}$ is the rms displacement. We have analyzed $x_{rms}$ by integrating the displacement spectral density in the vicinity of the cantilever resonance (Fig. D-8), and found it to be in agreement with the predicted thermal motion down to about 10 K (depending on the particular device), but to be inaccurate below 10 K due to slight mechanical disturbance by the refrigerator circuit. Below 10 K, we have therefore inferred $T$ using a combination of different bath temperatures and interferometer laser intensities, as
explained with Fig. 7-2(b). Using known values of $k_c$, $\omega_c$, $Q$ and $T$, we can then calculate the thermal force noise $F_{th}$ according to Eq. (7.2). For the cantilever shown in Fig. 7-2b, we find $F_{th} = 0.11 \text{fN} \cdot \text{Hz}^{-1/2}$ at room temperature, $6 \text{aN} \cdot \text{Hz}^{-1/2}$ at 3 K, and $0.54 \text{aN} \cdot \text{Hz}^{-1/2}$ at 100 mK (see Table 7.1). Other cantilevers in this study had a thermal force noise as low as $26 \text{aN} \cdot \text{Hz}^{-1/2}$ at room temperature and $3.5 \text{aN} \cdot \text{Hz}^{-1/2}$ at 3 K. These values are remarkable considering that the geometry of these test devices is not particularly optimized. With the present diamond material and processing method, we are confident that a cantilever thickness as small as 50 nm and a width of 1 $\mu\text{m}$ could be realized for a 240 $\mu\text{m}$-long cantilever. Such a cantilever has a projected thermal force noise of $9.4 \text{aN} \cdot \text{Hz}^{-1/2}$ at 300 K, $0.49 \text{aN} \cdot \text{Hz}^{-1/2}$ at 3 K and $45 \text{zN} \cdot \text{Hz}^{-1/2}$ at 100 mK, based on the scaling of $F_{th}$ with geometry (see Note 2 in Appendix D) and the $Q \propto t$ scaling of the quality factor.

### 7.6 Conclusions

In conclusion, we have presented measurements of mechanical dissipation in sub-micron-thick single-crystal diamond nanomechanical resonators. We find that single crystal diamond is an excellent material for mechanically resonant structures, with $Q$ factors that are between one and two orders of magnitude higher than corresponding polycrystalline diamond devices, and one order of magnitude higher than similar

<table>
<thead>
<tr>
<th>Material$^a$</th>
<th>Length (µm)</th>
<th>Width (µm)</th>
<th>Thickness$^b$ (nm)</th>
<th>$\omega_c/2\pi$ (Hz)</th>
<th>$k_c$ (mN·m$^{-1}$)</th>
<th>$Q$ (300 K)</th>
<th>$Q$ (3 K)</th>
<th>$F_{th}$ (300K) (aN·Hz$^{-1/2}$)</th>
<th>$F_{th}$ (3K) (aN·Hz$^{-1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>el-SCD</td>
<td>240</td>
<td>12</td>
<td>280(20)</td>
<td>13,168</td>
<td>4.8</td>
<td>380,000</td>
<td>800,000</td>
<td>50</td>
<td>3.5</td>
</tr>
<tr>
<td>o-SCD</td>
<td>120</td>
<td>12</td>
<td>100(25)</td>
<td>15,097</td>
<td>1.4</td>
<td>150,000</td>
<td>55,100</td>
<td>40</td>
<td>6.6</td>
</tr>
<tr>
<td>Si</td>
<td>170</td>
<td>4</td>
<td>135(5)</td>
<td>4,960</td>
<td>0.083</td>
<td>11,500</td>
<td>31,500</td>
<td>63</td>
<td>3.8</td>
</tr>
<tr>
<td>PCD</td>
<td>200</td>
<td>18</td>
<td>270(5)</td>
<td>14,197</td>
<td>5.0</td>
<td>6,680</td>
<td>22,000</td>
<td>370</td>
<td>21</td>
</tr>
<tr>
<td>el-SCD</td>
<td>240</td>
<td>12</td>
<td>660(20)</td>
<td>32,140</td>
<td>67</td>
<td>412,000</td>
<td>1,510,000</td>
<td>115</td>
<td>6.0 (0.54$^c$)</td>
</tr>
</tbody>
</table>

Table 7.1: Mechanical Properties for Selected Cantilevers $^a$el-SCD = electronic-grade single-crystal diamond, o-SCD = optical-grade single-crystal diamond, Si = single crystal silicon, PCD = polycrystalline diamond. $^b$Thickness values are reported as the average between the thickest and thinnest parts of each cantilever along its length, with values in parentheses denoting the difference between this average and the extrema. For most diamond devices, the extrema occurred at the base and the tip. $^c$At 93 mK.
silicon resonators. Measurements of the $Q$ factor at room and cryogenic temperatures furthermore underline the importance of both surface quality and low-defect bulk material. Several possible avenues for reducing dissipation exist in both departments, including different surface chemistries [236], atomic surface flatness [242], reduction of intrinsic defects through high-temperature annealing [243], or even the use of isotopically pure diamond material [244]. Moreover, we expect that geometry can be significantly optimized without unduly compromising device yields, moving thermally-limited force sensitivities from the current $\sim 0.54 \text{aN} \cdot \text{Hz}^{-1/2}$ into the $10 - 100 \text{zN} \cdot \text{Hz}^{-1/2}$-range.

Beside the demonstrated high mechanical quality factors and low mechanical dissipation, we believe that broad applicability of reported fabrication methods is a second main advance presented here. The facile and robust wafer-bonding approaches result in general diamond-on-insulator (DOI) or quartz-bonded substrates that are amenable to essentially any type of follow-up lithography. Due to its low absorption and high refractive index, for example, high-quality single-crystal diamond would be ideally suited for use in optomechanical cavities or as photonic crystal material [207]. Diamond further possesses interesting lattice defects, such as nitrogen-vacancy centers, that could be directly embedded in high-$Q$ diamond NEMS and enable direct coupling between mechanical, spin and optical degrees of freedom [203,221]. Such on-chip devices are considered key components for hybrid quantum systems in quantum science and technology, underscoring the prominent material platform diamond can offer to future applications.
Chapter 8

Additional Materials Exploration

Aside from the successful experiments using single-crystal diamond, we have explored several other materials that we discuss in this section. We investigated silicon nitride, silicon dioxide, and an amorphous-polyacrylonitrile microwire.

8.1 PECVD Silicon Nitride Torsional Oscillators

Silicon nitride, specifically LPCVD silicon nitride, has been a favored material for making doubly-clamped beam and drum resonators \[7, 11, 245, 246\]. The ability to produce the material with inherent tensile stress has been found to increase the mechanical quality factor \(Q\) and frequency \(f\) of such resonators \[245, 246\]. Unfortunately, in contrast to the one order of magnitude increases in \(fQ\) product, the mechanical dissipation only decreases by a factor of 2. The reason is simple; mechanical dissipation is \(\Gamma = \frac{k}{2\pi fQ}\), where \(k\) is the spring constant, \(f\) is the frequency, and \(Q\) has its usual meaning. Scaling of dissipation based on \(f\) and \(Q\) alone, without \(k\), is easily obtained by substituting in \(f \propto \sqrt{k/m}\), where \(m\) is a constant during stress application. Therefore, \(\Gamma \propto \frac{f}{Q}\). A quick division of published values shows that dissipation levels decreases by a factor of 2 between the relaxed and the maximally stressed states right before the plateau of \(Q\) (Fig. 2 in \[246\]).

For resonators designed to perform ultrasensitive force measurement, doubly-clamped geometry with inherent tensile stress is therefore not the most effective
approach; a doubly-clamped geometry is incompatible with scanning and the gain in dissipation is very small. For singly-clamped cantilevers, inherent stress in material could cause released cantilevers to undergo extensive curling [247], making it next to impossible to monitor the resonator motion by optical methods and to use its tip as a scanning element. Therefore, we chose to investigate SiN in its (nearly) stress-free state. Even so, substantial curling still happens (Fig. 8-1).

Ideally, one would study single-crystalline SiN. Unfortunately, single-crystalline SiN material amenable to batch fabrication is not yet available. Alternative SiN materials with tunable stress are LPCVD and PECVD SiN. A commercial LPCVD cantilever was measured and found to have comparable $Q$ as native oxide-covered silicon (Fig. B-2). Very importantly, the material was available in-house for our quick experimentation. Film deposition and oscillator processing were undertaken by Dr. Paolo Navaretti. Material was deposited on a silicon wafer with a thermal oxide layer using an Oxford Plasmalab 80plus PECVD System. Parameters were tuned to provide a low-stress material. The film was processed into torsional oscillators using standard photolithography and etching steps. Due to the use of buffered-HF etching during processing and the finite etch rate of low stress nitride in this etchant, the final thickness of the resulting devices is not known exactly, but is around 100-200 nm. A picture of resulting devices is shown in Fig. 8-1 along with an example of their thermal spectrum. Several points merit discussion.

Figure 8-1: PECVD SiN Torsional Resonators (Left) Bright-field optical micrograph of PECVD SiN torsional resonators fabricated by Dr. Paolo Navaretti. (Right) The thermal spectrum of the resonator in the center of the picture. Scale bar is 100 $\mu$m.
First, we note that due to imperfect stress cancelation during film deposition or during subsequent processing, most devices were curled, as evidenced by the changing brightness in the optical image (Fig. 8-1). The curling made it difficult to determine the position of the laser spot during focusing. As a result, it was impossible to properly measure the effective spring constant of torsional motion by thermal peak integration. Nevertheless, the size of the fundamental mode is very large, indicating large thermal excursion that was on par with, and possibly even greater than, that of the nanoladder resonators (Fig. 9-6A). These devices therefore have very small spring constants in the low $\mu$N/m to sub-$\mu$N/m range.

Second, the three devices are connected to each other via a thin membrane (four rectangles supporting the torsional resonators). Motion of neighboring devices could be seen in the spectrum (small peaks near 10 kHz Fig. 8-1). Future devices would need better clamping.

Finally, due to symmetry, it was more difficult to actuate the fundamental torsional mode in these devices by piezo-electric driving. There was also a second major mode (8-9 kHz) due to the trampoline motion in and out of the device plane. It is expected that the orthogonal motion going up and down, in plane, is also active. This would be problematic for scanning applications, as snap-in and sticking to scanned surface will certainly occur. The above points need to be born in mind when designing devices for feedback-controlled scanning applications.

<table>
<thead>
<tr>
<th>Device Type</th>
<th>$L$ ($\mu$m)</th>
<th>$W$ ($\mu$m)</th>
<th>Surface state</th>
<th>$f_1$ (Hz)</th>
<th>$Q_{1st}$</th>
<th>$f_2$ (Hz)</th>
<th>$Q_{2nd}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiN Torsional</td>
<td>80</td>
<td>10</td>
<td>As-Fabricated</td>
<td>5937</td>
<td>3,500</td>
<td>9964</td>
<td>1,560</td>
</tr>
<tr>
<td>SiN Torsional</td>
<td>100</td>
<td>10</td>
<td>As-Fabricated</td>
<td>3733</td>
<td>4,100</td>
<td>8495</td>
<td>1,500</td>
</tr>
<tr>
<td>SiN Torsional</td>
<td>120</td>
<td>10</td>
<td>As-Fabricated</td>
<td>3362</td>
<td>3,600</td>
<td>8743</td>
<td>2,650</td>
</tr>
</tbody>
</table>

Table 8.1: Frequency and Quality Factors of PECVD SiN Torsional Resonators

The frequency and quality factors of the devices are compiled in Table 8.1. The room temperature quality factors are decent given the fact that the oscillator is in essence a nanowire undergoing torsional motion. Coupled with the small torsional spring constant evident from Fig. 8-1, we expect the room-temperature force sensitivity of the fundamental torsional mode to be similar to that of Si nanoladder
resonators. The second mode is flexural and have uniformly lower quality factors. It would be very interesting to make the same type of structures in silicon to find out whether a change from the usual flexural mending mode in cantilever to a torsional mode of nanowires can provide a route to improvement in Q.

8.2 Commercial Wet Thermal Silicon Dioxide

Another important material in nano- and microfabrication technology is silicon dioxide (SiO₂). In bulk form, fused quartz is a favored low-loss material at room temperature [248–250], but not at low temperatures (Fig. 2-5 and Section 2.5.2). We investigated two types of SiO₂. In a first approach, we fabricated SiO₂ cantilevers directly from a film of thermally grown SiO₂ on top of a silicon wafer. The material was from an SOI wafer (Soitec) on which the top lightly B-doped silicon device layer (10-20 Ωcm) had been completely etched away. Fig. 8-2 shows as-fabricated devices and after an additional thermal annealing step in air.

Right after fabrication, devices were slightly curled. The deformation could be due to a combination of compressive strain in the material and residual surface contamination by photoresists and waxes used during processing. Annealing in air at 600°C was found to be effective at straightening out the devices, presumably by ox-
idizing any residual organic surface contamination and providing enough energy for thermal relaxation of strains. Higher annealing temperatures (700°C and 800°C) led to drooping and severe deformations of the devices. The flow point of this type of SiO₂ is therefore substantially lower than what has been reported for the bulk material. This could be due to the presence of substantial residues from the annealing step, which makes the material impure.

The quality factors of these thermal oxide cantilever were poor at both room temperature ($Q_{rt} \approx 1000\text{-}3500$) and liquid helium temperatures ($Q_{4K} \approx 2000$). The low temperature result is consistent with results in the next subsection. The room temperature value could be due both to increased surface contamination or to unknown differences in material structure.

8.3 Thermal Silicon Dioxide Produced in Air

Alternatively, we formed SiO₂ cantilever via the thermal oxidation of single-crystal Si cantilevers. We chose to explore this approach because the condition for SiO₂ formation appeared to be important for device properties based on our silicon surface studies. A separate calibration experiment showed that up to 70 nm of SiO₂ was grown on top of a silicon wafer after 3 hours (Fig. 8-3D). Given that the thickness of our silicon cantilevers were uniformly below 140 nm, the shortest oxidation time of 3 hours was already sufficient to convert the entire shaft to SiO₂. Further oxidation time presumably could have led to rearrangement of the material’s microstructure. We can see an initial increase in vibration frequency, followed by a decrease between 20 h and 196 h of oxidation.

It is remarkable that after the Si had completely oxidized, no flowing or drooping of the quartz was observed, in contrast to what was observed for cantilever fabricated directly from buried oxide. This may be an indication of a difference in the quality of fused quartz formed by oxidation in dry air vs. via commercial, presumably wet, oxidation processes. As mentioned, surface contamination is another explanation. The quality factors do not show significant change with the duration of oxidation.
Figure 8-3: SiO₂ Cantilever Fabricated by Thermal Oxidation of Si Devices

(A) Si cantilevers after 4h thermal oxidation in air at 950°C. (B) Si cantilevers after 20h thermal oxidation in air at 950°C. (C) Si cantilevers after 196h thermal oxidation in air at 950°C. (D) Kinetics of thermal oxidation in air at 950°C measured by ellipsometry. Scale bar is 100 μm. Solid line in (D) is a guide to the eye.
<table>
<thead>
<tr>
<th>Cantilever Shaft Length (μm)</th>
<th>$W$ (μm)</th>
<th>Oxidation Duration (h)</th>
<th>$f_{RT}$ (Hz)</th>
<th>$Q_{RT}$</th>
<th>$f_{4K}$ (Hz)</th>
<th>$Q_{4K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>4</td>
<td>3</td>
<td>8574.9</td>
<td>14136</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>4</td>
<td>3</td>
<td>8610.2</td>
<td>13781</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>4</td>
<td>4</td>
<td>10207</td>
<td>11600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>4</td>
<td>4</td>
<td>10424</td>
<td>12300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>4</td>
<td>4</td>
<td>11057</td>
<td>10300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>4</td>
<td>4</td>
<td>10845</td>
<td>9100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>4</td>
<td>20</td>
<td>12832</td>
<td>14748</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>4</td>
<td>20</td>
<td>12827</td>
<td>19662</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>4</td>
<td>20</td>
<td>15664</td>
<td>20094</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>4</td>
<td>20</td>
<td>15664</td>
<td>20094</td>
<td>15556</td>
<td>1983</td>
</tr>
<tr>
<td>90</td>
<td>4</td>
<td>196</td>
<td>12893</td>
<td>15714</td>
<td>12768</td>
<td>2436</td>
</tr>
<tr>
<td>90</td>
<td>4</td>
<td>196</td>
<td>12973</td>
<td>15806</td>
<td>12845</td>
<td>2449</td>
</tr>
<tr>
<td>105</td>
<td>4</td>
<td>3</td>
<td>6889</td>
<td>14628</td>
<td></td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>4</td>
<td>3</td>
<td>6914</td>
<td>14536</td>
<td></td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>4</td>
<td>4</td>
<td>8326</td>
<td>11649</td>
<td></td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>4</td>
<td>4</td>
<td>8453</td>
<td>12059</td>
<td></td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>4</td>
<td>4</td>
<td>8923</td>
<td>8402</td>
<td></td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>4</td>
<td>4</td>
<td>8714</td>
<td>5515</td>
<td></td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>4</td>
<td>20</td>
<td>10655</td>
<td>15347</td>
<td></td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>4</td>
<td>20</td>
<td>10438</td>
<td>14635</td>
<td></td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>4</td>
<td>20</td>
<td>12656</td>
<td>20210</td>
<td>12561</td>
<td>2353</td>
</tr>
<tr>
<td>105</td>
<td>4</td>
<td>20</td>
<td>12850</td>
<td>20100</td>
<td>12701</td>
<td>1829</td>
</tr>
<tr>
<td>105</td>
<td>4</td>
<td>196</td>
<td>10455</td>
<td>16530</td>
<td>10354</td>
<td>2300</td>
</tr>
<tr>
<td>105</td>
<td>4</td>
<td>196</td>
<td>10482</td>
<td>15693</td>
<td>10380</td>
<td>2057</td>
</tr>
<tr>
<td>120</td>
<td>4</td>
<td>3</td>
<td>5666</td>
<td>15456</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>4</td>
<td>3</td>
<td>5710</td>
<td>15658</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>4</td>
<td>4</td>
<td>6918</td>
<td>11378</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>4</td>
<td>4</td>
<td>6963</td>
<td>11393</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>4</td>
<td>4</td>
<td>7451</td>
<td>77412</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>4</td>
<td>4</td>
<td>7291</td>
<td>4743</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>4</td>
<td>20</td>
<td>8929</td>
<td>15293</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>4</td>
<td>20</td>
<td>10640</td>
<td>20702</td>
<td>10519</td>
<td>1867</td>
</tr>
<tr>
<td>120</td>
<td>4</td>
<td>20</td>
<td>10608</td>
<td>19251</td>
<td>10487</td>
<td>1801</td>
</tr>
<tr>
<td>120</td>
<td>4</td>
<td>196</td>
<td>8706</td>
<td>16161</td>
<td>8623</td>
<td>2178</td>
</tr>
</tbody>
</table>

Table 8.2: Frequency and Quality Factors of Fused Quartz Cantilever Produced by Thermal Oxidation of Si Cantilevers

The averages of all cantilevers for each duration all fall within $Q_{RT} = 14,000 - 18,000$, which is exactly the same range as for the starting single crystal silicon cantilevers with a native oxide layer. $Q_{4K}$ is very consistently scattered around 2000. This result confirms that dissipation due to TLS's is the dominant source of energy loss at liquid helium temperatures (Section 2.5.2).
8.4 Organic Material Resonator: Polyacrylonitrile Microwire

In light of the many desirable properties of carbon allotropes, many research groups have tried to emulate its structural perfection and dimensionality-control using synthetic polymers and self-assembled crystals. An example is self-assembly and controlled polymerization of 2D organic polymers [251]. When sufficiently pure and ordered, there is no a priori reason why synthetic organic materials could not exhibit low mechanical dissipation. It would therefore be interesting to test resonant organic structures when they become available.

As an example of organic resonant structure, we accidentally produced some microwire of polyacrylonitrile. The microwires had length in the hundreds of micrometers to the millimeter range and width in the micron range (Fig. 8-4A). They were grown at 120°C under the saturation vapor pressure of acrylonitrile over a period of 48 hours. The material was non-crystalline despite their impressively straight morphology. Nevertheless, we tested one of the longest wire by mounting it onto a silicon cantilever chip via gluing. The frequency and quality factor of the fundamental mode at 300 K and 4 K are listed in Table.
<table>
<thead>
<tr>
<th>Device Type</th>
<th>$L$ ($\mu$m)</th>
<th>diameter ($\mu$m)</th>
<th>Surface state</th>
<th>$f_{rt}$ (Hz)</th>
<th>$Q_{rt}$</th>
<th>$f_{4K}$ (Hz)</th>
<th>$Q_{4K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylonitrile Microwire</td>
<td>$&gt; 1$ mm</td>
<td>$\approx 10$</td>
<td>As-Grown</td>
<td>1956.6</td>
<td>560</td>
<td>1672.6</td>
<td>1,630</td>
</tr>
</tbody>
</table>

Table 8.3: Frequency and Quality Factors of Polyacrylonitrile Microwire Resonator

### 8.5 Conclusion

In this Chapter, we presented resonators fabricated from several amorphous materials, both inorganic and organic. The dissipation levels, especially at low temperature, are consistently higher than what have been measured in single-crystalline silicon and diamond. This is inline with dissipation due to TLS’s that are abundant in amorphous solids. Future material screening efforts should therefore concentrate on single-crystalline materials.
Chapter 9

Geometric Optimization

9.1 Introduction

In the past decade, there has been a trend toward nanomechanical resonators with ever-smaller dimensions [1, 4, 116, 194, 195, 225, 252, 253]. Much progress has been made; the ultimately reduction to the molecular and atomic scales has already been achieved in examples like carbon allotropes and trapped ions [8, 9, 12, 254–256]. The encouraging progress has also allowed the verification that size reduction in most cases leads to reduction in mechanical dissipation and a corresponding increase in force sensitivity [116, 257]. Concurrent drawbacks include increased difficulty in readout and increased susceptibility to noise fluctuations of electrical and magnetic origins [116, 257–259].

9.2 Three Inspirations

Three types of nanoscopic mechanical resonators are of particular interest for magnetic resonance force microscopy and for ultrasensitive force detection in general. These are bottom-up nanowires, carbon nanotubes, and laser-trapped nanoparticles. We give a brief overview of these types of resonators to motivate the main work in the current chapter.
9.2.1 First Inspiration

Silicon nanowires, as a natural, bottom-up extension of top-down silicon cantilevers, have been intensively investigated by Nichol et al. [37,116,257]. Alternative nanowire materials have been studied in the literature, but have not demonstrated dissipation parameters that are drastically superior to that of silicon. These include SiC and GaN nanowires [195,252]. Nichol and colleagues employed relatively long nanowires (10-20 μm) with thicknesses between 50 nm and 200 nm. Compared to the more commonly accessible short nanowires, longer nanowires present several advantages, including easier motional detection, lower spring constant, lower clamping loss due to the larger aspect ratio, and the possibility of sample loading via optical micromanipulation at the nanowire’s extremity. The small diameter of the nanowires have been shown to be an advantage for close approach toward surfaces while maintaining the quality factor [257], as we have also confirmed for diamond nanowire-tipped Si cantilevers (Chapter 10). Using SiNW resonator, Nichol et al. successfully demonstrated a novel MRFM detection protocol ideally suited to nanoresonators with high frequency [257]. The method was further used to demonstrate Fourier transform imaging at 10 nm resolution [37], on par with the best results achieved using conventional MRFM methods [35].

Further improvement in performance has been envisioned to require improvements in the NW sensor’s mode and frequency stabilities. For example, due to the radial symmetry of as-grown SiNW, two mechanical modes that are orthogonal to each other are very close together in frequency space. This proximity has sometimes led to unwanted coupling of the modes during scanning and data acquisition. Progress toward splitting the modes via secondary, post-growth fabrication have been made. In the work presented here, we exploit the small dissipation of nanowire structures, while avoiding the coupling between orthogonal mechanical modes by geometry engineering.
9.2.2 Second Inspiration

A second promising category of bottom-up resonators are low-dimensional carbon allotropes [9, 254, 260]. These include graphene resonators and carbon nanotube resonators. As far as sensing applications are concerned, graphene resonators are less suitable compared to CNT resonators. Graphene suffers higher dissipation due to larger surface-to-volume ratio and difficulties in fabrication and manipulation. The largest $RQ$ product is only $14,000 \text{ nm}^{-1}$, where $R$ is surface-to-volume ratio [9]. This value is not much higher than what has been achieved using conventional silicon cantilevers, where $R = 7,000 \text{ nm}^{-1}$ (Chapter 5). Due to its extreme floppiness, graphene resonators need to be doubly or circularly clamped. It is nearly impossible to use a graphene resonator as a scanning element to approach a sample surface in pendulum geometry. Even if the sample is on a scanning tip and could be brought close to a graphene membrane, thermal excursion would still likely induce unwanted sticking events between the resonator and the scanning tip. Foreseeable complications and the modest gain in dissipation therefore discourage considering graphene for next-generation mechanical sensors in scanning experiments.

Carbon nanotubes, on the other hand, have been shown to possess significantly lower intrinsic dissipation than any other material system studied to date [12]. This result can be attributed to three special aspects of CNT. First, a single-wall carbon nanotube is a chemically perfect structure without any dangling bonds. This self-enclosed geometry therefore circumvents the unavoidable presence of surface-termination layer on any three dimensional material, including the diamond allotrope. Secondly, the tubular shape of the carbon nanotube effectively increases its stiffness, while avoiding the extra weight of a solid core. The increased bending moment boosts the resonance frequency and alleviates the need for clamping under tension as in the graphene case. Finally, the electrical conductivity of CNT enables *in situ* cleaning of resonator surface via joule heating. This capability thus enables the preparation of a pristine resonator surface *in situ* under measurement conditions. The capability to desorb unavoidable carbonaceous adsorbates from the atmosphere is inaccessible.
to non-conducting materials. These advantages together impart carbon nanotubes with the lowest dissipation parameter of any material that have been studied, and will likely stay a record for the foreseeable future.

The major inconvenience when using CNT as a sensor for MRFM is the difficulty in detecting its mechanical motion. Currently, only conductance measurements have been successful at accurately monitoring the motion. A doubly clamped geometry is therefore necessary, which places stringent requirements on the type of samples that can be studied: either carbon nuclei resident in the CNT itself or surface adsorbates. Another inconvenience is the difficulty of approaching a magnetic field gradient source to within the tens of nanometers range necessary for good signal generation. Therefore, we take from carbon nanotube the inspiration of a hollow structure that imparts structural integrity while minimizing mass.

9.2.3 Third Inspiration

A third promising category of approaches to low-dissipation resonators goes one step further to completely sever any covalent contact between the oscillating element and the surrounding. This is achieved by suspending the oscillator in vacuum with the aid of laser beams [48, 58, 60, 61, 63, 64, 255]. Recent works from the Novotny group have demonstrated impressively high quality factors for the mechanical motion of suspended nanoparticles [255]. Fully laser-suspended systems achieves three advantages. First, the lack of physical contact between the oscillator completely eliminates clamping loss. Secondly, suspension enables decoupling of center of mass motions from internal, intra-particle deformations, which means that quality factor can become very high and is not dependent on the material. This is because material deformation in conventional resonators is what drives energy dissipation, regardless of the loss pathway. Thirdly and perhaps most importantly for future MRFM, the spring constant of trapped oscillators can be tuned by optical trapping intensity. Since the trapping field is almost non-dissipative, this has been advantageously exploited to increase the quality factor and the frequency of a weakly tethered SiO$_2$ resonator [261]. We want to engineer our system to be compatible with this future tunability.
In this chapter, we describe an approach combining useful elements from each of the three approaches described above. It is a top-down method using conventional fabrication techniques to push geometric optimization to the limit. The resulting devices showed excellent dissipation levels, while remaining amenable to conventional handling, motion detection, and scanning probe applications.

### 9.3 The Nanoladder Cantilever

The smallest force signal that a cantilever sensor is capable of detecting is

\[
F_{\text{min}} = \left( \frac{WT^2}{LQ} \right)^{1/2} (E\rho)^{1/4}(k_BTB)^{1/2}
\]  

where \( E \) is the Young’s modulus, \( \rho \) is the density, \( k_BT \) is the thermal energy, and \( B \) is the measurement bandwidth [222]. An alternative and more general presentation of the same equation is
\[ F_{\min} = \sqrt{4k_B T T B} = \sqrt{4k_B T B \frac{(km)^{1/4}}{Q^{1/2}}} \] (9.2)

This second version summarizes material and geometric parameters in two simple parameters, the spring constant \( k \) and the effective mass \( m \). To minimize \( F_{\min} \), one needs to make light-weight devices that are soft.

Keeping in mind the intended scanning probe application and drawing experience from successful literature approaches, we arrive at a set of four principles for resonator design:
1) Maximize Length (\( L \))
2) Minimize Width (\( W \)) and Thickness (\( T \))
3) Minimize Mass
4) Constrain Oscillation in One Dimension

Items 1) and 2) essentially seek to minimize \( k \) for the singly clamped cantilever geometry.

Among everyday common objects, we single out the ladder geometry as ideally suited for achieving all of the above criteria. Macroscopic ladder structures are lightweight, achieve high aspect ratios, and are mechanically stable. Long ladders are used by firefighters in fully-gear to climb tall buildings tens of meters high. Even using wood as construction material, a ladder as tall as 41 meters and with 120 rungs can been constructed (www.guinnessworldrecords.com). A well-designed nanoscale ladder-shaped resonator built from single-crystal materials, as shown in Fig. 9-1, combines advantages of the three successful dissipation minimization approaches reviewed in the introductory section.

First, the spatial mass-distribution of material in a ladder is analogous to the hollow structure of a carbon nanotube. Such designs maximize strength with minimum mass. A single rail is flexible and approximately radially isotropic. Introducing rungs between rails constrain their relative movements to impart structural stability and deformation anisotropy. With the rail bases attached to a solid support, the struc-
ture is constrained to move by synchronized rotation around an axis defined by the attachment points. Analogously, a graphene sheet is too floppy for resonator application unless held in tension by multiple clamping points. Rolling up graphene to form CNT imparts long-range constraints on relative motion between distant atoms. In both cases, a high moment of inertia for bending (in a selected direction) is achieved without substantial increases in the effective mass.

Second, the ladder geometry can be composed of nanowire segments that are easily accessed via ebeam lithography technology. The structure would thus profit from the demonstrated low dissipation and mechanical stabilities of nanowire oscillators. An additional advantage of the nanoladder is their suitability for batch production at design locations on cantilever chips with precisely controllable properties.

Third, the increased stability of the nanoladder compared to isolated nanowires would allow fabrication of much longer structures that have negligible clamping loss and better force sensitivities. In addition, the presence of a large laser-reflecting paddle near the extremity facilitates readout of what amounts to a nanowire resonator. It further could enable the $f$ and $Q$ tuning by optical trapping. This aspect partially captures the advantage of laser-suspended nanoparticle oscillators.

### 9.3.1 Comsol Simulation of Nanoladder Resonators

We used finite element methods implemented in Comsol to study the mechanical parameters of nanoladder resonators. We chose silicon and diamond as materials for the simulation due to easy experimental implementation. An illustration of the nanoladder structure is shown in Fig. 9-1. Geometric parameters include the total length ($L$), width of rails and rungs ($W$), common thickness of the whole structure ($T$), pitch of the rungs ($P$), and size of the laser-reflecting paddle near the tip of the resonator ($W_{\text{paddle}} \times L_{\text{paddle}}$). The number of rungs is obtained by dividing $L$ by $P$. A scanning tip is added to decrease noncontact friction in an eventual scanning application. Its other function is to ensure adequate distance between the scanned surface and the laser-reflector paddle for efficient interferometric readout. For the purpose of simulation, we have kept the tip geometry constant with a length of 5 $\mu$m.
Material | $L$ ($\mu$m) | $W$ (nm) | $T$ (nm) | $L_{\text{paddle}} = W_{\text{paddle}}$ ($\mu$m) | $f$ (kHz) | $k$ ($\mu$N/m) | $Q_{\text{Low T}}$ ($10^5$) | $\Gamma$ (fg/sec) | $F_{\text{min}}(4K)$ (aN) | $F_{\text{min}}(300mK)$ (aN)
--- | --- | --- | --- | --- | --- | --- | --- | --- | --- | ---
Silicon | 50 | 200 | 100 | 10 | 10.1 | 63 | 64 | 15 | 1.9 | 0.51
Silicon | 50 | 200 | 100 | 5 | 17.0 | 75 | 64 | 11 | 1.6 | 0.43
Silicon | 50 | 200 | 100 | 1 | 40.8 | 97 | 64 | 5.9 | 1.4 | 0.31
Silicon | 50 | 50 | 50 | 10 | 5.10 | 8.0 | 43 | 5.8 | 1.1 | 0.31
Silicon | 50 | 200 | 50 | 5 | 8.46 | 9.4 | 43 | 4.1 | 0.96 | 0.26
Silicon | 50 | 200 | 50 | 1 | 20.4 | 12 | 43 | 1.2 | 0.70 | 0.19
Silicon | 100 | 200 | 100 | 10 | 3.79 | 11 | 64 | 7.3 | 1.3 | 0.35
Silicon | 100 | 200 | 100 | 5 | 5.96 | 14 | 64 | 3.0 | 0.82 | 0.22
Silicon | 100 | 200 | 100 | 1 | 1.89 | 1.4 | 43 | 2.7 | 0.78 | 0.21
Silicon | 100 | 200 | 50 | 5 | 2.98 | 1.5 | 43 | 1.9 | 0.65 | 0.18
Silicon | 100 | 200 | 50 | 1 | 5.88 | 1.8 | 43 | 1.1 | 0.50 | 0.14
Diamond | 50 | 200 | 100 | 10 | 21.4 | 420 | 146 | 21 | 2.2 | 0.56
Diamond | 50 | 200 | 100 | 5 | 35.6 | 505 | 146 | 15 | 1.9 | 0.51
Diamond | 50 | 200 | 100 | 1 | 86.0 | 649 | 146 | 8.2 | 1.4 | 0.37
Diamond | 50 | 200 | 50 | 10 | 10.7 | 50.4 | 98 | 7.7 | 1.3 | 0.36
Diamond | 50 | 200 | 50 | 5 | 17.8 | 60.6 | 98 | 5.6 | 1.1 | 0.30
Diamond | 50 | 200 | 50 | 1 | 43.0 | 81.2 | 98 | 3.1 | 0.83 | 0.23
Diamond | 100 | 200 | 100 | 10 | 8.0 | 75 | 146 | 23 | 1.5 | 0.41
Diamond | 100 | 200 | 100 | 5 | 12.5 | 83 | 146 | 16 | 1.3 | 0.35
Diamond | 100 | 200 | 100 | 1 | 24.7 | 96 | 146 | 9.6 | 0.97 | 0.26
Diamond | 100 | 200 | 50 | 10 | 4.0 | 9 | 98 | 8.4 | 0.90 | 0.25
Diamond | 100 | 200 | 50 | 5 | 6.3 | 10 | 98 | 5.9 | 0.76 | 0.21
Diamond | 100 | 200 | 50 | 1 | 12.4 | 12 | 98 | 3.6 | 0.59 | 0.16

Table 9.1: Parameters and Mechanical Properties of Nanoladder Resonators $L$, $W$, $T$, $L_{\text{paddle}}$, and $W_{\text{paddle}}$ are defined in Fig. 9-1. Fundamental frequency ($f$) and spring constant ($k$) are computed via Comsol simulation. Quality factor at low temperature, $Q_{\text{Low T}}$, are calculated based on the established linear scaling of $Q^{-1}$ with surface-to-volume ratio. As a reference device, we use $Q_{4k}=150,000$ measured for a standard 4 $\mu$m-wide passivated with a propenyl monolayer (Fig. 10-4). Higher values, up to 250,000, can be achieved with an octyl monolayer, but is less stable in air (Fig. 4-1 and Fig. 5-4).

For ease of fabrication, we restricted the thickness of the structure to be uniform everywhere. We also intended to make the first prototypes via ebeam lithography and dry etching. These constraints dictate that the ladder resonator be composed of nanowire segments with rectangular cross-section. We investigated $T$ of either 50 nm or 100 nm. These are thicknesses that can be controllably accessed for both diamond and silicon and that are improvements over existing standard device thickness of roughly 120 nm. We further restricted the width of the nanowires to be 200 nm. This width can be very comfortably produced with ebeam lithography with good quality of the edge, so surface quality degradation due to roughness effects can be minimized. We finally restricted the range of rail lengths to three values of 50 $\mu$m, 100 $\mu$m, and
Figure 9-2: Ebeam Lithography and ICP Etching of Nanoladders (A) Bright-field optical, dark-field optical, and SEM micrographs of 100 μm-long nanoladders. The device pattern had been transferred from HSQ resist to the underlying silicon via ICP etching. Charging in the SEM is due to the 1 μm buried oxide of the SOI wafer. (B) Zoom-in view of the tip area of a nanoladder. (C) Zoom-in view at the intersection of a rung with a rail. Both are around 80 nm wide. Structures in (B-C) are HSQ resist. (D) Zoom-in view of a rung and the rails. Structure is silicon after HF etching removal of resist. Scale bars are 20 μm, 1 μm, 100 nm, and 1 μm respectively.
200 μm. A constant pitch of 20 μm was chosen due to the proven mechanical stability of SiNW with such length. A longer pitch up to 50 μm may be feasible, but would likely decrease the yield of high-quality devices due to sticking together of the rails. Shorter pitch increases oscillator mass and are not required for the stability. Results for 50 μm and 100 μm-long are shown in Table 9.1.

In calculating the force sensitivities, the only variable parameter is Q. The values used are calculated based on the well-characterized scaling of Q with thickness [13] or, in the case of similar W and T, with surface-to-volume ratio [1]. Therefore, we are optimistic that these values can be achieved. Encouragingly, sub-attonewton sensitivities are achievable even for operation at 4K.

9.3.2 Fabrication of Nanoladder Resonators

The fabrication of nanoladder resonators followed standard ultrasensitive silicon cantilever fabrication protocols except for the resonator definition step. Instead of the usual photolithography, we used ebeam lithography with HSQ as negative resist. Fig. 9-2A-C shows optical and SEM images of ebeam-written ladder structures. Nanowire segments with width down to 30 nm could be written reproducibly, although the relative roughness of the edges became unacceptably large. Thinner lines displayed rare defects along the hundreds of microns lengths that would jeopardize the structural integrity of devices. As a compromise between miniaturization and edge quality, we have chosen conditions such as the resulting resist structure was around 80 nm Fig. 9-2C. The resist pattern was transferred to the underlying silicon or diamond substrate via ICP etching. Fig. 9-2D shows an example of structure in silicon after the removal of HSQ mask in HF.

After the cantilever patterning step, the silicon handle layer was removed from the backside using a standard Bosch process (Fig. 9-3B). Inspection of the sample at this stage revealed significant stress in the oxide film and the formation of crack patterns. Roughly half of the cantilever structures were destroyed by crack lines running across them. A large crack is clearly visible at bottom of Fig. 9-3B. Using SOI wafers with thinner oxide layers is thus a promising future approach for maximizing the final yield.
of cantilevers.

The final step for removing buried oxide was achieved via vapor-phase HF etching. Liquid phase HF etching followed by drying in a new critical point dryer is another option for suspending these delicate mechanical devices. As can be seen in Fig. 9-4, released nanoladder cantilevers were tilted out of the wafer plane, indicating the presence of unbalanced surface stress in the structure. However, due to the extremely low spring constants of these devices, any unbalance is very low and could be caused by a small amount of nonvolatile impurity left onto the cantilever during vapor phase SiO$_2$ etching, or from any other surface asymmetry induced during processing.

The final yield of devices was 40 percent. We have not noticed a relationship between yield and cantilever length or nanowire aspect ratio. Even the longest nanoladder devices (300 μm) survived. These results confirm buried oxide cracking as the major yield-limiting mechanism. We were unable to obtain an SEM image of the release devices, as the scanning electron beam, even when zoomed out, caused the nanoladders to bend severely due to static charging and/or electron bombardment.

We have also fabricated nanocantilevers with width of 500 nm. 100 μm examples are shown in Fig. 9-5. These devices are an optimization of standard devices by a width reduction. Measuring their quality factors is useful for figuring out the dissipation channel in nanoladder resonators.
9.3.3 Nanoladder Mechanical Characterization

<table>
<thead>
<tr>
<th>Device Type</th>
<th>$L$ (µm)</th>
<th>$W$ (nm)</th>
<th>$T$ (nm)</th>
<th>Surface state</th>
<th>$f$ (Hz)</th>
<th>$Q_{rt}$ (measured)</th>
<th>$Q_{300 \text{ mK}}$ (projected)</th>
<th>$k$ (µN/m)</th>
<th>$F_{\text{min}}$ (300 mK) (zN/√Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoladder</td>
<td>200</td>
<td>90</td>
<td>90</td>
<td>As-Fabricated</td>
<td>2237.91</td>
<td>2.650</td>
<td>10,600</td>
<td>0.7</td>
<td>260</td>
</tr>
<tr>
<td>Nanoladder</td>
<td>200</td>
<td>90</td>
<td>90</td>
<td>As-Fabricated</td>
<td>2162.16</td>
<td>1.920</td>
<td>7,700</td>
<td>0.7</td>
<td>350</td>
</tr>
<tr>
<td>Nanoladder</td>
<td>200</td>
<td>90</td>
<td>90</td>
<td>As-Fabricated</td>
<td>1781.05</td>
<td>2.113</td>
<td>8,400</td>
<td>0.7</td>
<td>320</td>
</tr>
<tr>
<td>Nanoladder</td>
<td>200</td>
<td>90</td>
<td>90</td>
<td>HF Vapor</td>
<td>1774.85</td>
<td>3.100</td>
<td>12,400</td>
<td>0.7</td>
<td>200</td>
</tr>
<tr>
<td>Cantilever</td>
<td>100</td>
<td>500</td>
<td>90</td>
<td>As-Fabricated</td>
<td>6442.98</td>
<td>5.320</td>
<td>21,300</td>
<td>15</td>
<td>590</td>
</tr>
<tr>
<td>Cantilever</td>
<td>100</td>
<td>500</td>
<td>90</td>
<td>As-Fabricated</td>
<td>11591.28</td>
<td>5.110</td>
<td>20,400</td>
<td>15</td>
<td>620</td>
</tr>
</tbody>
</table>

Table 9.2: Mechanical Parameters of Nanoladder Resonators and Nanocantilevers $Q$ values at 300 mK are conservative projections assuming $\times 4$ gain upon cooling. $F_{\text{min}}$ values are calculated using the projected 300 mK $Q$ values.

We have measured the room-temperature frequency and quality factors of four nanoladder devices (Fig. 9-6). We have also measured two nanocantilevers with 100 µm length and 500 nm width. These results are presented in Table 9.2. The spring constants of the devices could not be measured accurately because the average thermal excursions of these resonators (80 nm at 300K) were so large that it went beyond the linear response range of the interferometer. This is manifested in the
**Figure 9-5: Ultrasensitive Nanocantilever** A) Bright-field, dark-field optical, and SEM micrographs of patterned devices before backside release. B) SEM micrograph of the tip and paddle region. C) Bright-field and dark-field optical micrographs of a release device. Scale bars are 20 μm in (A,C) and 1 μm in (B).

**Figure 9-6: Thermal Spectrum and Ringdown Curve of a Nanoladder Resonator**
spectrum as peaks at multiples of the fundamental flexural mode frequency (Fig. 9-6A). Measured spring constant values were around 1-2 µN/m, very close to Comsol prediction of 0.7 µN/m. Calculated spring constants were found to be very accurate in our diamond cantilever study. For these reasons, we believe the Comsol value to be more accurate and have used it for force sensitivity estimations.

As can be seen in the table, the quality factors of the 200 µm nanoladder resonators are roughly 2200±500. This value is significantly smaller than what one would expect based on a simple scaling of surface-to-volume ratio. Assuming a rectangular cross section with width \( W \) and thickness \( T \), surface dissipation is proportional to \( \left( \frac{1}{W} + \frac{1}{T} \right) \). Our standard devices fabricated using the same SOI material have width 4 µm and thickness 120 nm. Nanoladders measured here are composed of nanowires with width and thickness both equal to 90 nm. A quick calculation shows that one should expect a factor of 2.6 reduction in \( Q \) compared to \( Q = 15,000 \) in standard devices. So nanoladders, in case they had the same surface quality, should have \( Q = 5,800 \). The measured \( Q \) is therefore \( 2.6(6) = \frac{5800}{2200(500)} \) times smaller than expectation. By the same analysis, 500 nm wide nanocantilevers are expected to have \( Q = 9,900 \). The actual values are \( 1.9(1) = \frac{9900}{5200(150)} \) times smaller. Both values are significantly different from unity and confirm that the sample has more dissipation than what is achievable with this particular SOI material.

The inferior \( Q \) may be due to three factors. First, the vapor phase release may leave significant amount of impurities on the cantilevers. Fig. 9-5C, for example, shows significant amount of light-scattering impurity on the paddle of the device. Secondly, ebeam irradiation during lithography may have induced damage to the silicon lattice. It is known that thermal SiO\(_2\) can be directly patterned by ebeam irradiation, and that nanoscale silicon devices may be modified by high irradiation doses. Finally, sidewall produced during ICP etching may have different intrinsic dissipative properties compared to surfaces on the top and bottom sides of the resonators. The surface roughness, which translates into larger effective surface area, may be larger on sidewalls. The difference between the \( Q \) reduction factors, 2.6(6) for nanoladders and 1.9(1) for nanocantilevers, is marginally significant and would be
consistent with the third possibility.

Device quality can thus be improved by three simple modifications during future fabrication runs. First, one should start the process using SOI wafers with thinner buried oxide. The amount of non-volatile impurities left on release devices is presumably proportional to the oxide thickness. We believe that a buried oxide thickness of 200 nm should be sufficient to serve as etch-stop in the Bosch process. This modification would simultaneously solve the oxide cracking issue that reduces yield. To minimize or reverse potential ebeam damage, an annealing step may be added after ICP etching to release any strain for defect produced during lithography. Finally, to minimize side-wall dissipation, future protocol should consider using anisotropic wet etching. We have performed a preliminary experiment to show that high-quality, atomically smooth side walls can be produced this way (Fig. 9-7). The resulting Si(111) surfaces would in addition improve the stability of chemical surface protection by hydrosilylation (Fig. 4-4C).

9.4 Conclusion and Outlook

This chapter demonstrated that geometric optimization of top-down devices with the aid of ebeam lithography is capable of producing nanomechanical resonators with force sensitivities similar to those achieved in bottom-up synthesis method. The
batch production-compatibility and controllability are important advantages that justify applying the approach to alternative materials including single-crystal diamond. Straight-forward optimization of the fabrication steps, especially the cantilever definition-etch and the final release steps, is expected to further improve the already excellent force sensitivities.
Chapter 10

Single-Crystal Diamond Nanowires and Tips for Ultrasensitive Force Microscopy

This chapter is submitted for publication as:


Abstract

We report the fabrication, integration and assessment of sharp diamond tips for ultrasensitive force microscopy experiments. Two types of tips, corresponding to the upper and lower halves of a diamond nanowire, were fabricated by top-down plasma etching from a single-crystalline substrate. The lower, surface-attached halves can be directly integrated into lithographically-defined nanostructures, like cantilevers. The upper, detachable halves result in diamond nanowires (DNW’s) with tunable diameter and lengths of a few microns. Tip radii were around 10 nm and tip apex angles around 15 degrees. We further demonstrate the integration of DNWs as scanning tips onto ultrasensitive pendulum-style silicon cantilevers. We find the non-contact friction and frequency jitter to be exceptionally low, with no degradation in the intrinsic mechanical quality factor ($Q \approx 150,000$) down to tip-to-surface distances of about 10 nm. Our results are an encouraging step towards further improvement of the sensitivity and resolution of force-detected nuclear magnetic resonance imaging.
Nanomechanical detection of ultrasmall forces is of great interest for a number of applications, including magnetometry of nanoscale magnetic particles [76,77,262], measurement of persistent ring currents [66,67], fundamental tests of physics [263,264], and various types of force microscopy [265]. In particular, the detection of nuclear magnetic resonance signals using magnetic resonance force microscopy (MRFM) [34,36] requires sensitivity of forces in the zeptonewton to attonewton range ($10^{-21} - 10^{-18}$ N). Attonewton force detection has been demonstrated with several types of mechanical sensors, including silicon [222] and diamond [147] cantilevers, silicon nitride beams and membranes [50,56], and silicon nanowires [257]. Excellent force sensitivities, of order Zeptonewtons, were recently demonstrated with suspended carbon nanotube resonators [71] and trapped ions [224]. With the exception of Ref. [257], all of these force sensitivities were demonstrated for freely vibrating beams that were far ($\gtrsim 100$ nm) from a surface.

It is well known in force microscopy that force sensitivities deteriorate as a tip is approached closely to a surface. This undesired non-contact friction effect is due to dissipative forces between the moving tip and the surface [266,267]. Several mechanisms are believed to be effective, including dielectric fluctuations [268], radiative heat transfer [269], and the presence of static or fluctuating surface charge [182,270]. The reduction of surface dissipation has important implications for ultrasensitive force microscopy [34] and other fields, like surface-electrode ion traps [224,271]. Empirical evidence suggests that thin metal layers are effective at screening trapped charges, and that surfaces with low dielectric constants and low loss tangents show the lowest friction. Friction is also reduced by minimizing the tip-surface interaction area, that is, by using tips with a small radius of curvature.

Guided by these design considerations, we have fabricated diamond nanowires (DNW’s) for use as ultrasensitive force microscopy tips. Diamond has a low dielectric constant ($\varepsilon_r = 5.7$), low loss tangent ($\tan \delta < 0.00005$), is wear-resistant and mechanically robust, and is therefore an ideal candidate for a low-friction tip material. We have integrated DNW’s with tip radii down to 10 nm onto ultrasensitive silicon cantilevers and assessed their non-contact friction over a gold surface. We find that such
Figure 10-1: One-Step Fabrication of Single-Crystal Diamond Nanowires with Ultrasharp Tips  
(A) Diamond nanowires formed on a (100) diamond substrate via ICP etching and intrinsic micromasking. Scale bar is 10 μm. (B,C) Zoom-in views of an individual nanowire and its ~15 nm-thin waist region. Scale bars are 1 μm and 100 nm, respectively. (D-J) Time lapse of diamond nanowire growth after (D) 1 min, (E) 3 min, (F) 5 min, (G) 10 min, (H) 20 min, (I) 30 min, and (J) after cleavage of the top and bottom halves. Scale bars are 200 nm.

Tip-modified cantilevers can be approached very close to a surface, less than 10 nm, without increasing mechanical friction or frequency jitter. Diamond nanowire tips thus present an ideal platform for ultrasensitive force measurements with nanometer imaging resolution.

Two processes were developed to fabricate DNW’s with small tip radii. Both recipes followed a top-down approach using masked etching of single-crystal substrates by inductively coupled plasma (ICP) reactive ion etching \[215,272,273\]. In the first approach we exploited intrinsic micromasking by surface defects, while the second approach relied on a lithographically defined etch mask. Although bottom-up methods derived from carbon nanotube growth recipes have also been explored \[274,275\],
top-down etching has the advantage that single crystal material of high quality can be used.

In the micromasking approach, no surface patterning was applied and commercially available optical-grade diamond (100) single crystals (ElementSix Ltd.) were introduced as-received into an ICP etcher. Etching for 30 minutes in 10 mtorr O\(_2\) (30 sccm) using 2100 W ICP and 100 W bias powers led to the formation of randomly distributed pillar structures (Fig. 10-1A-C). The micromasking is most likely due to the unintended presence of impurities on the starting diamond substrate [273]. Indeed, we found that the pillar density can be controllably increased by deliberately introducing additional masking impurities, for example by covering part of the sample with a glass coverslip (SiO\(_2\)) during the etching (Appendix E).

The pillars had two segments, with a pyramidal base connected to a nanowire-like tip via a thin waist. Similar structures have been observed by Hausmann et al. before [215]. We believe that the bi-partite shape of the pillars is controlled by a combination of chemical etching anisotropy, directional etching and electron shading effects. Some of the pyramidal bases distinctly showed what appeared to be crystallographic planes and roughly exhibited four-fold symmetry, suggesting the presence of chemical etching anisotropy. The upper nanowire-like segment is mostly formed by directional etching. Electron shading effects [276] are in addition expected to lead to negative charge build-up near the tip and positive charge build-up near the base (Appendix E), which would promote formation of the waist. A time-lapse of the etching process (Fig. 10-1D-I) shows that both the pyramidal base and nanowire tip grow at roughly the same rate. The pillar structures were found to be stable when the waist diameter was above 10 nm. Additional ICP etching could then be used to completely erode the waist until the two segments separated (Fig. 10-1J). Both segments – the released nanowire and the substrate-bound pyramidal tip – could then be considered for use in scanning probe applications.

We have also fabricated diamond nanowires starting from an electron-beam-defined alumina (Al\(_2\)O\(_3\)) etch mask [215]. Etching a patterned sample with 2500 W ICP and 40 W bias powers for 30 minutes led to an array of structures very similar to pillars
obtained previously by stochastic micromasking (Fig. 10-2A). This demonstrates that DNW’s can be controllably produced at predefined locations. A noticeable difference was the thickness of the upper segment, which was much larger for the lithographically defined pillars due to the much larger size of the etch mask as compared to micromasking impurities (Fig. 10-2B). Again, additional etching was used to controllably pinch off the waist to yield arrays of sharp tips with radii $\lesssim 10$ nm (Fig. 10-2C). The ability to controllably produce diamond tips at predefined locations is an important advantage of lithographically-defined nanowires. For example, tips could be directly integrated onto cantilevers to make, for example, monolithic diamond AFM probes. Single-crystal diamond cantilevers have recently been shown to exhibit outstandingly low internal mechanical friction [213, 277].

In order to assess the potential of diamond tips for sensitive force microscopy, we have measured their non-contact friction over a gold surface. For this purpose, a few nanowires were manually attached at the end of ultrasensitive silicon cantilevers whose mechanical frequency and quality factor could be accurately monitored. The silicon cantilevers were of the kind used in recent nanomagnetometry [66, 67, 76, 77, 262] and mechanical spin detection [69, 278] experiments (see Fig. 10-3(A)), with a mechanical resonance frequency of $f_c \sim 7$ kHz and a spring constant of 160 $\mu$N/m. The cantilevers were surface-passivated (Section A.1.3) so as to increase the low-temperature quality factor to $Q \approx 150'000$ (Chapter 5). DNW’s were first transferred onto a piece of
Figure 10-3: Integration of Diamond Nanowire Tips on Ultrasensitive Silicon Cantilevers (A) Bare silicon cantilever with a nominal length of 90 \( \mu m \), shaft width of 4 \( \mu m \) and thickness of 135 nm. Scale bar is 10 \( \mu m \). (B) Batch of DNW’s (upper halves) transferred onto a Si substrate for manual pick-up. Scale bar is 10 \( \mu m \). (C,D) Zoom-in onto the end region cantilevers where a DNW tip had been attached. Scale bars are 15 \( \mu m \) and 1 \( \mu m \).
gel material (Gel-Pak-4), and then stamped onto a piece of silicon wafer (Fig. 10-3B). Subsequently, individual nanowires could be picked up via van der Waals forces using a pulled glass tip maneuvered by a micromanipulator. The nanowire was then deposited at the tip of the cantilever, where a dab of epoxy glue had been applied. Fig. 10-3(C-E) shows examples of integrated DNW tips.

We have measured the non-contact friction of DNW tips using a pendulum configuration as illustrated in Fig. 10-4(A). Experiments were performed in a custom magnetic resonance force microscope [147] and cooled to $T = 4\, \text{K}$ in a high vacuum environment. The tip was controllably approached to a gold surface via a piezo positioning system. The gold surface was produced epitaxially on c-cut single crystal sapphire following a literature protocol originally developed for the fabrication of single-crystal gold nanowires [279]. To determine the exact separation between the DNW tip and the surface, the cantilever was excited to a constant oscillation amplitude of about 5 nm-pk via feedback-controlled self-oscillation [280] while the distance between the cantilever and the surface was slowly decreased. We defined the $z = 0$ point to be reached when the $z$-piezo extension caused the cantilever oscillation to stop due to the tip physically sticking to the surface. The zero point can also be estimated from the $z$ height at which the diverging cantilever resonance frequency extrapolates to $f_c \to 0$ (see Fig. 10-4(B)) and the two values agreed to within $< 2\, \text{nm}$.

Repeated approach over the same $(x, y)$ location showed that the zero point was reproducible with a standard deviation of less than 1 nm (SI).

Fig. 10-4(C) plots the mechanical quality factor $Q$ as a function of tip-to-surface separation $z$. The $Q$ values were measured using the ring-down method [182]. The $Q$ factor is the key quantity that determines the total mechanical dissipation $\Gamma = k_c(\omega_c Q)^{-1}$ and the force noise $S_F = 4k_B T \Gamma$ of the cantilever. Fig. 10-4 shows that negligible changes in $Q$ are observed up until the tip-surface distance decreased to below 10 nm. Remarkably, even just before reaching contact with the surface ($z \approx 1\, \text{nm}$) the $Q$ factor remained above 40,000. If we subtract the intrinsic mechanical dissipation, given by the baseline value of $\Gamma$ at large tip-to-surface separation (see Fig. 10-4(D)), we find very low values of non-contact friction, about $3 \times 10^{-15}\, \text{kg/s}$.
Figure 10-4: DNW tips experience very little noncontact friction over a gold surface at 4K. (A) Schematic illustration of the experimental configuration. The diamond-tipped silicon cantilever oscillates along $x$ over a gold surface in a pendulum geometry. (B) Cantilever resonance frequency as a function of tip-surface spacing $z$. Different symbols and colors represent measurements over different $(x, y)$ locations on the surface. Vertical dashed line indicates $z = 10$ nm. (C) Mechanical quality factor $Q$ as a function of tip-surface spacing $z$. (D) Mechanical dissipation $\Gamma$ and thermal force noise $S_{F}^{1/2}$ as a function of tip-surface spacing $z$. Dashed line indicates the intrinsic dissipation of $\Gamma_0 = 24 \cdot 10^{-15}$ kg/s. Solid line is a guide to the eye. Values for an equivalent cantilever without DNW tip are given for comparison (open symbols). (E) Frequency jitter $\langle \delta f_{c}^2 \rangle$ as a function of tip-surface spacing $z$. 
at $z = 10\text{ nm}$ and $9 \times 10^{-15}\text{ kg/s}$ at $z = 5\text{ nm}$. Similar low values of non-contact friction have to our knowledge only been observed with silicon nanowire resonators operating at high frequencies ($\sim 1\text{ MHz}$) [257] where dissipative fluctuations are much reduced [271, 281].

In addition to low non-contact frictions, the DNW tips also showed very little frequency jitter $\langle \delta f^2 \rangle$ (see Fig. 10-4E). No additional frequency noise was seen down to a tip-to-surface separation of $z \approx 10\text{ nm}$, and the frequency noise stayed below $10\text{ Hz}^2$ even at the closest separation. Frequency jitter is an issue for ultrasensitive force measurements, because signal pickup requires a stable reference frequency and phase [278]. Moreover, frequency noise can parametrically upconvert to force noise and directly compromise the force sensitivity [282].

The low level of non-contact friction observed in this work is an encouraging step toward nanomechanical detection of nuclear magnetization [33, 34, 36]. Force detection has played an important role in extending nuclear magnetic resonance to the nanometer scale [36], and has, for example, enabled the three-dimensional magnetic resonance imaging (MRI) of single virus particles with about 5 nm spatial resolution [35]. A key requirement for force-detected magnetic resonance is that the sample of interest can be approached as closely as possible to a magnetic gradient source, like a nanoscale ferromagnetic tip [43, 283] or electromagnet [257]. The large magnetic gradient serves to generate a strong magnetic force $F_{\text{spin}}$ on a spin, and it determines the achievable spatial imaging resolution. Gradients of up to $G = 60\text{ G/nm}$ have recently been demonstrated at a tip-to-surface separation of $z \sim 25\text{ nm}$. Even higher gradients could be expected if the tip-to-surface spacing could be reduced. Non-contact friction, however, impedes a further reduction of $z$.

Our experiments suggest that $z \lesssim 10\text{ nm}$ are possible with DNW tips at no cost in force sensitivity. Assuming that the gradient scales inversely with distance $z$, a gradient of order $G = 150\text{ G/nm}$ can be expected at a distance of $z = 10\text{ nm}$ with a tip similar to those in Ref. [283]. Such gradients have, in fact, been demonstrated for magnetic recording heads [284]. The force on a single proton spin in this gradient is about $F_{\text{spin}} \approx 210\text{ zN}$. This force can be compared with the minimum detectable
force for a DNW-tipped cantilever at a tip-to-surface distance of $z = 10\,\text{nm}$, which is about $S_{F/2} = \left[4k_B T/(f_c Q)\right]^{1/2} \approx 3.7\,\text{aN/Hz}^{1/2}$ at $T = 4\,\text{K}$. If we would allow the measurement to be carried out at $T = 300\,\text{mK}$ [69], the minimum detectable force would improve to $S_{F/2} = 1.0\,\text{aN/Hz}^{1/2}$. Such a sensitivity would bring single nuclear spin detection within the reach of acceptable measurement averaging times [69].

In summary, we have presented a simple and effective method for the fabrication of single-crystal diamond nanowires (DNW’s) with typical lengths of a few micrometers and diameters around 100 nm. Tip radii of the nanowires were of order 10 nm, making them suitable probes for scanning probe applications that need very sharp tips. We have assessed the non-contact friction and frequency jitter of DNW-equipped ultrasensitive silicon cantilevers, and find those to be exceptionally low, with no degradation down to tip-to-surface distances $z < 1\,\text{nm}$. Our results are an encouraging step towards further improvement of the sensitivity and resolution of force-detected nuclear magnetic resonance imaging.
Chapter 11

Outlook

11.1 Summary

In this thesis, a mK-temperature magnetic resonance force microscope was constructed to enable device characterization for the development of next-generation ultra-low-dissipation nanomechanical force sensors. The resulting devices have low intrinsic dissipations and force sensitivities in the zN to single-digit aN range at liquid helium temperatures. Another key advance toward single nuclear spin detection was achieved with the reduction of non-contact friction by two orders of magnitude for a tip-surface separations between single-digit to double-digit nm range (Fig. 10-4).

A first method in low-dissipation sensor fabrication consisted of straightforward upgrading of standard ultra-sensitive silicon cantilevers by surface chemical engineering. The modular, post-fabrication processing achieved between a factor of 3-5 improvement in $Q$. A second method explored alternative resonator materials with lower intrinsic dissipation than silicon. High-purity single-crystal diamond exhibited an order of magnitude increase in $Q$ compared to silicon devices of comparable thicknesses, thus representing a viable replacement. A third method is the nanofabrication of a new type of resonator in the shape of a nanoladder. By virtue of its small mass, dissipation is reduced by an order of magnitude. Reduction in non-contact friction was achieved by the integration of a diamond nanowire as the scanning tip.
11.2 Outlook

Magnetic resonance force microscopy has undergone two decades of slow but steady development to advance from a proposal to an instrument with unique capabilities among modern scientific instruments. Numerous exciting advances have been reported in recent years and multiple parallel approaches are being explored by several groups around the globe. A major common goal is to push detection sensitivity by two orders of magnitude to the single nuclear spin level. With the advances described in the present thesis, it is our opinion that such sensitivity is now within reach. We propose the following next steps that could lead to the demonstration of single-nuclear-spin force detection:

Sample Preparation. Due to their large gyromagnetic ratio, the easiest nuclei to use in a single nuclear spin detection demonstration experiment are $^1$H and $^{19}$F. However, protons are omnipresent as part of the physisorption layer on every surface exposed to the atmosphere. Therefore, the use of $^{19}$F may be beneficial if isolated spin on the scanning tip were to be prepared. Several avenues exist for the preparation of such samples.

For $^{19}$F, one may consider the covalent attachment of fluorinated alkyl chains to a diamond nanowire surface, using methods similar to what we have used for silicon passivation. One can alternatively use plasma fluorination, followed by partial thermal desorption to tune the surface concentration of fluorine atoms.

Magnetic Gradient Source. Nanomagnetic gradient source suitable for single nuclear spin detection must exhibit gradients above $10^7$ T/m. A candidate is harddrive write heads that are reported to have gradients as high as $2 \times 10^7$ T/m [284] for a sample-to-write head distance of 35 nm. This distance is easily accessed by a DNW-tipped cantilever (Chapter 10) without additional dissipation, if a smooth metal layer between 10-20 nm thick could be deposited above the write pole. A single proton spin would
experience a force of 0.28 aN in such a gradient. This force is about the same as the design sensitivities of the nanoladder resonators (Tables 9.1 and 9-6). We have already demonstrated that a commercial write head device can be integrated into our MRFM system [285].

**Smooth Metal Layer Deposition.** The smooth epitaxial gold used as the interacting surface is likely to have contributed to the excellent non-contact friction demonstrated in Chapter 10. When the surface has roughness in the single-digit nm range, dissipation is expected to increase more quickly with distance of approach. This could be due to both the tip simply colliding with peaks and/or due to trapped charges at sharp edges. To extend the excellent force sensitivity to thin metal layer deposited directly above the write pole of a harddrive write head, one would need to find conditions for the deposition of 5-10 nm of a low-dissipation surface material with close to atomic smoothness. This should be possible with a screening of deposition methods, including variable-temperature evaporation and atomic layer deposition recipes.

<table>
<thead>
<tr>
<th>Spin</th>
<th>Magnetic Moment ($10^{-28}$ J/T)</th>
<th>Gradient at 10 nm (MT/m)</th>
<th>Single-Spin Force (aN)</th>
<th>Sensor</th>
<th>$F_{min}$-4K (aN/$\sqrt{Hz}$)</th>
<th>SNR= T in (sec)</th>
<th>$F_{min}$-300mK (aN/$\sqrt{Hz}$)</th>
<th>SNR= T in (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>141</td>
<td>20</td>
<td>0.28</td>
<td>Si Nanoladder</td>
<td>0.18</td>
<td>2.9</td>
<td>0.13</td>
<td>0.22</td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>133</td>
<td>20</td>
<td>0.27</td>
<td>Si Nanoladder</td>
<td>0.48</td>
<td>3.2</td>
<td>0.13</td>
<td>0.23</td>
</tr>
<tr>
<td>$^{31}$P</td>
<td>57.1</td>
<td>20</td>
<td>0.11</td>
<td>Si Nanoladder</td>
<td>0.48</td>
<td>19</td>
<td>0.13</td>
<td>1.4</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>35.4</td>
<td>20</td>
<td>0.071</td>
<td>Si Nanoladder</td>
<td>0.48</td>
<td>46</td>
<td>0.13</td>
<td>3.4</td>
</tr>
<tr>
<td>$^{15}$N</td>
<td>14.3</td>
<td>20</td>
<td>0.029</td>
<td>Si Nanoladder</td>
<td>0.48</td>
<td>270</td>
<td>0.13</td>
<td>20</td>
</tr>
<tr>
<td>$^1$H</td>
<td>141</td>
<td>20</td>
<td>0.28</td>
<td>SCD Nanoladder</td>
<td>0.75</td>
<td>7.2</td>
<td>0.098</td>
<td>0.12</td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>133</td>
<td>20</td>
<td>0.27</td>
<td>SCD Nanoladder</td>
<td>0.75</td>
<td>7.7</td>
<td>0.098</td>
<td>0.13</td>
</tr>
<tr>
<td>$^{31}$P</td>
<td>57.1</td>
<td>20</td>
<td>0.11</td>
<td>SCD Nanoladder</td>
<td>0.75</td>
<td>46</td>
<td>0.098</td>
<td>0.79</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>35.4</td>
<td>20</td>
<td>0.071</td>
<td>SCD Nanoladder</td>
<td>0.75</td>
<td>110</td>
<td>0.098</td>
<td>1.9</td>
</tr>
<tr>
<td>$^{15}$N</td>
<td>14.3</td>
<td>20</td>
<td>0.029</td>
<td>SCD Nanoladder</td>
<td>0.75</td>
<td>678</td>
<td>0.098</td>
<td>11</td>
</tr>
</tbody>
</table>

**Table 11.1: Comparing Dipole-Gradient Forces from Single Spins with Force Sensitivities of Optimized Mechanical Sensors**
11.3 Applications

Results from this thesis project allows realistic projections of the force sensitivities of optimized sensors and to compare them with the signal from single nuclei to determine the length of averaging time required to achieve a signal-to-noise ratio of 1 (Table 11.1). A field gradient of 20 MT/m is expected from a nanomagnet with $M_s$ of 1.5 T at 10 nm standoff (Chapter 10). Such, and better, values have been achieved in single-crystal FeCo nanowires we recently developed (not described in this thesis due to constraints of space). The result of the calculation is encouraging; a range of single nuclei should be detectable within reasonable averaging times. Given that MRFM is an intrinsically multiplexed method as a result of the spatial extent of the resonance slice, imaging of 3D volumes with dimensions in the hundreds of nanometers with single-spin sensitivities should be possible.

With the attainment of single nuclear spin sensitivity, it would become possible to perform imaging of macromolecules with sub-nm spatial resolution on a routine basis. This would be an experimental game-changer for the structural analysis of heterogenous biological samples and intrinsically disordered proteins. The technique would also have an extensive impact on material science and engineering, such as for the nondestructive 3-dimensional imaging of interstitial protons and other NMR-active dopant atoms in materials.
Appendix A

Gas-Phase Processing of Silicon Surface

A.1 Experimental Methods

A.1.1 Substrate Preparation

Boron-doped, single-side-polished 2-inch wafers with 10-20 Ω-cm resistivity were used in this study. The Si(100) wafers were cut into 6mm x 6mm squares and Si(111) wafers were cut into similarly-sized trapezoids for easy differentiation. The cutting was done in a cleanroom environment by scribing on the unpolished back side of the wafers. Before cracking along a scribing line (over a piece of particle-free cleanroom towel), the damage track was blown clean with N\textsubscript{2} gas and wiped free of particles with isopropanol-drenched cleanroom towel. Polished side on sample chips thus obtained were free of particles and in the as-received condition.

A.1.2 Preparation, Purification, and Storage of Reagent Gases

The gases used in this study were subjected to additional preparation and purification before use. We have used acetylene (99.6%, PanGas AG, Switzerland), propyne (99%, GFS Organic Chemicals®), 3,3,3-trifluoropropyne (98%, SynQuest Laboratories, Inc.), octene (98%, Sigma-Aldrich®), trivinylphosphine (Toronto Research
Chemicals, 65% in THF over hydroquinone stabilizer), and cyanoacetylene.

Rationale behind the choice of reagents other than cyanoacetylene was laid out in the main text. Motivation for exploring cyanoacetylene was three-fold. First, the cyano group is expected to stabilize a radical at the $\beta$-carbon position, and may facilitate/hinder the hydrosilylation reaction depending on the identity of the rate-determining step. Conjugated alkynes, for example, have been found to provide superior results [135]. Second, the small effective size of the cyanogroup compared to the methyl and trifluoromethyl groups may favor higher saturation surface coverage. Third, once grafted onto the silicon surface, the electro-withdrawing ability of the cyano group may stabilize the surface against oxidation. Cyanoacetylene was syn-

![Figure A-1: The Custom-Built Reactor Used for the Passivation Experiments](image-url)
thesized by the dehydration of propiolamide (97%, Sigma-Aldrich®) by phosphorus pentoxide (99%, Sigma-Aldrich®) using a literature recipe adapted to our CF vacuum systems [286]. Inside a glovebox, powders of propiolamide (1.00 g, 14.5 mmol) and anhydrous phosphorus pentoxide (2.06 g, 14.5 mmol, 1 equiv. based on P₂O₅) were combined and thoroughly mixed in a glass beaker with maximum 32 mm outer diameter (to fit into the inner diameter of CF40 parts). The beaker’s opening was tightly plugged with glass wool to both minimize moisture absorption during transfer from the glovebox to the reactor and prevent powder dispersal during vacuum pumping. The beaker was loaded into the perpendicular branch of a CF40 T-piece and sealed with a blank-flange with a 3 mm-diameter, 2 cm-deep side hole, drilled to accommodate a hotplate thermocouple. A second branch of the T-piece had been connected, via a CF/KF adaptor and a KF valve, to a turbo-molecular pump. The third branch of the T-piece had been connected, via an angled CF valve, to a stainless steel-glass container filled with phosphorus pentoxide (about 1g) sandwiched between 2 pieces of glass wool. The closed system was pumped to a pressure of 5×10⁻⁶ mbar. The valve on the pump side was closed and the blank-flange of the T-piece, above which sat the glass beaker with reactants, was heated on a hotplate to 200°C for 3 hours. During this period, a liquid nitrogen bath was used to freeze any gaseous product into the stainless steel-glass reservoir. About 1-2 cm³ of white solid was collected at liquid nitrogen temperature. The metal CF valve was sealed off and the system was allowed to cool to room temperature before the CF valve-glass reservoir module was dismantled from the preparatory setup. This modular gas source was attached to the main reactor system via one of three available ports.

For all the gases used in this study, phosphorus pentoxide was used as a desiccant to ensure rigorously anhydrous reagents. To load one of the commercial gases, the gas bottle was connected to the reactor setup via a pressure reducer, Swagelok lines/parts, and finally a Swagelok/CF adaptor. The reactor chamber, the gas reservoir, the lines, and all the spaces before the bottle were evacuated to a pressure in the 10⁻⁶ mbar range. The valve before turbo pump was closed and the gas bottle was opened. The chamber was filled to a pressure of 1.2 atm. The source bottle was closed and the
gas was condensed into the reservoir using liquid nitrogen. After closing the reservoir valve and venting the chamber with Ar, the gas source was detached and the system was sealed with a blank flange. To rid the gases of residual oxygen and water, they were each subjected to 5 rounds of freeze-pump-(thaw-evaporate/sublimate)-condense cycles. In the evaporation/sublimation phase, the gas was allowed to fill the entire reactor volume by passing through the phosphorus pentoxide sandwiched between glass wool. The base pressure of the system during the final pumping step was in the range of $10^{-6}$ mbar. The alkynes were then ready for use in the reactions.

To load octene, the liquid and phosphorus pentoxide were directly loaded into the stainless steel-glass CF piece. The reservoir was attached to the system via an angled all-metal valve. The liquid was purified by standard freeze-pump-thaw cycles before use. The octyl-terminated surfaces were prepared at the saturation vapor pressure of octene at room temperature by leaving the gas source open to the chamber during the reaction. Much lower pressure was sufficient for good coverage in the case of decene, but required a continuous flux and consumption of material [152].

100 mg of trivinylphosphine dissolved in THF and stabilized with hydroquinone was purchased for the dopant precursor monolayer attachment experiment described in the main text. The as-received bottle was opened inside an Ar-purged glovebox and its content, around 0.10 ml of liquid, was transferred into a stainless steel-glass CF piece. Phosphorus pentoxide was not added for this experiment due to uncertain reagent compatibility. The stainless steel-glass piece was sealed by connecting to an angled all-metal valve. The closed module was taken out of the glovebox and mounted onto the reactor. The tiny amount of liquid was frozen in liquid nitrogen and purified by 2 cycles of freeze-pump-thaw cycles. Due to the limited amount of material, the vapor pressure during the actual hydrosilylation step was estimated to be around a few percent of an atmosphere assuming complete vaporization.

The gases, when not in use, were allowed to go into the gas-phase inside the reservoirs. For security, a thick polymer tube was fixed around the glass part of the reservoir to protect against possible mechanical failure due to overpressure. There was visible discoloration of the phosphorus pentoxide drying agent overtime, and some
powders may fall down into the bottom of the glass if the bottom glass wool plug was loose. Recondensed gases, however, were colorless, indicating that any colored reaction products (most likely polymers), were not volatile. We have not noticed a difference in the passivation result as the gas sources age.

A.1.3 The Passivation Procedure

To remove the native oxide and passivate the silicon surfaces, scribed wafer chips were subjected to a 3-step sequence. Step # 1 is removal of surface organic contaminants by either a 30-min UV-ozone cleaning (UV Ozone Cleaner-ProCleaner™ Plus) or a 1-min oxygen plasma (Ashers in ETH FIRST Laboratory and BRNC at IBM, Rueschlikon). We have used 200W power at an oxygen pressure of 100 mtorr. An XPS control experiment showed that oxide regrowth rates were indistinguishable on samples pre-cleaned in these two methods and subsequently processed in parallel.

Step # 2 is vapor-phase HF etching. Within minutes of the oxidative cleaning, the samples were loaded into a small custom Teflon chamber equilibrated to the target temperature on top of a hotplate. We have used 50°C for the experiments described in this study, but other temperatures can be used as well. In general, higher temperature leads to lower etching rate, but may lead to better material selectivities in real application scenarios. Lower temperatures may lead to liquid condensation that may compromise NEMS structural integrity. We have, for example, used 65°C to achieve selectivity over ebeam-evaporated alumina. HF/H₂O vapor was applied to the inlet nozzle of the Teflon chamber by bubbling in-house N₂ gas at a rate of 50-200 sccm through ≈ 20 ml of 49% hydrofluoric acid (Sigma-Aldrich) in a polyethylene bubbler. Similar procedures were used for water- and methanol-diluted solutions of HF. Vapor etching was allowed to proceed for 10 minutes. Much shorter durations are probably sufficient for native oxide removal. This is a point that can be optimized in future applications.

An alternative, simpler method is vapor etching in enclosed space without active gas flow. One drop of HF solution was added to a plastic vial with a small block on which the sample could be placed. After introducing the sample, the vial was
sealed with a cap and the etching was allowed to proceed at room temperature for the required length of time. Experiments in Fig. 4-5A, for example, were performed using this method. In future studies of gas-phase HF etching condition for optimal Si-H quality, specialized equipment that permit independent control of sample and source temperature, atmosphere composition, lighting, etc., will be necessary. Future workers are cautioned to become fully aware of the dangers and corrosive properties of hydrogen fluoride and its solutions before starting work in this area!

Step # 3 is surface passivation by gas-phase hydrosilylation. Within 30 seconds of HF treatment, the samples were loaded into the high vacuum reactor chamber that was constantly flushed with Ar (99.9999%, ALPHAGAZ™) to keep out air and moisture during sample loading. A new copper gasket was used for every experimental run to ensure good vacuum. The reactor was pumped down to a pressure around $1 \times 10^{-5}$ mbar within 5 minutes of the HF step, at which point a valve between the turbo molecular pump and the all-CF reactor chamber space was closed. The all-metal construction of the reactor space and sufficient backout of the reactor before the reaction ensured that outgassing did not degrade vacuum to above $1 \times 10^{-4}$ mbar after pumping was stopped. Valve to the gas source was then opened to fill the reactor volume with 1-atm pressure of the reagent gas. The sample plate (modified blank flange) was heated to the required reaction temperature with a hotplate. The reactions were allowed to proceed for 24h. The gas was recondensed back into the reservoir during cooling. The system was pumped back to $10^{-6}$ mbar range before closing the gas source and before venting the system to retrieve samples and, if needed, start a new experimental run.

Propyne samples were prepared at various temperatures between 25°C and 180°C. Acetylene samples were prepared between 80°C and 200°C. 3,3,3-trifluoropropyne samples were prepared between 25°C and 150°C (150°C was optimal). Cyanoacetylene samples were prepared between 120°C to 180°C. Octene samples were prepared at 180°C. Trivinylphosphine samples were prepared at 150°C.

We have also tested sequential thermal hydrosilylation using combinations and permutations of two gases. We have not obtained evidence that sequential treatment
would yield better oxidation protection than optimized recipes using only propyne or using only acetylene. This result may suggest that the optimal recipes led close to full Si-C coverage.

Visible light and UV light were also used for promoting deposition of alkynes on silicon in the gas phase. Instead of a all-metal blank flange as in the thermal reactions, a deep-UV-compatible CF quartz window viewing port was used to pass UV light into the reactor chamber from underneath. Visible light was from an LED flashlight (Energizer: Hi-Tech LED 2-in-1 Light). UV light was produced from a double-bore mercury lamp (Jelight Company, Inc.). Samples were supported, upside down, over a custom copper sample holder with through holes to let the light pass. Samples were within 2 cm from the light source. Visible light reactions were allowed to proceed for 24h. UV exposure was allowed to proceed for 12h.

A.1.4 Samples Storage

After the passivation procedure, samples dies were stored in 4×4 plastic waffle pack sample trays. The closed waffle packs were furthermore wrapped in aluminum foil during storage and transport. Storage temperature and humidity was that of a typical chemistry laboratory (23 ± 2°C, 50 ± 10% humidity).

A.2 XPS Data Acquisition

XPS data were acquired using a Quantum 2000 from Physical Electronics Inc. (Chanhassen, MN 55317 USA). Monochromatized aluminum $K_\alpha$ X-rays with photon energy $\hbar \nu = 1486.7$ eV were used for excitation. The background base pressure in the measurement chamber was $< 2 \times 10^{-9}$ Torr. Samples were fixed onto the sample holder using exclusively metal clamps and screws. The binding energy was calibrated using Au 4f 7/2 at 84.0 eV to an uncertainty of ± 0.1 eV. The electron take-off angle was 45° and the analyzer was operated in the constant pass energy mode of 117.4 eV (calibrated to a total analyzer energy resolution of 1.62 eV for Ag 3d electrons) for survey scans and an analyzer pass energy of 46.95 eV for fine scans (to yield a total analyzer
Figure A-2: XPS Survey Spectra of Si-octyl and Si-propenyl Surfaces No elements other than the ones discussed in the main text could be found.

Figure A-3: XPS Survey Spectra of Si-3,3,3-trifluoropropenyl and Si-ethenyl Surfaces No elements other than the ones discussed in the main text could be found. The ethenyl surfaces were analyzed 1 month after preparation and have 0.04 nm and 0.06 nm oxides on Si(111) and Si(100) surfaces at the time of these acquisitions.

energy resolution of 0.95 eV for Ag 3d electrons). An area of 100 \( \mu \text{m} \) diameter was analyzed.
Figure A-4: XPS Survey Spectra of Si-2-cyanoethenyl Surfaces The surfaces were analyzed 3 weeks after preparation and have substantial oxide growth at the time of these acquisitions. The cyano nitrogen peak is visible.

Figure A-5: XPS Survey Spectra of Si-propenyl Prepared by UV Light-Promoted Reaction Substantial polymerization of the propyne had occurred. The thickness of the product film was proportional to the intensity of illumination. The light was shone from below on a sample supported on top of a sample holder with a hole drilled through. Due to the finite thickness of the sample holder, illumination on the sample was not uniform, with the center receiving most light.

A.3 XPS Survey Spectra

The survey spectra for the types of surfaces studied in this work are presented here. The presented spectra, except those for the Si-2-cyanoethenyl and Si-Ethenyl surfaces, were measured on samples with a maximum of two days of air exposure after preparation and had no measurable SiO$_x$ contribution to the oxygen peak. The preparation procedure for the Si-2-cyanoethenyl surfaces has not been optimized and the kinetics of degradation has not been studied in detail. Their spectra presented here are from 150°C reactions and are measured 3 weeks after preparation, by which point
Figure A-6: XPS Survey Spectra of Si-Trivinylphosphine Surfaces

Beside the expected elements, copper was also observed (around 933 eV). The presence of copper is likely due to the production of an organo-copper species by the reaction of the phosphine with the copper gasket used for sealing. This copper ring was also heated during the reaction, which may have promoted a side reaction. Future applications may need to take place in vacuum chambers without copper parts or prevent copper heating to circumvent this mode of contamination.

0.17(1) nm of oxides had grown. Si-Ethenyl spectra are from surfaces measured one month after preparation. Between 0.04-0.06 nm of oxides had grown by the time of the measurement.

A.4 XPS Fine Scan

In order to obtain quantitative contributions of each detectable element detected on the surfaces, spectral fitting of the different core level peaks using mixtures of Gaussian and Lorentzian line shapes was applied. The total peak area for each element was then divided by the corresponding sensitivity factor. The resulting values were then used to calculate surface atomic percentages.

The key requirement in atomic percentage analysis is to faithfully capture the peak areas. As a result, over-fitting using more components than the spectral shape would warrant, in the presence of a priori information about the chemical structures, is not an issue. Similarly, using a smaller number of chemical components than that we know to be present is also permissible as long as the peak area were well-captured by the resulting fit.

We present representative XPS fine scan spectra in this section. The silicon peaks
Figure A-7: XPS Fine-Scan Spectra of Si(100)-octyl Surface and Modeling Used to Extract Out Peak Areas for Composition Analysis

were found to be completely free of oxides after the gas-phase passivation process. We have used an asymmetric, 2-component peak to model the silicon elemental peak. We note that each of these components is composed of the $p = 1/2$ and $p = 3/2$ orbital contributions with 1:2 area ratio and 0.6 eV separation. To extract elemental silicon contribution from sample spectra with SiO$_x$ contribution, we have used this 2-component asymmetric model with fixed relative position, fixed relative area, and fixed relative line width. The oxygen spectra and most fluorine spectra were satisfactorily fitted using one single component. Fluorine spectra for Si-3,3,3-trifluoropropenyl and Si-trivinylphosphine were fitted using two components.

Due to the presence of adventitious adsorbates, we have not explicitly separated
the carbon peak of Si-octyl surfaces into Si-C and aliphatic components. We have instead simply used an aliphatic ($\approx 285$ eV) and a C-O ($\approx 286$ eV) components. For Si-propenyl and Si-3,3,3-trifluoropropenyl carbon peaks, we have separated the signal into components based on the expected product structure. In the former case, we have used literature chemical shift difference of 1.2 eV between the Si-C carbon and the other two distal propenyl carbons (Components 1 and 3 in Fig. A-8) [119]. In the latter case, the well-resolved -CF$_3$ carbon peak was used as a calibration signal to fix the areas of the 2 other carbon components in the propenyl chain (components 1, 2, and 3 in Fig. A-9). Because the well-resolved -CF$_3$ provides an unequivocal calibration, this analysis suggest that the amount of non-specific carbon adsorbates
Figure A-9: XPS Fine-Scan Spectra of Si(100)-3,3,3-trifluoropropenyl Surface and Modeling Used to Extract Out Peak Areas for Composition Analysis

was roughly similar to the amount of covalently bounded carbon.

### A.5 Silicon Peak Fitting using 5-Component Model

A 5-peak model that takes into account the presence of silicon in different oxidation states is necessary for an accurate analysis of thin oxides on silicon, especially when the total thickness is below 0.2 nm [110]. We have implemented this model used for quantitative oxide thickness determination by XPS analysis, as described in detail by M. P. Seah et al [110]. The 5 components are states with empirical formulae SiO$_2$, Si$_2$O$_3$, SiO, Si$_2$O, and elemental Si. In this model, the chemical shift values for
Figure A-10: XPS Fine-Scan Spectra of Si(111)-ethenyl Surface and Modeling Used to Extract Out Peak Areas for Composition Analysis

We have not measured this type of surface immediately after preparation. The Si(111) variety is presented here as a best available approximation of the pristine state due to the small amount of regrown oxides.

the suboxides are fixed with respect to that of the elemental peak, whereas the full oxide peak (SiO₂) is allowed to move during fitting. We show two examples of the resulting fits, for 1 month-old Si(100)-propenyl samples passivated at 120° and 180° (Fig. A-12).
Figure A-11: XPS Fine-Scan Spectra of Si(100)-trivinylphosphine Surface and Modeling Used to Extract Out Peak Areas for Composition Analysis The phosphorus data are presented in the main text. The reaction was performed at 150°C. The samples were exposed to air for 3 hours between preparation and measurement. The amount of regrown oxide is consistent with the measured surface concentration of phosphine, which would translate into < 30% conversion of Si-H bonds to Si-C even when all phosphine molecules were covalently attached.

A.6 Conversion between SiOₙ/Si Ratio and SiOₙ Thickness

Many authors report oxide regrowth as a ratio between measured SiO₂ and Si elemental peaks. We decided to use thickness units for intuitive clarity and to make it easy for readers to appreciate the atomic scale at which workers in the field are
Figure A-12: Example of Silicon 2p Peak Fitting Using the 5-Peak Model [110]
Top row is a sample processed at 120°C. The bottom row is a sample processed at 180°C. The right column are zoom-in (×10) views.

trying to control surface corrosion. Data from Web and Lewis were provided in both thickness and ratio units, so no conversion was necessary [151]. Data from Puniredd et al. were only reported as ratios [119]. A rigorous conversion between SiO$_x$/Si ratio and SiO$_x$ thickness is model-dependent and would require access to the original raw data, but a direct conversion with errors below order 0.1-nm can be done by a simple multiplication with the proper scaling factor. We have used the data of Web and Lewis and our own data to confirm that for the thin oxide thicknesses studied in these works, the two quantities are very well described via a linear relationship. Therefore, a simple scaling can be used to plot existing literature data against new
Figure A-13: Using our data as training sets, we find that a direct multiplicative factor is sufficient for converting between peak ratio and thickness units. The values of the slopes obtained from this analysis was used to plot literature values on a thickness axis.

As a side note, we remark that in the simplest 2-component model (Si and SiO$_2$), thickness of oxide, $d_{\text{SiO}_2}$, is related to the peak area ratio, $\frac{I_{\text{SiO}_2}}{I_{\text{Si}}}$, via

$$d_{\text{SiO}_2} \propto \ln(1 + A \frac{I_{\text{SiO}_2}}{I_{\text{Si}}}) \quad (A.1)$$

where $A$ is a constant near unity. Therefore, for small $\frac{I_{\text{SiO}_2}}{I_{\text{Si}}}$, oxide thickness and the ratio are linearly related. The situation is more complicated in the case of the 5-component model we used and the direct proportionality, though intuitively evident, is not as easily represented mathematically. We therefore use the empirical illustration described below to justify the conversion procedure by simple scaling.

The data from Puniredd et al. were measured at a take-off angle of 59.5°. Using this value to process our data sets, we obtained plots for calculated thickness vs measured SiO$_x$/Si ratios (Fig. A-13). We have divided the datasets into Si-H, Si-octyl, and Si-propenyl to account for possible systematic differences between the different surfaces, mainly with regards to potential differences in the relative amounts of suboxide and full SiO$_2$ oxides. Given the overlapping confidence intervals of the slope values, performing the analysis with all data lumped together would not have changed the conclusions. We chose to stick to the separation for optimal direct comparability.

The Si-Me(l) data from Puniredd et al. were converted using the value for Si-
octyl(g): 2.84±0.23 nm. Due to structural and electronic similarity, the Si-propynyl(l) data were converted using the value for Si-propenyl(g): 2.98±0.35 nm. Literature peak ratio values were multiplied by these conversion factors to obtain thickness equivalents with error reflecting uncertainty in this direct estimation method.

A.7 Atomic Concentration Evolution on Si(100)

Si(100) data, analogous to those for Si(111) in Fig. 4-2, are presented in Fig. A-14.

![Figure A-14: Atomic percentages of surface carbon (A), silicon (B), and oxygen (C) change as samples were exposed to air for up to three months. Data are for Si(100) samples. Solid lines are guides to the eye.](image)

A.8 Monolayer Reactivity

Fig. 4-1 shows that with the exception of Si-octyl surfaces, other surfaces incorporated oxygen species in forms other than SiO$_x$. The other locations for additional oxygen species to go were either inside or on top of the monolayer. Covalent incorporation of oxygen into the carbon chain of the monolayer, or a change in the oxygen content of the physisorbed layer, would both shift the carbon spectrum. We overlaid peak height-normalized fresh and aged C1s spectra and noticed a visually compelling correlation between the degree of the spectral change with the measured amount of oxygen incorporation. We have verified that the shift in C1s is not due to a simple overall shift of the entire XPS spectra.
Figure A-15: Evolution of C1s Carbon Spectra on Si-octyl Samples We have normalized the plots using maximum peak height. We have further plotted the difference in the normalized spectra as a first step to quantify the change.

To quantify the spectral change, we used a model-independent method. Our approach has the important advantage that no assumption about the identity of the chemical reaction or physical process underlying the change is necessary. We take the
Figure A-17: Evolution of C1s Carbon Spectra on Si-propenyl Samples We have normalized the plots using maximum peak height. We have further plotted the difference in the normalized spectra as a first step to quantify the change.

Figure A-18: Evolution of C1s Carbon Spectra on Si-3F-propenyl Samples We have normalized the plots using maximum peak height. We have further plotted the difference in the normalized spectra as a first step to quantify the change.

difference spectrum between aged and fresh spectra (bottom rows in Fig. A-15-A-18), and sum the absolute value of the difference spectrum to obtain a quantity we call
‘C1s Spectral Change’ in Fig. 4-3G.

It is important to realize that the summation of |spectral difference| gives a quantity that is linearly proportional to the fraction of carbon atoms undergoing chemical change, through reaction and/or dynamic exchange. This fact constitutes a second advantage of our approach. To see why this is the case, imagine that a sample initially had a single peak at 285 eV with peak area of 50 (in arbitrary units). Let’s assume that by a hypothetical process, 100% the carbon in this peak became -CF$_3$ and moved to 292 eV. The spectral difference would contain a negative peak at 285 eV with area 50 and a positive peak at 292 eV with area 50. Then the summation of the absolute value of the spectral difference would give 100. If, say, only 20% of the initial carbon changed to -CF$_3$, the difference spectrum would show a negative peak of area 10 at 285 eV and a positive peak of area 10 at 292 eV. The summation would give 20. Therefore, summation of |spectral difference| gives a quantity that is directly proportional to the ‘conversion’ of carbon. This quantity is the ‘C1s Spectral Change’ on the y-axis in Fig. 4-3G.

One technical detail in the required calculation is the proper handling of statistical error. As a result of the absolute-value operation, random measurement noise add ‘constructively’ in the subsequent summation step. Therefore, a subtraction of the contribution from |random noise| becomes necessary to back out the net spectral shift. To calculate the noise contribution to the summation, we assumed that measurement noise followed Gaussian distribution with standard deviation $\sigma$ and was uncorrelated between successive measurement points. All subsequent additive and subtractive operations on the data sets would then conserve the Gaussian shape, but would broaden the width of the noise term distribution. For example, the standard deviation of noise in the difference spectra would be $\sqrt{2}\sigma$. We took the point-to-point difference in the original spectra. In spectral regions without signal, this point-to-point difference would have zero mean and standard deviation also equaling to $\sqrt{2}\sigma$. By taking its absolute value and summing, we effectively calculate the expectation value of a half-Gaussian distribution multiplied by the number of samples: $2N\sigma/\sqrt{\pi}$. The extra noise contribution, per datum, when summing over the absolute value of
the difference spectrum is therefore: $2\sigma/\sqrt{\pi}$. We subtracted this value (multiplied by the number of data) from the sum to give results presented in Fig. 4-3G of the main text. We noticed that the direction of spectral shift is different for the Si-octyl samples as compared with the other types of surfaces. We adopt the sign convention that a shift to higher binding energies is positive, whereas a shift to lower binding energies is negative.

The spectral region used for background noise calculation is 290 eV-298 eV for Si-H, Si-octyl, and Si-propenyl data. It is 295 eV-298 eV for Si-3,3,3-trifluoropropenyl data.

In the analysis, the normalization of fresh and aged spectra is justified because carbon atomic percentage stayed constant in time (Fig. 2A). Normalizing peak area is more rigorous, but the error is negligible due to small change in the overall line shape, and the same conclusions would result from either a height- or an area-normalization.

### A.9 System Base Pressure and Acetylene-Propyne Comparison

By the end of this study, the base pressure of our vacuum system deteriorated by an order of magnitude due to an unknown, sudden deterioration of performance of the rotary pre-pump (Oil change did not solve the problem and the pump was still ‘too’ operational to enable easy trouble shooting.). We present preliminary data suggesting that the quality of the vacuum could be important for hydrosilylation results (Fig. A-19). This parameter can thus be explored in future efforts.

The data in addition show that around 180°C is the optimal reaction temperature for acetylene. 100-120°C is the optimal range for propyne. Another clear difference that emerges when comparing Fig. A-19 and Fig. 4-1C is the much better protection by propyne exposure at low temperatures. This difference is to be expected based on the stability of hydrosilylation reaction intermediates: a secondary radical in the
Figure A-19: Regrowth of SiO$_x$ after One Month of Air Exposure on Si-ethenyl Surfaces Prepared at Different Hydrosilylation Temperatures

The two open data points were obtained while the vacuum had an excellent base pressure of $2 \times 10^{-7}$ mbar, where as the closed symbols represent samples prepared with vacuum system base pressure of $3 \times 10^{-6}$ mbar.

We also noticed a subtle difference that might contain hints for the importance of Si-C coverage for stability: The difference in oxide regrowth between the crystal orientations might be slight more dramatic on Si-propenyl samples. Given the larger steric bulk of the propenyl group compared to the ethenyl group and the fact that Si(100) surfaces has more dangling bonds, one would expect higher incremental surface coverage of Si(100) when changing from propyne to acetylene. Higher coverage would lead to better oxidation resistance. Test for this hypothesis would require STM-type studies that we have not undertaken.

A.10 Water Contact Angle Measurements

Si-ethenyl samples were prepared at several hydrosilylation temperatures and characterized by static water contact angle measurements using 2 µL sessile droplets. The
Figure A-20: Water contact angle for freshly-prepared Si-ethenyl samples is almost independent of hydrosilylation temperature.

data are presented in Fig. A-20. The results show that this analytical method is not suitable for verifying the quality of such films, as opposed to long-chain hydrocarbon films for which the method is most useful. Therefore, the one-month oxide regrowth thickness we have used seems to be a more sensitive metric of film quality that is also directly relevant for most applications.

We have also measured the water contact angles of bare silicon samples after UV-ozone (or oxygen plasma) cleaning and after either liquid-phase HF or vapor-phase HF treatment. The results are summarized in Table A.1. Each measurement was repeated on 3 samples and the reported uncertainty is their standard deviation. All Si-H samples were measured within 30 seconds of preparation, as we have noticed considerable decrease in the measured value within a couple of minutes of air exposure.

The results show that samples changed from completely hydrophilic to significantly hydrophobic following HF exposure (Fig. A-21). Si(100) sample showed significantly higher water contact angles than Si(111) samples, possibly because of the higher Si-H bond areal density on the former. Existing literature values for hydrogen-terminated silicon surfaces are scattered between 60-80 degrees, consistently lower than what we have measured. Two reasons have likely contributed to this difference. Many workers perform a water rinse after HF etching, effectively prolonging air ex-
posure [287]. The saturation water contact angle may also differ based on the doping level of the silicon material [288].

![Figure A-21: Example WCA Measurements](image)

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Treatment</th>
<th>Static Water Contact Angle (degrees)</th>
<th>Uncertainty (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(100)</td>
<td>30 min UV-ozone</td>
<td>$&lt;2$</td>
<td>NA</td>
</tr>
<tr>
<td>Si(111)</td>
<td>30 min UV-ozone</td>
<td>$&lt;2$</td>
<td>NA</td>
</tr>
<tr>
<td>Si(100)</td>
<td>1 min O₂ Plasma</td>
<td>$&lt;2$</td>
<td>NA</td>
</tr>
<tr>
<td>Si(111)</td>
<td>1 min O₂ Plasma</td>
<td>$&lt;2$</td>
<td>NA</td>
</tr>
<tr>
<td>Si(100)</td>
<td>5 min Liquid HF (49%)</td>
<td>94.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Si(111)</td>
<td>5 min Liquid HF (49%)</td>
<td>87.8</td>
<td>2.7</td>
</tr>
<tr>
<td>Si(100)</td>
<td>10 min Vapor HF (49%)</td>
<td>92.2</td>
<td>2.4</td>
</tr>
<tr>
<td>Si(111)</td>
<td>10 min Vapor HF (49%)</td>
<td>85.1</td>
<td>1.6</td>
</tr>
</tbody>
</table>

**Table A.1: Static Water Contact Angle of Oxidatively cleaned and Hydrogen Terminated Silicon Crystals**

Liquid HF-etched samples showed a slightly higher level of hydrophobicity that was border-line significant (Table A.1). To test whether this difference in the quality of the intermediate Si-H surface were the reason behind the different levels of stability between liquid-phase and gas-phase Si(111)-propenyl surfaces, we have performed gas-phase hydrosilylation simultaneously on gas-phase Si-H and liquid-phase Si-H samples using acetylene at 150°C. The resulting surfaces did not show a significant difference in the thickness of regrown oxide after 1 month, with gas-phase Si-H-derived samples growing 0.19(3) nm and liquid-phase Si-H-derived samples growing 0.21(1) nm of oxides. We therefore conclude that the quality-limiting step in the gas-phase
protocol is not due to a difference in liquid or gas HF oxide stripping, but may be due to the high concentration of residual Si-F bonds formed by concentrated HF etching compared to NH₄F etching, as discussed in the main text. Alternatively, the microscopic heterogeneity of HF etched surfaces, compared to NH₄F etched Si(111), may contribute to the difference.

A.11 Wilcoxon Sign-Rank Test for Statistical Significance–Difference in Kinetics of Fluorine Desorption From Si(111) and Si(100)

![Figure A-22: A pair-wise analysis using Wilcoxon’s signed rank test confirms crystal-orientation dependence of F desorption.](image)

In Fig. A-22, we plot the difference in surface fluorine concentration between all identically treated pairs of Si(111) and Si(100) surfaces measured in this study as a function of air-aging time. We have excluded 3,3,3-trifluoropropenyl samples from this analysis as the relevant fluorine peak overlaps with and is overwhelmed by the CF₃ peak in the XPS spectra, so could not be determined with confidence (Fig. A-9).

We found that the great majority of sample pairs (28 out of 37 pairs) exhibited higher surface fluorine concentration on Si(111) than on Si(100). With the assumptions that the initial and final residual fluorine concentrations are the same on the
two crystal orientations, Wilcoxon signed-rank test showed that the difference was significant with a Z-value of 3.52 ($p < 0.0005$). Together, data in Fig. 4-4A and A-22 show that the difference was initially small, grew in the first week, and decayed over the first a couple of months as surface fluorine concentrations approach 0.6% for both crystal orientations. Si(100) surfaces suffered an initially precipitous drop in surface fluorine concentration, whereas Si(111) crystals experienced a much more gradual rate of loss. We note that the initial difference as plotted on Fig. A-22 was not zero. Given the observed kinetics in fluorine loss from Si(100), this is likely due to the couple of hours of air exposure during transport before measurement for the ‘$t = 0$’ samples. A rigorous calibration of the $t = 0$ difference would require in situ HF treatment in a XPS system. Any initial offset will not likely exceed order 0.1% and would not change the conclusions.

A.12 Phosphorus Peak Background Subtraction

The phosphorus 2p data presented in Fig. 4-5C are presented after a background subtraction procedure. As can be seen in Fig. A-6, P 2p signal is riding on top of a broad silicon plasmonic peak. In order to properly subtract out this background, we first analyzed a total of 11 survey spectra (none-phosphine samples) in the region of interest in order to extract, by curve fitting, the position, the width, and the lineshape (Gaussian/Lorentzian ratio) of the plasmonic feature. The analysis showed that the
plasmonic peak is stable across all sample types, is centered at 134.36(20) eV binding energy, had a width 6.67(33) eV, and was > 98% Gaussian. An example is shown in Fig. A-23A. These parameters were then entered as fixed inputs in the plasmonic background substraction procedure, in which the height of the plasmonic background was allowed to vary. A linear component was also added. The sum of a linear and the gaussian components were fitted to the raw data in the ranges of 127-130 eV and 138-147 eV. An example of the raw data and the fitted background is shown in Fig. A-23B.

A.13 Comments about Future Loadlocked System

![Graph showing comparison between Si(111)-H and Si(111)-ethenyl samples after different exposures.](image)

**Figure A-24:** Better vacuum may be necessary for further improvement.

We have obtained evidence that even brief air exposure was sufficient to promote the growth of oxides on freshly HF-treated samples. This limits the starting quality for Si-C protection and should thus be avoided in optimized protocols. Fig. A-24 compares the Si2p spectrum of a 30 days-old Si-ethenyl sample with that of a 3 minutes-old Si-H sample. The data show that minutes of air exposure was enough to induce the growth of about 0.04 nm of oxide, the same amount as on the one month-old Si-ethenyl sample (Fig. A-24 zoom-in view on right). The data also show a 4 orders of magnitude improvement in air stability via Si-C protection. Future efforts should therefore consider loadlocked systems with ideally *in situ* HF treatment capability that completely avoids air exposure between steps.
A.14 Comments about Light-Promoted Hydrosilylation

![Figure A-25: Si 2p Spectrum of a Si(111)-propenyl Sample Fabricated using UV-Catalyzed Reaction](image)

UV and visible light are standard methods for promoting Si-C formation by hydrosilylation, and have the advantage of energy efficiency over thermal methods. Visible light did not provide increased protection over room-temperature background thermal hydrosilylation of propyne and 3,3,3-trifluoropropyne. UV light was effective but will need further optimization to circumvent/control polymerization. Fig. A-5 shows polymerization of alkyns is a side reaction under UV illumination that may or may not be desirable depending on the particular application. Fig. A-25 shows the Si 2p fine scan of a sample irradiated with UV light at room temperature during hydrosilylation. The sample was exposed to air for several hours before the measurement. The sub-monolayer growth of SiO$_x$ indicates that covalent bond formation between surface Si atoms and propyne had taken place. Future efforts should explore different wavelengths, intensity, dose, and gas pressure.
A.15 Last Comments on Si-F

The presence of Si-F may hasten film aging via several mechanisms. First, their presence deceases the maximum attainable Si-C coverage by taking up sites intended for carbon chains. This is additionally problematic on the Si(100) surface, as the reactivity of the neighboring FSi-H bond might also be reduced. Second, we have seen that alkenyl monolayers may undergo oxidative degradation within the carbon layer. Reduced packing density and steric hindrance due to the presence of Si-F or Si-OH facilitates the infiltration of oxygen and water molecules. A surface silanol group may also catalyze the oxidation of surrounding carbon chains. Third, Si-F hydrolysis leaves ‘pin-hole’ defects for the initiation of silicon suboxide growth. For electrical and mechanical devices, the creation of inhomogeneous point defects may be equally detrimental as the regrowth of native oxide itself. Future research should thus aim to control the amount of residual fluorine after native oxide removal.
Appendix B

Surface Chemical Modifications of Silicon Resonators

B.1 Review of surface reactions on single-crystal silicon

The surface chemistry of single-crystal silicon has been developed extensively in the last sixty years. Methods can be divided into two major categories depending on the presence (I) or absence (II) of the native oxide layer (Fig. B-1). One can
conceptually envision at least three sub-categories of strategies for both I and II: (a) growing a dielectric layer of controlled thickness by the reaction of the resident silicon crystal lattice with other elements, (b) forming a self-assembled monolayer (SAM), and (c) depositing an arbitrary thin film(s) of controlled thickness, crystalline or amorphous, by any available method.

A native oxide-covered surface is the default state for current silicon devices (Rectangle in Fig. B-1). From this starting point, the simplest example of dielectric layer growth (Ia) is the thermal oxidation of silicon [289]. We investigated this process to qualitatively compare the bulk dissipative property of amorphous SiO$_2$ with that of LPCVD Si$_3$N$_4$. SAM formation (Ib) is generally based on S$_N$2 reaction between incoming electrophiles and resident Si-OH nucleophile on the surface. Chlorosilanes, alkoxylsilanes, and silazanes are the most common types of electrophiles in such a silanization strategy that alters surface properties such as surface friction and surface energy, but conserves the properties of the bulk substrate as originally found in the defect-rich Si/SiO$_x$ bimorph. For the purpose of improving $Q$ and electrical performance of silicon NEMS, both intuition and a relevant literature report [15] seem to argue against the utility of this approach. Unexpectedly, however, results presented in this study show that reality may in fact be more complicated (Dashed Arrow in Fig. B-1). While possibilities within Ic are infinite, we have refrained from pursuing this route because mechanical dissipation is additive in layered structures [13].

The second category of approaches to silicon surface modification has focused on the construction of thin dielectric layers (IIa and IIC) and of SAM (IIB) directly on the outermost layer(s) of lattice silicon atoms. The development of these approaches are driven on the one hand by an effort to eliminate the native oxide layer, the formation of which correlate with the degradation of certain electronic properties of the material [151,290], and on the other hand by a quest for high-permittivity dielectric replacements to SiO$_2$ as a gate dielectric for DRAM and FET fabrication [291,292].

IIa contains few possibilities, and is represented by the thermal growth of thin nitrides and oxynitrides on hydrogen-terminated silicon using either N$_2$ gas or NH$_3$ gas
as the nitridizing agent [186, 293–295]. Sub-category IIb is by far the most mature technology; listed approximately in decreasing order of stability to ambient conditions, Si-C, Si-O, Si-N, and Si-X (X=F, Cl, Br) bonds have been demonstrated. Si-C bond construction has been achieved using thermal, radical-initiated, photochemical, sonochemical, or spontaneous hydrosilylation of terminal alkenes and alkynes by a H-terminated silicon surface [121, 127, 130–133, 135, 296–298], via the nucleophilic substitution between an activated Si-X surface [187] with a carbon nucleophile [124], via cyclocondensation on reconstructed surfaces in UHV [299], and by grafting of both carbon-centered electrophiles and nucleophiles onto Si-H surface with or without electrochemical assistance [123, 125, 126, 129]. Most strategies leading to Si-O and Si-N linkages have proceeded under conditions analogous to those for Si-C construction, such as by hydrosilylation of an aldehyde with a Si-H surface [300, 301] and the nucleophilic substitution of activated Si-X by an oxygen- [302] or nitrogen-centered nucleophiles [188, 189]. In the case of Si-N, pericyclic modes of reactivity having no carbon and oxygen analogues have also been reported recently [303]. Finally, high-quality surfaces belonging to sub-category IIc are the most difficult to achieve and are prominently exemplified by the growth of thin crystalline strontium titanate (SrTiO₃) layers in perfect register with a silicon <1,0,0> surface in dedicated molecular-beam epitaxy systems [291]. We have refrained from this last method after consulting with experts in the field, who believe that epitaxial strontium titanate is generally defect-rich and does not significantly slow down oxygen infiltration and oxidation of the silicon crystal.

**B.2 Experimental Methods**

**General** Reagents were purchased from Sigma-Aldrich unless otherwise specified. All solvents used in cleaning and rinsing were of HPLC grade or better. Argon was of 99.9999% purity. Nitrogen was from an in-house supply line. Glassware, Teflonware, titanium sample holders and all surfaces that may come into contact with or in the proximity of the samples and reagent liquids were rigorously cleaned in acetone,
methanol, boiling piranha solution (2:1 H₂SO₄:H₂O₂), and finally DI water. Glassware and stainless steel cannula used for the purification and transfer of alkenes, alkynes, and amines were dried by dehydration bake at 300°C for >30 minutes immediately before use.

**Fabrication** The silicon cantilevers used in this experiments were fabricated from undoped SOI wafers with a 1.5 μm device layer and 1 μm of buried oxide. Procedures similar to those reported in [3] were used. The key difference is the following: The original work uses Si epitaxy from an initially-thin 0.1 μm device layer for forming the mass loading at the tip of the cantilevers. We have, instead, used ICP etching or TMAH wet etching steps from an initially thicker device layer for forming the mass loading. Our as-fabricated devices perform essentially identically to those reported in [3] in terms of frequency, spring constant, and quality factor (cf. Table B.9, Section 0).

**H-termination** This transformation was performed with a two-step procedure. The samples were first UV-ozone cleaned for 10 minutes to remove organic contaminants. They were then placed inside a small, custom Teflon chamber that had been thermally equilibrated to 40°C atop a hotplate. This Teflon reactor chamber is equipped with a receptacle for the hotplate’s feedback thermometer as well as gas inlet/outlet valves. After 5 minutes of thermal equilibration, HF/water vapor generated in a teflon bubbler containing 49% hydrofluoric acid using N₂ as the carrier gas was flushed through the chamber at rates between 50-200 sccm for 10 minutes. Ar gas was then used to flush the chamber for 5 minutes to remove residual HF. Following exposure to air for the desired duration, the sample was mounted into the measurement setup and kept in high vacuum during measurement.

**D-termination** This transformation was performed by a similar procedure, except that DF vapor was generated by bubbling N₂ through a solution of 2.0 M potassium fluoride (KF, anhydrous, powder, >99.99%) and 1.0 M sulfuric acid-d₂ (D₂SO₄, 96-98 wt.% in D₂O, 99.5 atom % D) in deuterium oxide (D₂O, >99.9 atom
% D). The mixture was prepared by adding a solution of KF (0.581 g in 1.15 ml D₂O) to a solution of D₂SO₄ (0.266 ml in 3.00 ml D₂O). The N₂ gas was first dried by passing it through a CaSO₄ drying column to minimize proton contamination from H₂O vapor.

**Oxide formation in the presence of different silane vapors**

These treatments were performed immediately following H-termination by switching the inlet feed gas to the Teflon chamber from HF vapor to silane vapor produced by gently bubbling N₂ through 1ml of the silane contained in a small glass bubbler maintained at 40°C by water bath. N₂ was passed at a gentle rate such that all of the silane evaporated in 20-30 minutes. The procedure was considered completed upon exhaustion of the liquid silane source.

**Liquid-Phase Hydrosilylation**

The alkenes and alkyne were each dried over excess CaH₂ for two days with vigorous stirring and then distilled from CaH₂ under reduced pressure. The distillates were deoxygenated via 4 freeze-pump-thaw cycles under the high vacuum generated with a turbo-molecular pump and finally warmed up to room temperature under a slightly positive Ar pressure. The cantilever samples were mounted onto a titanium holder, treated via the usual UV-ozone/vapor HF sequence, and quickly moved into an aluminum foil-covered 2-ml cylindrical vial (minimize light-induced oxidation before reagent addition) and tightly sealed with clamped septum. The flask was flushed with Ar for 5 min. The freshly purified alkene or alkyne was then added to the vial via cannula under slight Ar pressure to completely cover the devices. The vial was then immersed for the required duration in a temperature-controlled oil bath pre-equilibrated to the required temperature: octadecene (200°C, 2h), octene (120°C, 24h), hexyne (70°C, 12h). After the reactions, samples were rigorously rinsed with gentle agitation in toluene (3x), chloroform (3x), and ultra-pure anhydrous ethanol (12x). Finally, samples were dried from ethanol using a dedicated (brand-new) critical point drier (Tousimis).

**Gas-Phase Hydrosilylation of Alkene and Aldehyde**

The proce-
dure described below was used before the better method presented in Chapter 4 and Appendix A. We recommend that the extra resources be spent for the purchase and assembly of the CF system for better performance, reproducibility, and simplified procedures.

The procedure was performed with the aid of a standard glass distillation head having 4 connection joints. The vacuum/inert gas inlet was connected to a turbo-molecular pump. The thermometer outlet was connected, via a valve, to an Ar line. A 20-ml pear-shaped flask containing 5 ml of octene and excess P$_2$O$_5$ (or octanal over excess 4 Å molecular sieves) was connected to the source joint. The distillate collection joint was temporarily closed with a small, 5-ml round-bottom flask. All joints were greased and gas-tight.

The alkene (aldehyde) was deoxygenated via 4 freeze-pump-thaw cycles under high vacuum and allowed to warm to room-temperature under Ar. Meanwhile, freshly H-terminated cantilever samples were quickly loaded into an aluminum foil-covered 10-ml pear-shaped flask (to minimize light-promoted re-oxidation during the ≈ 30 second air exposure during transfer). The sample flask was then attached to the distillate collection joint of the distillation head under moderate Ar flow. Ar flow was stopped and the system was immediately brought under high vacuum while the alkene source was simultaneously solidified in liquid nitrogen. After two additional rounds of freeze-pump-thaw cycles to remove dissolved Ar, the liquid was frozen and the system was brought under high vacuum one last time. Vacuum valve was closed, the alkene (aldehyde) was allowed to thaw and warm to room temperature, and the silicon sample flask was immersed into a 180°C oil bath for 6 hours. The alkene (aldehyde) source was maintained at room temperature throughout the process.

**Two-step Alkylation and Amination** Following H-termination, the samples were transferred to a nitrogen-flushed glove box maintained at 0.0% relative humidity. The samples were exposed to a vapor of dry (over excess P$_2$O$_5$) and deoxygenated Br$_2$ by creating a partial vacuum over the sample container before opening a valve to the Br$_2$ source. The brown Br$_2$ vapor was seen to immediately fill the
sample container. The exposure lasted 30 minutes. Sample and the Grignard reagent solution (or dry, deoxygenated heptylamine) were added into 2-ml vials and sealed by clamped septum. The vials were heated to the required temperature and for the required duration: methyl magnesium bromide (3.2 M in 2-methyltetrahydrofuran, 90°C, 12h), 1-propenylmagnesium bromide (0.5 M in THF, 110°C, 24h), heptylamine (120°C, 12h). After the alkylation reactions, samples were rigorously rinsed with gentle agitation in THF (3x), methanol (3x), CH₂Cl₂ (3x), acetic acid (3x), toluene (3x), chloroform (3x), and finally ultra-pure, anhydrous ethanol (12x) before drying from ethanol using a brand-new CPD. After the amination reaction, samples were rigorously rinsed with gentle agitation in CH₂Cl₂ (3x), toluene (3x), chloroform (3x), and finally ultra-pure, anhydrous ethanol (12x) before drying from ethanol using a dedicated CPD.

**Thermal Nitridation using NH₃** was conducted using a commercial rapid thermal processing (RTP) system (Annealsys). The reactor chamber volume is roughly 2 liters. Sample is placed on a 4-inch silicon carrier wafer with 1 μm of thermal oxide. The temperature of the sample was assumed to be in equilibrium with that of the carrier wafer, which was monitored using a pyrometer. Within 30 seconds of the usual vapor HF treatment, cantilever and bulk-crystal samples were loaded, via brief air exposure, into the RTP chamber and immediately pumped down to a pressure below 10⁻⁵ mbar. The chamber was back-filled with Ar and evacuated again to below 10⁻⁵ mbar. Under vacuum, the sample was rapidly heated to 450°C at a constant 30% power over about 20 seconds. Temperature was allowed to stabilized to 450°C for 30 seconds under PID feedback. NH₃ was then introduced at a flow rate of 500 sccm for 30 seconds. Ammonia flow was decreased to 100 sccm and the chamber temperature was simultaneously ramped (>35°C/min) to the target temperature and held there for 60 seconds. Following the 60-second treatment, power supply to the heater was cut and the chamber temperature quickly fell to below 450°C. At this point, 100 sccm NH₃ flow was stopped and replaced with N₂ (purity 5.0) purge at 2000 sccm. The sample was allowed to cool to ambient temperature over several
minutes under constant $N_2$ flow.

**THERMAL NITRIDATION USING $N_2$** The same RTA and sample arrangement used for $NH_3$ nitridation were also used here. $N_2$ used in these experiments (except for the post-anneal cooling purge) was purchased at a purity of 6.0 and further purified at the point of use using an inline filter cartridge. Within 30 seconds of the usual vapor HF treatment, cantilever and bulk-crystal samples were loaded, via brief air exposure, into the RTP chamber and immediately pumped down to a pressure below $10^{-5}$ mbar. The chamber was back-filled with $N_2$ and evacuated again to below $10^{-5}$ mbar. $N_2$ was introduced at a flow rate of 1000 sccm for 60 seconds. $N_2$ flow was kept constant at 1000 sccm throughout the following steps. The sample was rapidly heated to 450°C at a constant 30% power over about 20 seconds and allowed to stabilized to 450°C for 5 seconds under PID feedback. The chamber temperature was ramped (>70°C/min) to the target temperature and held there for 60 seconds. Following the 60-second treatment, power supply to the heater was cut and the chamber temperature quickly fell to below 450°C. At this point 1000 sccm ultra-high purity $N_2$ flow was stopped and replaced with N2 (purity 5.0) purge at 2000 sccm. The sample was allowed to cool to ambient temperature over several minutes under constant $N_2$ flow.

Cursory XPS examination showed substantial oxidation in addition to some nitrogen incorporation. Nitridation in $N_2$ is therefore a more finicky procedure than nitridation in $NH_3$. We have refrained from measurement the $Q$ of $N_2$-nitrided samples in light of the XPS results.

**THERMAL NITRIDATION USING $N_2$ AND $H_2$** The treatment was conducted using a recipe similar to that for $N_2$ nitridation. The only difference is that 970 sccm $N_2$ and 30 sccm $H_2$ flows were used in place of the 1000 sccm $N_2$ flow.

**SAMPLE CHARACTERIZATION** Mechanical properties of silicon nanoresonators were measured in a custom-built scanning force microscope originally designed for magnetic resonance force microscopy [69]. Cantilevers were prepared and mounted under ambient conditions and then mounted in a high-vacuum chamber ($<10^{-6}$ mbar)
at the bottom of a dilution refrigerator (\(\sim 65\,\text{mK} - 300\,\text{K}\)). Resonator frequency \(f_c\) and quality factor \(Q\) were measured using the ring-down method [13], and the spring constant \(k_c\) calibrated via a thermomechanical noise measurement at room temperature [222]. As a consistency check \(f_c\) and \(k_c\) were independently calculated from the geometry using a finite element software (Comsol). Resonator motion was detected using a low-power fiber-optic interferometer [115] operating at a wavelength of 1550 nm and producing less than 10 nW of laser light incident at the cantilever. To exclude cavity effects, it was verified that the same \(Q\) factor was obtained whether the measurement was done on the positive or negative (red- or blue-shifted) side of the interferometer fringe. To measure temperature dependence of quality factors, temperature was measured the usual way by slowly (\(\lesssim 0.2\,\text{K/min}\)) sweeping refrigerator temperature and assuming thermal equilibrium between resonator and bath.

**B.3 Tabulation of Key Results**

Some of the key results are given in Table B.1.

**B.4 Quality Factor vs Temperature for Some Important Samples**

We have measured the temperature-dependences of \(Q\) of a commercial LPCVD \(\text{Si}_3\text{N}_4\) cantilever and of a \(\text{SiO}_2\) cantilever produced by thermal oxidation of a silicon device (Fig. B-2). Given the additive nature of mechanical dissipation, this result suggests that replacing the native oxide by a nitride could improve the low-temperature \(Q\) of silicon cantilevers. This result is also the original motivation for investigating thermal nitridation methods.

Fig. B-3 plots the temperature dependance of mechanical quality factor for several important samples. The dip in \(Q\) between 10-20 K observed for the octene sample is most likely not related to the surface treatment, but is likely due to some defect in the bulk for that particular cantilever device. Similar dips has been observed in other
Table B.1: Quality Factors of Cantilevers Follow Various Surface Modifications

All reported $Q$ values are averages from between 5 to 46 measured cantilever devices. The corresponding standard deviations are in the parentheses. Significant improvements over native oxide-covered bench mark devices (Top entry) are marked in red and in bold. $a$: Standard errors in the $Q$ ratios are dominated by the spread of $Q$ values in the native-oxide covered devices, $Q_{300K}$-$SiO_2$. $b$: Not Applicable, such as when $Q$ values represent no improvement over native oxide baseline. $c$: Not Determined. $d$: $Q$ decreased from 72 (28) to 16.7 (2.0) with 15 hours of air exposure. The kinetics of $Q$ evolution suggest that no or little reaction had occurred with this mono-chloride. $e$: Si(CH$_2$)$_2$(CF$_2$)$_5$CF$_3$Cl$_3$;

<table>
<thead>
<tr>
<th>Section</th>
<th>Material</th>
<th>Surface Treatment</th>
<th>$Q_{300K}$ (10$^3$)</th>
<th>$Q_{300K}$-$SiO_2$ (SE)$^a$ (σ)</th>
<th>$Q_{4K}$ (10$^3$)</th>
<th>$Q_{4K}$-$SiO_2$ (SE) (σ)</th>
<th>Air Stability</th>
<th>Time Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Silicon</td>
<td>None, Native Oxide</td>
<td>15.7 (5.7)</td>
<td>1</td>
<td>59 (26)</td>
<td>1</td>
<td>&gt;months</td>
<td>&gt;months</td>
</tr>
<tr>
<td>and Oxides</td>
<td>Si wafer 1 + 2</td>
<td>1000°C in Air, 20h</td>
<td>14.3 (4.0)</td>
<td>0.91 (0.42)</td>
<td>2.13 (0.25)</td>
<td>0.036 (0.016)</td>
<td>&gt;months</td>
<td>&gt;months</td>
</tr>
<tr>
<td>1</td>
<td>Thermal</td>
<td>NH$_3$, 600°C</td>
<td>24.5 (1.3)</td>
<td>1.6 (0.6)</td>
<td>108 (14)</td>
<td>1.8 (0.8)</td>
<td>days</td>
<td>days</td>
</tr>
<tr>
<td>and Nitridation</td>
<td>Si wafer 1</td>
<td>NH$_3$, 700°C</td>
<td>25.8 (0.7)</td>
<td>1.6 (0.6)</td>
<td>114 (2)</td>
<td>1.9 (0.9)</td>
<td>days</td>
<td>days</td>
</tr>
<tr>
<td>and LPCVD Si$_3$N$_4$</td>
<td>Si wafer 1</td>
<td>NH$_3$, 1000°C</td>
<td>36.7 (0.4)</td>
<td>2.3 (0.8)</td>
<td>99 (3)</td>
<td>1.7 (0.7)</td>
<td>days</td>
<td>days</td>
</tr>
<tr>
<td>2</td>
<td>Hydrosilylation</td>
<td>Si wafer 2</td>
<td>SiMe$_2$Cl$_2$ on native oxide</td>
<td>18 (5)</td>
<td>1.1 (0.5)</td>
<td>54 (6)</td>
<td>0.92 (0.42)</td>
<td>NA$^b$</td>
</tr>
<tr>
<td>and Si wafer 1 + 2</td>
<td>Liquid Octene on Si-H</td>
<td>24.5 (2.0)</td>
<td>1.6 (0.6)</td>
<td>188 (5)</td>
<td>3.2 (1.4)</td>
<td>≈ day</td>
<td>&gt;months</td>
<td></td>
</tr>
<tr>
<td>and Si wafer 1</td>
<td>Liquid Octadecene on Si-H</td>
<td>14.0 (1.9)</td>
<td>0.89 (0.35)</td>
<td>126 (7)</td>
<td>2.1 (0.9)</td>
<td>≈ day</td>
<td>&gt;months</td>
<td></td>
</tr>
<tr>
<td>and Si wafer 1</td>
<td>Liquid Hexyne on Si-H</td>
<td>10.7 (3.1)</td>
<td>0.68 (0.32)</td>
<td>125 (15)</td>
<td>2.1 (1.0)</td>
<td>≈ day</td>
<td>&gt;months</td>
<td></td>
</tr>
<tr>
<td>and Si wafer 1</td>
<td>Vapor Octanal on Si-H</td>
<td>41.6 (4.8)</td>
<td>2.7 (1.0)</td>
<td>186 (9)</td>
<td>3.2 (1.4)</td>
<td>≈ day</td>
<td>&gt;months</td>
<td></td>
</tr>
<tr>
<td>and Si wafer 1</td>
<td>Vapor Octene on Si-H</td>
<td>44.7 (7.6)</td>
<td>2.8 (1.1)</td>
<td>261 (22)</td>
<td>4.4 (2.0)</td>
<td>≈ day</td>
<td>&gt;months</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Traditional</td>
<td>Si wafer 1</td>
<td>SiMe$_2$HCl on Si-H</td>
<td>16.7 (2.0)$^d$</td>
<td>1.1 (0.4)</td>
<td>ND</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>and</td>
<td>Si wafer 1</td>
<td>SiMe$_2$Cl$_2$ on Si-H</td>
<td>39 (5)</td>
<td>2.5 (1.0)</td>
<td>57 (2)</td>
<td>1.0 (0.4)</td>
<td>&gt;months</td>
<td>&gt;months</td>
</tr>
<tr>
<td>and</td>
<td>Si wafer 1</td>
<td>SiEt$_2$Cl$_2$ on Si-H</td>
<td>32 (2)</td>
<td>2.0 (0.8)</td>
<td>ND$^c$</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Novel Si wafer 1</td>
<td>SiMe$_2$Cl$_2$ on Si-H</td>
<td>16.7 (2.0)$^d$</td>
<td>1.1 (0.4)</td>
<td>ND</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>and</td>
<td>Si wafer 1</td>
<td>TCTHPPOS$^e$ on Si-H</td>
<td>11.7 (0.5)</td>
<td>0.75 (0.27)</td>
<td>ND</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Protocols</td>
<td>Si wafer 1</td>
<td>HMDS on Si-H</td>
<td>0.90 (0.09)</td>
<td>0.057 (0.022)</td>
<td>ND</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Figure B-2: Quality Factors of a LPCVD Si$_3$N$_4$ Cantilever and of a SiO$_2$ Cantilever as a Function of Temperature
B.5 X-ray photoelectron spectroscopy (XPS) Analysis of Silicon Surfaces

Samples for XPS analysis were cut into 5mm x 5mm square chips from a bulk boron-doped Si(1,0,0) wafer with resistivity between 1-10 Ohm cm. After dicing, the samples were cleaned by sonication in organic solvents, boiling in Piranha solution (10 minutes), extensive rinsing with deionized water, and blow-drying with nitrogen. They were then processed alongside silicon cantilever samples so that both the cantilever devices and the XPS monitor samples receive identical chemical modifications. Upon termination of chemical treatment, the samples were kept under high-purity (6.0) Ar gas for transportation to the XPS instrument (1-2 hours). They were finally analyzed
following the indicated duration of air exposure (between opening of the Ar-filled container and start of pumpdown in the loadlock of the XPS instrument).

Detailed XPS studies were conducted for vapor HF-treated samples (Fig. B-4, Table B.2), thermal nitridation samples (Fig. B-5, Table B.3), SiH samples exposed to dichlorodimethylsilane vapor (Fig. B-6, Tables B.4 and B.5), and SiH as well as native-oxide samples exposed to trichloro(1H,1H,2H,2H-tetrahydroperfluorooctyl) silane vapor (Fig. B-7, Table B.6). They are presented in this section. The determination of SiO$_x$ thicknesses was based on methods described in reference [110]. Hydrosilylation samples were only cursorily examined and were found to agree with extensive literature reports and are not presented here.

![Figure B-4: XPS Analysis of the ⟨1,0,0⟩ Si-H Surface Prepared by Vapor HF Treatment as a Function of Ambient Air Exposure Time Data are for Si2p emission. A, 2 minutes of air exposure. B, 10 minutes of air exposure. C, 60 minutes of air exposure. D, 1 month of air exposure.](image-url)
Table B.2: Summary of XPS Analysis of the Thicknesses of Regrown Native Silicon Oxides Following Vapor-Phase H-Termination and Air Exposure

<table>
<thead>
<tr>
<th>Air Exposure (Minutes)</th>
<th>SiO$_2$ Total Area A.U.</th>
<th>Si Peak Area A.U.</th>
<th>SiO$_2$ Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>48</td>
<td>1206</td>
<td>0.10</td>
</tr>
<tr>
<td>10</td>
<td>367</td>
<td>1458</td>
<td>0.58</td>
</tr>
<tr>
<td>60</td>
<td>342</td>
<td>943</td>
<td>0.80</td>
</tr>
<tr>
<td>48,000</td>
<td>428</td>
<td>979</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Table B.3: Summary of XPS Analysis of the Thicknesses and Compositions of Oxynitrides Formed on Si-H Surface during Thermal Nitridation in NH$_3$

<table>
<thead>
<tr>
<th>Process Temperature ($^\circ$C)</th>
<th>SiO$_2$ Total Area A.U.</th>
<th>Si Peak Area A.U.</th>
<th>SiO$_2$N$_x$ Thickness (nm)</th>
<th>Nitrogen Area A.U.</th>
<th>Oxygen Area A.U.</th>
<th>% Nitrogen (min Estimate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>569</td>
<td>1698</td>
<td>0.75</td>
<td>307</td>
<td>1329</td>
<td>25</td>
</tr>
<tr>
<td>700</td>
<td>607</td>
<td>1131</td>
<td>1.11</td>
<td>579</td>
<td>988</td>
<td>46</td>
</tr>
<tr>
<td>800</td>
<td>716</td>
<td>985</td>
<td>1.40</td>
<td>940</td>
<td>979</td>
<td>59</td>
</tr>
<tr>
<td>1000</td>
<td>1089</td>
<td>651</td>
<td>2.51</td>
<td>1753</td>
<td>1032</td>
<td>71</td>
</tr>
</tbody>
</table>

For nitrogen content as a percentage of total nitrogen and oxygen content, we have divided the raw measured peak areas by the relative sensitivity factors (RSF) of the emitting orbitals: 0.499 for N1s and 0.733 for O1s. Raw data and fits are presented in Fig. B-4.
Figure B-6: XPS Analysis of The $\langle 1,0,0 \rangle$ Si-H Surface After Treatment by Vapor-Phase Dichlorodimethylsilane as a Function of Ambient Air Exposure Time Data are for Si2p emission. A, 10 minutes of air exposure. B, 60 minutes of air exposure. C, 900 minutes of air exposure.

Table B.4: Summary of XPS Analysis of Poly-dimethylsiloxane Thin Film Formed on Si-H Surface The thicknesses and compositions of polydimethylsiloxane thin film formed by vapor phase exposure to dichlorodimethylsilane are presented as functions of air exposure time. Raw data and fits are presented in Fig. B-6.

<table>
<thead>
<tr>
<th>Air Exposure (Minutes)</th>
<th>SiO$_2$ Peak Area A.U.</th>
<th>-O-SiMe$_2$O- Peak Area A.U.</th>
<th>Si Peak Area A.U.</th>
<th>Polydimethylsiloxane Thickness (nm)</th>
<th>SiO$_2$ Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1171</td>
<td>2515</td>
<td>4351</td>
<td>0.96</td>
<td>0.62</td>
</tr>
<tr>
<td>60</td>
<td>1257</td>
<td>2671</td>
<td>3734</td>
<td>1.09</td>
<td>0.75</td>
</tr>
<tr>
<td>900</td>
<td>1388</td>
<td>2720</td>
<td>3756</td>
<td>1.08</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Table B.5: A surface atomic concentration analysis confirms that the empirical formula of the thin film obtained by treating Si-H with dichlorodimethylsilane vapor to be that of polydimethylsiloxane: (SiMe$_2$O)$_n$. These values are calculated assuming oxygen has the same level of contamination as carbon. Therefore, the values are the maximum amount of oxygen that could be found in the polymer film.

For dichlorodimethylsilane-treated samples, we also performed an analysis of the relative atomic concentrations of carbon (C1s), oxygen (O1s), and silicon (Si2p) to confirm that the none-SiO$_x$ component is consistent with a species with empirical formula (SiMe$_2$O)$_n$. 

221
Figure B-7: XPS Analysis of $\langle 1,0,0 \rangle$ Si-H Surface (Top Row) and $\langle 1,0,0 \rangle$ Si Surface with Normal Native Oxide (Bottom Row) after Treatment by Vapor-Phase trichloro(1H,1H,2H,2H-tetrahydroperfluorooctyl) Silane The silicon signals are satisfactorily fitted to 2 components. The carbon signal was fitted to 3 components, as expected. The oxygen and fluorine signals are well-modeled by single peaks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total C</th>
<th>Total F</th>
<th>Total O</th>
<th>Si: Crystal</th>
<th>Si: SiO$_2$</th>
<th>SiO$_2$ (nm)</th>
<th>SiO$_2$ (nm)</th>
<th>O$_2$Si-R SiO$_2$-equi. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor On Si-H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atomic Percent</td>
<td>11.5</td>
<td>19.3</td>
<td>37.3</td>
<td>11.7</td>
<td>14.6</td>
<td>2.07</td>
<td>1.94</td>
<td>0.13</td>
</tr>
<tr>
<td>Normalized to F</td>
<td>8.9</td>
<td>15</td>
<td>29</td>
<td>9.1</td>
<td>11.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor On Native Oxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atomic Percent</td>
<td>13.5</td>
<td>26.5</td>
<td>33.7</td>
<td>12.2</td>
<td>14.1</td>
<td>1.96</td>
<td>1.79</td>
<td>0.17</td>
</tr>
<tr>
<td>Normalized to F</td>
<td>7.6</td>
<td>15</td>
<td>19</td>
<td>6.9</td>
<td>7.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table B.6: Summary of Surface Atomic Concentration Analysis of Trichloro(1H,1H,2H,2H-tetrahydroperfluorooctyl) Silane Vapor-Treated Samples. Results confirm the formation of a fluoroalkyl monolayer on both types of starting surfaces. Compared to the structure formed on already-formed native oxide surface, the oxide grown from a Si-H surface appears slightly thicker and its surface fluoroalkyl monolayer, slightly less densely-packed.

B.6 Frequency and Quality Factor Data from Cyclic Oxide Removal-Native Oxidation Experiments

The devices used in this experiment come from Wafer 2 (see Table B.9), which displayed lower $Q$ at room temperature in the Si-H state.

In the present study, XPS measurements show negligible amount of silicon oxides remaining on the surface right after each hydrofluoric acid vapor step. In this oxide-free
Table B.7: Frequency and Room-Temperature Quality Factor Evolution During Cyclic DF/HF Exposure and 1h Air Oxidation Experiments

state, the mechanical frequency of the cantilever is directly proportional to the silicon crystal thickness. The ratio of frequencies between two successive DF treatment steps thus reflect the ratio of bare silicon thicknesses between those steps. The initial cantilever thicknesses are precisely known from fabrication, SEM characterization, and Comsol simulation. Without distinguishing the suboxides (maximum 0.12 nm per cantilever side [110]) from the dioxide, one can thus obtain the thickness of silicon lost as silicon oxides after each air-oxidation/DF cycle. This value in turn gives the thickness of corresponding native oxide film that had been present on the surface before vapor-phase removal. As a result, all quantities in Equation (1) of main text, with the exception of $E_{\text{SiO}_2}$, can be directly obtained from the data or literature. As shown in the main text, the data is consistent with theoretical predictions of a Si/SiO$_x$ bimorph cantilever, with a native oxide film having a thickness-independent, in-plane Young’s modulus of 97.1±1.7 GPa (assuming density is the same as for bulk fused quartz).

We note the presence of randomness in the thickness of oxide regrowth over different 1-h periods and among different devices on the same sample chip. Due to the marked dependence of native oxidation rate on various environmental factors like relative humidity, lighting, and temperature, this level of spread is to be expected for an experiment conducted over several days in our laboratory without temperature or humidity control. To our knowledge, this study is the first direct experimental determination of the Young’s modulus of sub-mm-thin native SiO$_2$ films.
**B.7 Si and SiO$_2$ Material Properties Used in Data Analysis**

In order to derive the Youngs’ modulus of native oxide films from measured cantilever frequency data, we used the following material constants: $E_{Si} = 171$ GPa, $\rho_{SiO_2} = 2.203$ g/cm$^3$, and $\rho_{Si} = 2.329$ g/cm$^3$. In the calculation, we assume that the density of the native oxide is the same as that of fused quartz. This assumption is equivalent to neglecting the presence of suboxides, which are expected to have densities between those of silicon and fused quartz, thus higher than the value for fused quartz. We also assume that the thickness of grown oxide to be directly proportional to the thickness of lost silicon crystal, via a proportionality constant of 2.27 based on the volume expansion in the reaction from Si to SiO$_2$.

**B.8 Oxide Growth Underneath Polydimethylsiloxane Thin Film**

![Graph](image)

Figure B-8: Fractional Frequency Change of Cantilevers that Had Been Exposed to Dichlorodimethylsilane (DCDMS) Vapor as a Function of Post-Treatment Air Exposure

XPS measurements show that surface oxide formation in the presence of DCDMS vapor lead to a 1 nm polydimethylsiloxane film covering a native oxide on top of crystalline silicon. XPS also shows that when exposed to air, the oxide layer underneath
this thin polymer film continues to grow. When DCDMS-treated cantilevers were monitored over a 40-day air exposure period, monotonic decrease in resonance frequencies was observed, suggesting continued thickening of the oxide layer (Fig. B-8, Table B.8). Here, we analyze the cantilever frequency data to extract the temporal evolution of SiO\(_2\) thickness and the Young’s modulus of the underlying oxide film formed in such a ‘template-directed’ native oxidation process.

We can neglect the 1 nm polydimethylsiloxane in the following analysis. We are justified to do so as long as its structure does not significantly change over time, so that its presence merely adds a small (relative to the resonance frequency) constant value to all measured frequencies. XPS measurements have confirmed that the thickness of this polymer film is constant in time.

We consider the sample upon the first frequency measurement as the reference and calculate additional SiO\(_2\) growth compared to this initial measurement. Let the thickness of the silicon core and the measured frequency at the first measurement be \(t_0\) and \(f_{0m}\), respectively. We call \(f_0\) the frequency that one would measure had it been possible to selectively remove the polydimethylsiloxane film and the initially-formed underlying oxide of thickness \(t_{SiO_20}\), leaving only the silicon core of thickness \(t_0\). Such a procedure is obviously not yet possible to achieve experimentally. To proceed further, we therefore need to express \(f_0\) as a function of measured values \(f_{0m}\) and \(t_{SiO_20}\), the oxide thickness upon first measurement.

The measured initial frequency, \(f_{0m}\), is related to \(f_0\) via \(f_{0m} = f_0 + \Delta f_0\), where

\[
\Delta f_0 = \left( \frac{3E_{SiO_2}}{2E_{Si}} - \frac{\rho_{SiO_2}}{2\rho_{Si}} \right) \frac{t_{SiO_20}}{t_0} f_0 \equiv \alpha \frac{t_{SiO_20}}{t_0} f_0 \tag{B.1}
\]

Here, \(E\) and \(\rho\) are the Young’s moduli and material densities. Therefore,

\[
f_0 = (1 + \alpha \frac{t_{SiO_20}}{t_0})^{-1} f_{0m} \tag{B.2}
\]

When an additional oxide thickness, \(\Delta t_{SiO_2}\), grows on the cantilever, the silicon core reduces in thickness to a value
where $\beta = 2.27$ is the volume expansion factor when silicon oxidizes to fused quartz. Due to the constrained geometry in a surface thin film, this volume expansion is confined to the thickness dimension perpendicular to the film surface.

At later measurements, we measure a frequency $f_m = f + \Delta f$, where $f$, analogous to $f_0$, would be the frequency of a cantilever had we been able to selectively remove the oxide, and $\Delta f$ is the contribution of the oxide layer to the experimentally accessible $f_m$. Similar to $f_0$, $f$ is beyond experimental reach, but can be expressed as $f = \frac{t}{t_0} f_0$ based on the scaling of frequency with cantilever thickness. Eliminating $f$ from the expression for $f_m$, we have

$$f_m = t \frac{f_0}{t_0} + \Delta f$$  \hspace{1cm} (B.4)

$\Delta f$ is found similarly to $\Delta f_0$:

$$\Delta f = \left( \frac{3E_{SiO_2}}{2E_{Si}} - \frac{\rho_{SiO_2}}{2\rho_{Si}} \right) t_{SiO_2} f \equiv \alpha \frac{t_{SiO_2}}{t} f = \alpha \frac{t_{SiO_2}}{t_0} f_0$$ \hspace{1cm} (B.5)

Combining Equations (B.2) to (B.5) and solving for $\Delta t_{SiO_2}$ we have,

$$\Delta t_{SiO_2} = \frac{\left[ f_m f_{m0} \left( 1 + \alpha \frac{t_{SiO_2}}{t_0} \right) - 1 \right] t_0 - \alpha t_{SiO_2} f_0}{\alpha - \frac{1}{\beta}}.$$ \hspace{1cm} (B.6)

It is clear that because $t_{SiO_20}$ is vanishingly small compared to $t_0$, the value of $\Delta t_{SiO_2}$ is practically independent of the value of $t_{SiO_20}$ one enters into the equation. For consistency, we use the value of 0.62 nm as determined by XPS in Table B.4. $t_0 = 115$ nm is known from fabrication and confirmed by SEM inspection as well as Comsol simulations. Therefore, $\Delta t_{SiO_2}$ only depends on $\alpha$, a parameter that summarizes the material properties. We had previously determined the Young’s modulus of natural native oxide to be 97.1(1.7) GPa, corresponding to $\alpha = 0.379$. However, it is not valid to assume that an oxide formed under a 1-nm polydimethylsiloxane should
have the same materials properties as the natural native oxide. Therefore, we used the XPS data presented in Table B.4 to calibrate the frequency change data. The calibration gives $E_{\text{SiO}_2} = 74.7$ GPa, corresponding to $\alpha = 0.181$. This value for the Young’s modulus is very close to commonly reported values of amorphous quartz. The differences in the Young’s moduli and dissipation of surface oxides formed under difference conditions may suggest differences in their atomic structures.

Table B.8: Frequency and Room-Temperature Quality Factor Evolution of DCDMS Vapor-Treated Cantilevers

<table>
<thead>
<tr>
<th>Device</th>
<th>$f$ (Hz) 10 min Air</th>
<th>$Q$ 10 min Air</th>
<th>$f$ (Hz) 1 h Air</th>
<th>$Q$ 1 h Air</th>
<th>$f$ (Hz) 15 h Air</th>
<th>$Q$ 15 h Air</th>
<th>$f$ (Hz) 3 days Air</th>
<th>$Q$ 3 days Air</th>
<th>$f$ (Hz) 40 days Air</th>
<th>$Q$ 40 days Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7374.5</td>
<td>38580</td>
<td>7371.2</td>
<td></td>
<td>36001</td>
<td>7369.5</td>
<td>37778</td>
<td>7365.0</td>
<td>37077</td>
<td>7359.0</td>
</tr>
<tr>
<td>2</td>
<td>6023.0</td>
<td>59966</td>
<td>6019.7</td>
<td>32127</td>
<td>6018.3</td>
<td>35186</td>
<td>6014.8</td>
<td>33102</td>
<td>6009.6</td>
<td>33255</td>
</tr>
<tr>
<td>3</td>
<td>4974.3</td>
<td>37441</td>
<td>4971.1</td>
<td>33807</td>
<td>4969.9</td>
<td>36259</td>
<td>4966.9</td>
<td>34649</td>
<td>4962.2</td>
<td>34307</td>
</tr>
<tr>
<td>4</td>
<td>4969.4</td>
<td>40040</td>
<td>4966.0</td>
<td>37778</td>
<td>4964.6</td>
<td>40815</td>
<td>4961.2</td>
<td>38297</td>
<td>4956.1</td>
<td>38174</td>
</tr>
<tr>
<td>5</td>
<td>5999.1</td>
<td>44181</td>
<td>5994.9</td>
<td>38407</td>
<td>5993.1</td>
<td>42545</td>
<td>5988.3</td>
<td>39002</td>
<td>5981.3</td>
<td>39715</td>
</tr>
<tr>
<td>6</td>
<td>7443.2</td>
<td>44429</td>
<td>7439.2</td>
<td>38543</td>
<td>7437.6</td>
<td>43156</td>
<td>7432.0</td>
<td>38101</td>
<td>7423.9</td>
<td>38059</td>
</tr>
</tbody>
</table>

Table B.8: Frequency and Room-Temperature Quality Factor Evolution of DCDMS Vapor-Treated Cantilevers Devices 1 and 6, 2 and 5, 3 and 4 are 90, 105, and 120 $\mu$m long, respectively.

B.9 Other Tested Silicon Surface Modification Strategies With Results That May be Optimized

B.9.1 Two-Step Alkylation and Amination Reactions (IIa)

These experiments are based on the now-standard halogenation/alkylation sequence first reported by Bansel et. al. [124]. These two-step procedures did not lead to improvement in $Q$. In the alkylation case, we attribute the result to visible reaction residues on the silicon surface due to inability to apply ultrasonic assistance during post-reaction solvent rinsing and cleaning (fragile cantilevers break instantaneously even with weak sonicator power).

B.9.2 Spontaneous Diazonium Salt Grafting (IIa)

This experiment was based on results in [304], where immersion of silicon $<1,0,0>$ wafers into a solution of diazonium salt and HF (2%) in CH$_3$CN/H$_2$O (1:1) led to
Table B.9: Quality Factors of Cantilevers Following 2-Step Alkylation/Amination Procedures

<table>
<thead>
<tr>
<th>Device From</th>
<th>Surface Treatment</th>
<th>$Q_{300K} (10^3)$</th>
<th>$Q_{300K}/Q_{4K}$ (SE)(^a)</th>
<th>$Q_{4K} (10^3)$</th>
<th>$Q_{4K}/Q_{4K-SiO_2}$ (SE)(^a)</th>
<th>Air Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si wafer 2</td>
<td>Heptylamine on Si-Br</td>
<td>12.2 (1.6)</td>
<td>0.78 (0.30)</td>
<td>55 (17)</td>
<td>0.93 (0.50)</td>
<td>NA</td>
</tr>
<tr>
<td>Si wafer 2</td>
<td>MeMgBr on Si-Br</td>
<td>6.3 (1.0)</td>
<td>0.40 (0.16)</td>
<td>52 (12)</td>
<td>0.88 (0.44)</td>
<td>NA</td>
</tr>
<tr>
<td>Si wafer 1</td>
<td>Allyl MgBr on Si-Br</td>
<td>9.3 (0.9)</td>
<td>0.50 (0.22)</td>
<td>46 (4)</td>
<td>0.78 (0.35)</td>
<td>NA</td>
</tr>
</tbody>
</table>

native oxide removal and the deposition of an organic thin film of controllable thickness (by adjusting reaction time). Based on Table 1 in [304], we chose to use an Ar-sparged 4-bromobenzenediazonium tetrafluoroborate (0.20 mM) solution in 2% HF in CH\(_3\)CN/H\(_2\)O (1:1) and a reaction time of 10 minutes.

We first established a method for reversibly dipping the cantilevers into a liquid and retracting them back into the air. The cantilever chip was mounted, tip pointing down, on a micromanipulator. The vertical movement of the sample could be controlled with about 5 \(\mu\)m accuracy by constantly monitoring the sample through a microscope. The sample was positioned over a small Teflon beaker of Ar-sparged 2% HF in 50% CH\(_3\)CN. The cantilevers shafts were lowered into the liquid (until 10 \(\mu\)m from the base) for 5 seconds and quickly retracted up, out of the liquid. It is essential to preventing the liquid from getting into contact with the base of the cantilevers, i.e. the silicon chip. Because otherwise, surface tension would cause the liquid to climb up and completely cover the small sample chip. If this wetting happens, tedious critical-point drying becomes necessary.

The frequencies and $Q$s measured following 5-min air exposure confirmed successful SiO\(_2\) removal. The sample was then mounted back onto the micromanipulator and immersed into the 0.20 mM 4-bromobenzenediazonium tetrafluoroborate solution for 10 minutes. The sample was remeasured after the grafting reaction. Results in Table B.10 suggest formation of a rather thick coating on the cantilevers. The color of the cantilevers in areas that had been exposed to the liquid vs areas that had stayed dry were markedly different, confirming the formation of a thick film.

Due to difficulties associated with precise control of coating thickness, this methods has not been pursued further. Future studies should consider a dedicated setup
inside a glovebox to eliminate potential complications such as O\textsubscript{2}-promoted polymerization and oxidation.

<table>
<thead>
<tr>
<th>Device</th>
<th>$f$ (Hz)</th>
<th>$Q$ (300 K)</th>
<th>$f$ (Hz)</th>
<th>$Q$ (300 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7,593</td>
<td>61,331</td>
<td>6,281</td>
<td>3,513</td>
</tr>
<tr>
<td>2</td>
<td>6,124</td>
<td>61,138</td>
<td>4,873</td>
<td>2,544</td>
</tr>
<tr>
<td>3</td>
<td>5,048</td>
<td>49,723</td>
<td>3,870</td>
<td>2,544</td>
</tr>
<tr>
<td>4</td>
<td>5,340</td>
<td>53,018</td>
<td>4,217</td>
<td>2,239</td>
</tr>
<tr>
<td>5</td>
<td>7,478</td>
<td>53,398</td>
<td>6,180</td>
<td>3,219</td>
</tr>
</tbody>
</table>

Table B.10: Results for Spontaneous Diazonium Alkylation

B.9.3 Atomic Layer Deposition (ALD) of Al\textsubscript{2}O\textsubscript{3} (IIc)

Samples were H-terminated as usual and loaded into a commercial ALD system with <1 min air exposure during transfer. Al\textsubscript{2}O\textsubscript{3} coating (10 cycles) was performed with 0.1 second reagent pulses and 4 sec pumping steps at a temperature of 110 °C. Measurements at room temperature were performed following 20 minutes and 2 hours of air exposure. The significant decrease in both frequency and quality factor points to the inefficiency of the treatment at preventing oxidation. Future efforts along this direction should consider thicker ALD films and alternative materials.

<table>
<thead>
<tr>
<th>Device</th>
<th>$f$ (Hz)</th>
<th>$Q$ (300 K)</th>
<th>$f$ (Hz)</th>
<th>$Q$ (300 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4313.97</td>
<td>20,591</td>
<td>4301.21</td>
<td>16,657</td>
</tr>
<tr>
<td>2</td>
<td>5091.05</td>
<td>22,282</td>
<td>5078.02</td>
<td>17,391</td>
</tr>
<tr>
<td>3</td>
<td>6342.76</td>
<td>17,428</td>
<td>6328.70</td>
<td>14,496</td>
</tr>
<tr>
<td>4</td>
<td>7305.94</td>
<td>22,791</td>
<td>7289.43</td>
<td>17,356</td>
</tr>
</tbody>
</table>

Table B.11: Results for ALD Al\textsubscript{2}O\textsubscript{3} Coating

B.9.4 Electron Beam Evaporation of Al\textsubscript{2}O\textsubscript{3} (IIc)

Samples were H-terminated as usual and loaded into the evaporator loadlock with <2 min air exposure during transfer. 2.0 nm of Al\textsubscript{2}O\textsubscript{3} were evaporated onto each side of the cantilevers at a rate of 0.10 nm/sec. Measurements were performed following 20 minutes air exposure. The results show significant dissipation from the thin Al\textsubscript{2}O\textsubscript{3} film at room temperature. The cantilever also appeared to have slight curva-
ture, indicating residual, unbalanced stress from the coatings. Variable-temperature measurement was not undertaken.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample Size</th>
<th>$Q(10^4) (300 \text{ K})$ (Standard Deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si Wafer 1</td>
<td>6</td>
<td>10.0 (0.4)</td>
</tr>
<tr>
<td>Si Wafer 2</td>
<td>6</td>
<td>12.7 (0.3)</td>
</tr>
</tbody>
</table>

Table B.12: Results for Ebeam Evaporated $\text{Al}_2\text{O}_3$ Thin Coating

### B.9.5 Simultaneous Exposure to HF Vapor and Alkene Vapor

We have subjected UV/Ozone-cleaned cantilever devices and silicon wafer dies to a gas mixture of wet HF vapor and alkene vapor (pentene, hexene, or heptene). The motivation of the experiment was to test whether the constant presence of HF vapor could maintain the silicon surface in an oxide-free state for the alkene to react with until saturation coverage was reached. The resulting surfaces were highly hydrophobic, suggesting the formation of a hydrocarbon top layer. XPS analysis showed the presence of substantial SiO$_2$ (1-2 nm) underneath a carbon-rich thin layer (data not presented here). The quality factors of the cantilevers were similar to those of the default, native oxide-covered devices. The results may suggest that the alkene can react with SiO$_2$ in the presence of HF and H$_2$O, perhaps via acid-catalyzed electrophilic addition to form Si-O-R. The surface alkyl layer may then protect the underlying oxide from attack by HF vapor.

### B.9.6 Hydrosilylations of Propyne and Trifluoropropyne

A procedurally even simpler extension of the gas-phase hydrosilylation procedure would be to use a reagent that is gaseous at room temperature and oxygen-free as-purchased. We have investigated the process using propyne and trifluoropropyne (Synquestlabs). These gases are chosen because the corresponding monolayer surface for propyne has been reported to be practically immune to oxidation in air [119]. The alkylation step was conducted similarly to that described above for octene and octanal, except that the reagent was introduced to the reaction space directly from
the purchased cylinder, eliminating the freeze-pump-thaw cycle step needed for the liquid reagents.

The resulting $Q$ values are comparable to and perhaps slightly better than the default values. Silicon monitor wafers process alongside cantilever devices became hydrophobic with contact angles $>90^\circ$, suggesting successful surface reaction. The rather low $Q$ values may either be due to sub-optimal alkylation conditions or to the possibility that an alkenyl monolayers induces intrinsically higher dissipation compared to alkyl monolayers.

<table>
<thead>
<tr>
<th>Device</th>
<th>$f$ (300 K) (Hz)</th>
<th>$Q$ (300 K)</th>
<th>$f$ (4K)</th>
<th>$Q$ (4K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9197.6</td>
<td>17161</td>
<td>9259.8</td>
<td>93696</td>
</tr>
<tr>
<td>2</td>
<td>7226.6</td>
<td>17135</td>
<td>7283.5</td>
<td>115019</td>
</tr>
<tr>
<td>3</td>
<td>5980.2</td>
<td>17600</td>
<td>6049.6</td>
<td>99364</td>
</tr>
<tr>
<td>4</td>
<td>5821.8</td>
<td>16730</td>
<td>5871.9</td>
<td>89901</td>
</tr>
<tr>
<td>5</td>
<td>7121.4</td>
<td>16905</td>
<td>7175.5</td>
<td>87573</td>
</tr>
<tr>
<td>6</td>
<td>8297.8</td>
<td>16620</td>
<td>8358.1</td>
<td>85940</td>
</tr>
</tbody>
</table>

Table B.13: Results for Propyne Hydrosilylation These results were from devices exposed to alkyne gas without careful purification as described in Appendix A. Proper procedure described there gave much better results (Fig. 5-4).

<table>
<thead>
<tr>
<th>Device</th>
<th>$f$ (300 K) (Hz)</th>
<th>$Q$ (300 K)</th>
<th>$f$ (4K)</th>
<th>$Q$ (4K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7841.3667</td>
<td>12107</td>
<td>7933.2304</td>
<td>66465</td>
</tr>
<tr>
<td>2</td>
<td>6294.7938</td>
<td>13982</td>
<td>6362.1972</td>
<td>82922</td>
</tr>
<tr>
<td>3</td>
<td>5313.7413</td>
<td>10217</td>
<td>5394.3866</td>
<td>81920</td>
</tr>
<tr>
<td>4</td>
<td>5327.1395</td>
<td>15274</td>
<td>5394.3594</td>
<td>88374</td>
</tr>
<tr>
<td>5</td>
<td>6404.847</td>
<td>15788</td>
<td>6481.8298</td>
<td>95040</td>
</tr>
<tr>
<td>6</td>
<td>7796.4194</td>
<td>14168</td>
<td>7876.515</td>
<td>79223</td>
</tr>
</tbody>
</table>

Table B.14: Results for Trifluoropropyne Hydrosilylation These results were from devices exposed to alkyne gas without careful purification as described in Appendix A.
Appendix C

Additional Diamond Fabrication

Experimental Notes

C.1 ICP Etching

In all ICP etching performed in this study, quartz carrier wafers was used in place of the usual silicon carrier wafer. This change was necessary because of the high etch rate of silicon in the Ar/Cl\(_2\) plasma, would have led to contamination of both the diamond sample and the ICP chamber by the shear quantity of released volatile and non-volatile etch products.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Diamond</th>
<th>Quartz</th>
<th>Sapphire</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar Flow (sccm)</td>
<td>5</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>Cl(_2) Flow (sccm)</td>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SF(_6) Flow (sccm)</td>
<td>0</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>BCl(_3) Flow (sccm)</td>
<td>0</td>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>Pressure (mtorr)</td>
<td>1.0</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>ICP Power (W)</td>
<td>500</td>
<td>1000</td>
<td>100</td>
</tr>
<tr>
<td>Bias Power (W)</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Etch Rate (um/h)</td>
<td>2.8</td>
<td>30</td>
<td>23</td>
</tr>
</tbody>
</table>

Table C.1: ICP Etching Recipes For Materials Used in Study
Table C.2: Precision Polishing, Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness Variation (As-Received) (µm)</th>
<th>Thickness Variation (Precision-Polished) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.76(13)</td>
<td>1.25(10)</td>
</tr>
<tr>
<td>2</td>
<td>10.65(5)</td>
<td>0.50(7)</td>
</tr>
<tr>
<td>3</td>
<td>6.45(12)</td>
<td>2.47(7)</td>
</tr>
</tbody>
</table>

C.2 Diamond Polishing Characterization

C.3 Fine Details of the Sandwich Method

We initiated the Sandwich method by removal of mechanical polishing damage on the sample surface by etching away 200 nm of material from the top side of the diamond film in a Ar/Cl$_2$ ICP plasma. Cantilevers were patterned on the same side via standard photolithography (PL) and plasma etching steps, using stress-free PECVD silicon oxide-silicon nitride alternating layers as the hardmask (300nm in total). Cantilever patterns were transferred into the diamond to a depth of 800nm - 900nm via cyclic O$_2$ and O$_2$/CF$_4$ reactive ion etching (RIE)$^1$. These depths ensured that release cantilevers would be sub-micron in thickness. After front-side cantilever patterning, the diamond film was turned upside-down and a 5 µm-deep square pitted frame having the same lateral dimension as the perimeters of the front-side pattern was etched into the back side surface using Ar/Cl$_2$ plasma. The edges of the square were aligned to the base of cantilevers on the front-side pattern so that the 5-µm-thick perimeter would serve as a clamping mass at the base of the cantilevers once they are released in an ICP etching step later. Hardmask used in this clamping-mass patterning step was a 5µm, stress-free, alternating layers of SiO$_2$ and Al$_2$O$_3$ deposited by e-beam evaporation and liftoff (Fig. 6-2A). After a HF wet etching to remove any residual hardmask and a short piranha cleaning to remove any residual organic contaminants, the diamond film is ready for sandwiching.

We proceeded to prepare the quartz (or sapphire) handles for sandwiching by first laser-cutting [305] square through-holes on the dies (Fig. 6-2B). The size of the

$^1$See Experimental for process parameters
through holes was adjusted to be larger than the perimeter of the diamond pattern by at least 200 μm on each side, while still smaller than the lateral dimensions of the diamond film. Next, a pit with dimensions slightly larger than those of the diamond film was etched into the quartz, fully spanning and encompassing the through hole. We found that a convenient and expedient method is to use a shadow mask pieced together using diced glass microscope cover slides (Fig. 6-2B). We ensured alignment of the shadow mask to the substrate using a macor alignment frame during ICP machining. 20-μm-deep diamond receptacle pit can be efficiently machined in about 40 minutes using a SF₆-based or a BCl₃-based ICP plasma on quartz and sapphire handle slides, respectively [306,307].

Right before sandwiching, we cleaned both the top and bottom handle slides for 10 minutes in a boiling piranha solution, followed by DI water rinses and drying under nitrogen flow. We nudged the diamond sheet into the receptacle pit and completed the sandwich with the upper slide (Fig. 6-2C). We loaded the assembly into a wafer bonder and performed wafer bonding at a temperature of 500 °Celsius and a pressure of 5,000 kPa for 30 minutes. After wafer bonding, the quartz-quartz or sapphire-sapphire interface became fused and optically invisible. The sample chip is cleaned again in a piranha solution before loading into the ICP for diamond bulk thinning and concurrent cantilever release (Fig. 6-2D). The progress of the thinning and release can be conveniently followed by ellipsometry, using an air-diamond-air model. Under the microscope, colorful optical thin-film interference fringes become apparent on the residual diamond film once its thickness has been reduced below 1μm. ICP etching was continued until the cantilevers were completely freed from the supporting diamond membrane.
Figure C-1: Plot of SEM-derived vs optical thin-film interferometry-derived cantilever thicknesses for several cantilevers at both the tip and the base confirms fringe color as an effective indicator of device thickness.

C.4 Monitoring Resonator Release Via Fringe Color
Appendix D

Diamond Cantilever: Additional Data and Analyses

D.1 Details of Device Fabrication

Diamond material and polishing: Diamond plates were purchased from ElementSix and Delaware Diamond Knives (DDK). Dimensions were roughly $3 \times 3 \text{ mm}^2$ laterally and $20 - 40 \text{ } \mu\text{m}$ in thickness, with a typical wedge of $5 - 15 \text{ } \mu\text{m}$ over the entire plate. Plates were laser-cut to size and had a surface polish of $< 5 \text{ nm}$. Both surfaces were briefly plasma etched to remove the first $\sim 100 \text{ nm}$ on each side to improve surface quality. Surface roughness after etching was not measured on these samples but was $\leq 0.4 \text{ nm} - \text{rms}$ over a $300 \times 300 \text{ nm}^2$ area for an equivalent sample in a different study. Wedged plates were repolished by placing them in a custom-made polycrystalline diamond mold of $\sim 20 \text{ } \mu\text{m}$ depth, resulting in an improvement of surface uniformity better than $1 \text{ nm}$. All plates had a $< 100 >$ surface orientation. Electronic-grade plates (ElementSix) had a doping concentration of $< 5 \text{ ppb \ N}_0$ and $< 5 \text{ ppb \ B}$. Optical-grade plates (DDK) had a doping concentration of $< 5 \text{ ppm \ N}_0$ and $< 5 \text{ ppm \ B}$. DOI wafer bonding: Both the diamond and the handling substrate were cleaned for 10 minutes in a boiling piranha solution and rinsed with DI water. Diamond was allowed to dry in air, placed on a cleanroom wipe, whereas the handling substrate was blown dry with nitrogen. After a 10-minute dehydration bake of both
pieces at 200 °C in air, HSQ resist was spin-coated onto the handling chip at 2000 rpm for 10 seconds. The diamond plate was quickly placed on top of the freshly spun HSQ layer, with its originally upward-facing surface making contact with HSQ. The assembly was annealed under a uniform pressure of 10^5 kPa at 500 °C for 30 minutes. Quartz sandwich wafer bonding: To sandwich the diamond between quartz slides, both quartz slides were cleaned in boiling piranha solution. Both slides had through holes in the center for access to the diamond membrane. One of them had a an additional 20-μm-deep pit patterned at the center to accommodate the ~20 μm-thick diamond plate and to allow for direct contact between the quartz slides. Bonding was achieved using a uniform pressure of 10^5 kPa at 500 °C for 30 minutes. Cantilever patterning and release: Cantilever patterns were defined using oxygen-based plasmas using PECVD oxide as the hardmask. Silicon wafer through-etch was performed using a standard Bosch process, with a 10-um positive photoresist. Release from the silicon oxide etch-stop membrane was performed in buffered HF, followed by copious rinsing in DI water and IPA. The cantilever chip was directly retractd from the IPA and allowed to dry in air. The progress of diamond thinning by Ar/Cl₂ ICP in the DOI approach was monitored by profilometry. The progress of diamond thinning and concurrent cantilever release by the same plasma in the sandwich method was monitored using thin-film ellipsometry. Surface modification: In the "as released" state, the surface had a mixture of covalently attached H, O, and Cl, as confirmed by XPS measurements. Moreover, SiO₂ particles were sometimes found to be present, as SiO₂ from the mask can re-deposit during plasma etching. Possible SiO₂ was later removed using an additional HF cleaning step. HF cleaning lead to a slight (2 ×) improvement of Q factors, but nowhere close to the Q factors found for O-terminated or F-terminated devices. For oxygen-termination of the diamond surface was achieved by a low-temperature (450 C) annealing in air [232]. The air annealing step has the added benefit of removing organic and graphitic contamination from the surface leading to a general improvement of surface quality. Fluorine-termination was achieved using exposure to a CF₄ plasma [234]. Polycrystalline diamond cantilevers: Polycrystalline diamond reference cantilevers were produced from ultrananocrystalline (3-5
nm grain size) material, available as a diamond-on-insulator wafer from Advanced Diamond Technology, using applicable steps from our DOI method.
Figure D-1: Thickness-Dependence of Q-Factor, Separated by Length, Width, Surface Termination, and Temperature
Figure D-2: Length-Dependence of Mechanical Dissipation. a. Quality factor vs. length for oxygen-terminated diamond cantilevers fabricated from electronic-grade (el-SCD) substrate. b. Quality factor vs. length for oxygen-terminated diamond cantilevers fabricated from optical-grade (o-SCD) substrate. c. Quality factor vs. length for fluorine-terminated diamond cantilevers fabricated from optical-grade substrate.

Figure D-3: Width-Dependence of Mechanical Dissipation. a. Quality factor vs. width for oxygen-terminated diamond cantilevers fabricated from electronic-grade substrate. b. Quality factor vs. width for oxygen-terminated diamond cantilevers fabricated from optical-grade substrate. c. Quality factor vs. width for fluorine-terminated diamond cantilevers fabricated from optical-grade substrate.
Figure D-4: Temperature Dependence of Mechanical Dissipation Between 3 and 300 K. a. Quality factor vs. temperature for diamond cantilevers fabricated from optical-grade substrate. b. Quality factor vs. temperature for diamond cantilevers fabricated from electronic-grade substrate.

Figure D-5: Cantilever Frequency Change of the Studied Materials vs. Temperature This figure shows the frequency variation with temperature for the cantilevers shown in Fig. 7-2. Among the cantilevers measured, single-crystal diamond resonators exhibited the lowest frequency variation in the temperature range of the experiments, consistent with diamond having the highest Debye temperature. In excellent agreement with literature results [308], we observed a monotonous frequency variation of 0.065(5)% over the 0 K-300 K temperature range for cantilevers thicker than about 200 nm. For thinner cantilevers, such as the optical-grade device shown here, frequency variation up to 0.11% is seen. Debye temperature of diamond was obtained via least-squares fitting of the data for several thicker cantilevers using Equation (25) given in a paper by Orson L. Anderson [309], and was found to range between 950 K-3500 K, with an average of 1750 K. These values are consistent with known values for diamond [310]. The large uncertainty is partly a result of the limited temperature range, compared to diamond Debye temperature, surveyed in the experiment.
Figure D-6: Fit of Low-Temperature data to Two Dissipation Models. a. $Q$ vs. $T$ plot. b. $1/Q$ vs. $1/T$ plot.

Figure D-7: 0.1-300 K Measurements of the $Q$ Factor for the Resonator Shown in Fig. 7-2b. a. Quality factor vs. temperature plot obtained by sweeping refrigerator temperature between 0.08-300 K. b. Quality factor vs. laser power plot for two refrigerator temperatures. c. Resonator temperature vs. laser power at refrigerator base temperature inferred from b as described in the text.
Figure D-8: Thermal Noise Measurement of a Representative Nanoresonator Displacement power spectral density is shown as a function of frequency for the electronic-grade cantilever shown in Fig. 7-2b and Table 7.1. a. At 294 K bath temperature. b. At 6 K bath temperature.

<table>
<thead>
<tr>
<th>Length (μm)</th>
<th>Width (μm)</th>
<th>Thickness (nm)</th>
<th>(f_{300\text{K}}) (Hz)</th>
<th>(f_{4\text{K}}) (Hz)</th>
<th>(f_{\text{mK}}) (Hz)</th>
<th>(Q_{300\text{K}})</th>
<th>(Q_{4\text{K}})</th>
<th>(Q_{\text{mK}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>240</td>
<td>16</td>
<td>580</td>
<td>30389</td>
<td>30405</td>
<td>30404</td>
<td>322000</td>
<td>1000000</td>
<td>797000</td>
</tr>
<tr>
<td>120</td>
<td>16</td>
<td>360</td>
<td>81529</td>
<td>81559</td>
<td>81554</td>
<td>311000</td>
<td>370000</td>
<td>239000</td>
</tr>
<tr>
<td>200</td>
<td>12</td>
<td>760</td>
<td>57141</td>
<td>57164</td>
<td>57163</td>
<td>255000</td>
<td>139272</td>
<td>593000</td>
</tr>
<tr>
<td>200</td>
<td>16</td>
<td>395</td>
<td>29710</td>
<td>29708</td>
<td>29685</td>
<td>78400</td>
<td>291000</td>
<td>420000</td>
</tr>
</tbody>
</table>

Table D.1: Mechanical frequencies \(f\) and quality factors \(Q\) of additional electronic grade resonators are measured at \(T = 300\) K, 4 K and refrigerator base temperature \((\text{mK})\). The table collects data from four additional electronic grade resonators that were cooled to the refrigerator base temperature \((80 \text{ mK})\). Due to laser heating by the 5 nW interferometer laser the resonator temperature for these measurements was significantly higher than the bath temperature, as is explained in Supplementary Note 1 below. Although we do not precisely know the resonator temperature for the millikelvin measurements in the above table, we estimate that \(T \approx 400 \text{ mK}\) based on the calibration of the device shown in Fig. 2(b) of the main manuscript. The data show that some, but not all devices display an increase in mechanical \(Q\) below 1 K. The variability could be easily attributed to the fact that single crystal diamond often has growth sectors of different quality even in the same crystal [231], or to variability in processing. On the other hand, not much change is seen in \(Q\) down 400 mK for the extensively studied device from Fig. 2(b). As a side note, we have never observed significant increase in \(Q\) in the 0.1 – 1 K regime for single crystal silicon devices.
<table>
<thead>
<tr>
<th>Material</th>
<th>Density $\rho$ [kg/m$^3$]</th>
<th>Young’s modulus $E$ [GPa]</th>
<th>$\sqrt{\rho E}$ [kg/(m$^2$. s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-crystal diamond</td>
<td>3,530</td>
<td>1220</td>
<td>$6.6 \cdot 10^7$</td>
</tr>
<tr>
<td>Polycrystalline diamond</td>
<td>ca. 3,300</td>
<td>ca. 850</td>
<td>$5.3 \cdot 10^7$</td>
</tr>
<tr>
<td>Single-crystal silicon</td>
<td>2,330</td>
<td>166</td>
<td>$2.0 \cdot 10^7$</td>
</tr>
</tbody>
</table>

Table D.2: Densities and Young’s Moduli of Resonator Materials.

**Supplementary Note 1: Dissipation and fitting of the data at $< 1$ K**

We have fitted the low temperature (100 mK – 1 K) $Q$ vs. $T$ data to two simple functional forms, a power law and a model for a thermally-activated two-level system.

**Power law.** Power-law fitting used the following equation,

$$Q^{-1} = Q_0^{-1}[1 + (T/T_0)\epsilon],$$

where $Q_0$, $T_0$ and $\epsilon$ are free parameters. For the data shown in Fig. 7-2B the fit yields $Q_0 = 6.8 \cdot 10^6$, $T_0 = 0.3$ K, and $\epsilon = 1.6$. Note that this $\epsilon$ is considerably larger than the $\epsilon = 0.5$ predicted by general standard tunneling model (STM) theory of surface friction [18], indicating that this model does not fully describe the dissipation in diamond nanoresonators at low temperatures.

**Thermally-activated ensemble of two-level systems.** Alternatively, we have fit the entire dataset (100 mK – 2 K) to model involving an ensemble of two-level systems (TLS), such as bulk or surface defects. In this model we assume that the harmonic oscillator interacts with an ensemble of like TLS that have one single energy separation $\Delta E$. Energy transfer occurs due to re-population between the two TLS states as the energy splitting is slightly modulated by the resonator oscillation. Energy transfer is at a maximum if the relaxation rate between the TLS states matches the resonator frequency. Moreover, dissipation is proportional to the occupation probability of the excited TLS state. As temperature is lowered below $T_0 = \Delta E/k_B$, the excited TLS state becomes depopulated and dissipation is suppressed.
Dissipation in this model will have the following functional form,

\[ Q^{-1} = Q_0^{-1} + Q_1^{-1} e^{-\beta \Delta E} e^{-\beta \Delta E} + e^{+\beta \Delta E}, \tag{D.2} \]

where \( Q_0 \) is the quality factor for \( T \to 0 \) and \( Q_1^{-1} = Q_\infty^{-1} - (2Q_0)^{-1} \), with \( Q_\infty \) being the quality factor for \( T \to \infty \). \( \beta = (k_B T)^{-1} \) is thermal energy.

A fit of this equation to our data is shown as a blue curve in Fig. D-6, and yields \( Q_0 = 5.9 \times 10^6 \), \( Q_\infty = 1.2 \times 10^6 \), and \( T_0 = 0.63 \) K. The corresponding energy splitting is about \( \Delta E/h = 13 \) GHz.
Supplementary Note 2: Scaling of resonator parameters and thermal force noise with geometry and material

Resonance frequency $f_c$ and spring constant $k_c$ can be calculated for a singly-clamped rectangular cantilever beam as (Ref. [13])

$$f_c = 0.162 \frac{t}{l^2} \sqrt{\frac{E}{\rho}}, \quad (D.3)$$

$$k_c = \frac{wt^3}{4l^3} E, \quad (D.4)$$

where $t$ is the thickness, $w$ is the width, $l$ is the length of the cantilever, $\rho$ is the density of the material, and $E$ Young’s modulus. Literature values for density and Young’s moduli of single-crystal diamond, polycrystalline diamond and single-crystal silicon are collected in Supplementary Table D.2.

Using Eqs. (D.3) and (D.4), thermal force noise per unit bandwidth can be expressed as a function of $t$, $w$ and $l$,

$$F_{\text{min}} = \left( \frac{4k_B T k_c}{2\pi f_c Q} \right)^{1/2} = \left( \frac{6.17 k_B T w t^2 \sqrt{E \rho}}{Q l} \right)^{1/2} \propto \left( \frac{\sqrt{E \rho t}}{Q l} \right)^{1/2} \left( \frac{w t}{l} \right)^{1/2} \propto \alpha^{1/2} \left( \frac{w t}{l} \right)^{1/2}, \quad (D.5)$$

where $\alpha = \sqrt{E \rho t}/Q$ is the geometry-independent dissipation factor that appears with Fig. 4 in the main manuscript. The last $\propto$ expression assumes that $Q$ scales linearly with thickness, and can be used to predict the scaling of force sensitivity with device dimensions at a given temperature. $\alpha$ is related to the mechanical dissipation or “loss parameter” $\gamma$ [13] as $\gamma \propto \alpha(w t^2/l)$. 

246
Supplementary Note 3: Estimation of cantilever temperature

Cantilever temperature was measured using two different experimental schemes. For elevated temperatures ($T = 0.4 - 300\, K$), refrigerator temperature was slowly swept and the $Q$ value continuously measured. At very low temperatures ($T < 2\, K$), where significant heating of the cantilever due to interferometer laser absorption was observed, refrigerator temperature was kept fixed and the laser power incident at the resonator varied. Moreover, the resonator mode temperature was inferred by integrating the thermal noise spectral density around the resonance frequency.

0.4 - 300 K measurements. The standard method for measuring cantilever parameters as a function of temperature involved slow sweeping of the refrigerator temperature while continuously recording the $Q$ value. This method assumes that resonator and refrigerator are always at thermal equilibrium. This method worked well for about $T > 0.4\, K$ when using slow sweep rates ($dT/dt < 0.2\, K/\text{min}$) and low laser powers ($P < 10\, \text{nW}$ incident at the resonator).

100 mK - 2 K measurements. At even lower temperatures, absorption of interferometer laser light combined with the $\propto T^3$ decreasing thermal conductivity of diamond leads to resonator heating, and resonator temperature is typically higher than refrigerator temperature. Since the temperature dependence of the thermal conductivity of diamond is well known [311], we can infer the resonator temperature by recording a series of measurements at different laser powers and refrigerator temperatures. This approach turned out to work well in the temperature range $T = 0.1 - 2\, K$. In particular, we found excellent agreement of both measurement techniques in the overlap region between 0.4-2 K.

To estimate the resonator temperature from heat absorption measurements, we consider thermal conduction through a slab of uniform cross-section $A$, given by the width times the thickness of the cantilever, and length $L$, given by the distance from the interferometer laser spot to the cantilever base. According to Fourier’s law of thermal conduction,

$$P = -k(T)A \frac{\partial T}{\partial L}$$  \hspace{1cm} (D.6)
where $P$ is absorbed power, $k(T)$ is the temperature-dependent thermal conductivity, and $\partial T/\partial L$ the temperature gradient. At low temperatures ($< 10$ K), the thermal conductivity of diamond scales as $T^3$, such that $k(T) \approx \alpha T^3$ [311]. We can integrate Eq. (D.6) up to $L$,

$$P \int_0^L dL' = -\alpha A \int_{T_b}^T T^3 dT', \quad \text{(D.7)}$$

$$PL = -\frac{\alpha A}{4} (T^4 - T_b^4), \quad \text{(D.8)}$$

where $T_b$ is the bath temperature (at the base of the cantilever) and $T$ the temperature at the location of the interferometer laser spot (the resonator temperature). We obtain an expression for $T$ as a function of absorbed laser power $P$,

$$T = \left( \frac{4L}{\alpha A} P + T_b^4 \right)^{1/4} = (\epsilon P + T_b^4)^{1/4} \quad \text{(D.9)}$$

An approximate value for $\epsilon$ is found by comparing quality factor measurements made at $T_{\text{bath}} = 80$ mK and $T_{\text{bath}} = 900$ mK (Supplementary Fig. D-7(b)). From the $T_{\text{bath}} = 900$ mK curve we find that $Q \approx 1.44 \cdot 10^6$ for vanishing laser power ($P = 1$ nW), and at this low laser power, resonator temperature $T_{\text{res}}$ will be very close to the bath temperature. From the $T_{\text{bath}} = 80$ mK curve we see that the laser power required to obtain the same $Q$ value is approximately $P = 10 \mu$W; thus, at this laser power, the resonator temperature is also about $900$ mK. Together these yield $\epsilon = (T_{\text{res}}^4 - T_{\text{bath}}^4)/P \approx 6.6 \cdot 10^4 K^4/W$ with $T_{\text{res}} = 900$ mK, $T_{\text{bath}} = 80$ mK, and $P = 10 \mu$W. Note that there is an excellent agreement between the two $Q$ vs. $T$ measurement methods in the 0.4-2 K overlap region (see Fig. 7-2(b)).

Using Eq. (D.9), we thus find that the resonator temperature at the lowest investigated laser power (0.5nW) and $T_{\text{bath}} = 80$ mK is about $T_{\text{res}} = 93$ mK.
Supplementary Note 4: Measurements of resonator thermal noise

In thermal equilibrium, a harmonic oscillator exhibits a random (Brownian) motion with rms-amplitude \( x_{\text{rms}}^2 = k_B T/k_c \), where \( k_B T \) is thermal energy and \( k_c \) is the spring constant. By measuring \( x_{\text{rms}} \) we can thus derive the noise temperature \( T_{\text{noise}} = k_c x_{\text{rms}}^2/k_B \) of the oscillating mode, and determine whether it is in thermal equilibrium with the physical temperature of the resonator. Alternatively, measurement of \( x_{\text{rms}} \) at known temperature can be used to infer the spring constant \( k_c \).

For the experiments presented in this study we performed a thermal noise measurement at room temperature to calibrate the spring constant \( k_c \). (This measured \( k_c \) can be compared to a theoretical \( k_c \) calculated from resonator geometry and material parameters, see Eq. (D.4), with good overall agreement). We also performed a thermal noise measurement at low temperatures (typ. 3 – 10 K) and found mode temperatures to be in thermal equilibrium down to about 10 K (depending on the particular device), but to be enhanced at lower temperatures due to slight mechanical disturbance by the refrigerator pumps. (We note that slight mechanical excitations do not change the \( Q \) factor, as that one is set by the physical temperature of the resonator. An example of a thermal noise spectrum is given in Fig. D-8.)
Appendix E

Diamond Nanowire Fabrication and Integration

E.1 Experimental Methods

E.1.1 Diamond Tip and Nanowire Fabrication

Optical grade, ⟨100⟩-oriented single-crystal diamond plates (3 mm × 3 mm × 0.5 mm) were purchased from Element Six. ICP etcher used for this study was an Oxford Instruments ICP 180. We have used a 4-inch quartz carrier wafer throughout this study. For the direct etching method, as-received samples were positioned at the center of the quartz carrier wafer and loaded into the ICP etcher. A 3 mm-tall Macor frame with an inner 10 mm x 10 mm area was put around the diamond to prevent the latter from slipping off of the quartz carrier wafer during automatic robotic arm transfer between the loadlock and the main chamber. Samples were etched in 10 mtorr O₂ (30 sccm) using 2100 W ICP and 100 W bias powers. It has been our experience that ICP etching rates typically vary by a factor up to 2-3 when executing an identical recipe on different instruments, even etchers of the same model. Therefore, the conditions reported here should only serve as a starting point guideline for instrument-specific fine tuning. We have also noticed significant interference between recipes from different users. It is recommended that chamber...
cleaning and preconditioning runs of at least 30 minutes be performed before etching experiments on diamond samples.

To fabricate pillars with lithographic placement, we first cleaned the samples in a boiling piranha solution for 10 minutes. They were then glued to a silicon carrier chip using a thin layer of G1 Epoxy (Gatan). Care was taken to use as little glue as possible while still obtaining a continuous film between the diamond and the silicon. This care was to increase the resistance of the glue to both wet and dry etching steps by decreasing the width for convective access. A flat substrate is also important for ebeam resolution. The glue was cured at 100°C over 1 hour. After the gluing, the sample were etched in buffered HF for 2 minutes (remove adventitious micromasks), rinsed in DI water, dipped into boiling piranha solution for 10 seconds, and finally blown dry with nitrogen gas after DI water rinsing. The samples were coated with a double layer of PMMA-PMAA/PMMA resist stack to facilitate lift off. The thickness of the bottom PMMA-PMAA layer was 800nm, and the thickness of the upper PMMA layer was 150 nm. 8 nm of Au was deposited by ebeam evaporation to serve as the charge dissipation layer during ebeam writing. After ebeam exposure and resist development, 500 nm of Al2O3 was deposited by ebeam evaporation at a rate of 0.5 nm/sec. Liftoff was performed by leaving the samples in acetone without agitation. ICP etching was performed with 2500 W ICP and 40 W bias powers for 30 minutes. To pinch off the waist of the resulting pillars, the sample was subjected to 10 more minutes of etching using 2500 W ICP and 60 W bias powers.

**E.1.2 Attachment of Diamond Nanowires to Silicon Cantilevers**

To facilitate visualization and micromanipulation under an optical microscope, we first transferred the diamond nanowires from the starting diamond substrate to a silicon wafer chip. A small piece of sticky Gel-Pak 4 material was broken off from the box using tweezers. The piece of gel was put on top of the donor diamond surface, and pressed tight with tweezers. The gel was peeled away and stamped on a clean silicon wafer chip at several locations. An example of optical image of freshly-transferred sample is shown in Fig. E-1A. Nanowires lying flat on a carrier wafer can be further
Figure E-1: Transfer of Diamond Nanowires to a Silicon Substrate (A) Optical micrograph of long diamond nanowires freshly transferred to a silicon substrate. (B)-(C) SEM micrographs of diamond nanowire on silicon, after the sample had been coated with 15 nm YF$_3$ and 10 nm Pt. Scale bars are 50 $\mu$m in (A), 1 $\mu$m in (B), and 100 nm in (C).

processed using standard cleanroom techniques. As an example, we evaporated a thin double layer of YF$_3$ (10 nm) and Pt (10 nm). The evaporated samples are shown in SEM micrographs (Fig. E-1B-C). The nanowires in this batch seemed to have roughly rectangular cross-section. We note that while we have not pursued the idea further, it should be possible to tune etching conditions to enable longer etches to obtain nanowires that are suitable to be used as mechanical resonators themselves. Wire length 10 $\mu$m is certainly possible. The oblong cross-sectional shape of the nanowires make them ideal nanowire mechanical oscillators with well-separated and stable mechanical modes [37].

To mount nanowires onto silicon cantilevers, we used a commercial micromanipulator system (Narishige Three-axis Hanging Joystick Oil Hydraulic Micromanipulator, model: MMO-202ND). A glass capillary (Narishige Model: G1) was pulled to two tips under a heating power of 56.5 using a capillary puller (Narishige, Model: PC-10). Resulting capillary tip radius was around 500nm. The tip was used to nudge a NW on the silicon substrate and to move in into an orientation that was either perpendicular or parallel to the capillary tip axis. For longer wires (> 5$\mu$m), parallel orientation was preferable. For shorter wires, only the perpendicular orientation worked well for subsequent re-deposition step. The capillary was pressed into the diamond nanowire, often repeatedly, until the latter stuck to the capillary and got lifted off of the surface. The capillary tip was retracted from the surface and cantilever chip.
was brought close to the microscope focal point. Note that we had previously deposited a dab ($\approx (1\mu m)^3$) of G1 epoxy (5:1 glue:hardener) at the tip of the cantilever. Cantilever chip was oriented so the cantilever was parallel to the $xy$ plane projection of the diamond nanowire on the capillary tip. The nanowire was brought into contact with the silicon tip, the sticking force with the glue was generally stronger than the van der Waals force with the capillary tip, allowing the nanowire to stay on the cantilever as the micromanipulator tip was gently moved away in a direction parallel to the Si cantilever. The glue was allowed to cure at room temperature over 24h.

### E.1.3 Silicon Cantilever Pretreatment

To decrease the intrinsic mechanical friction in the silicon cantilever, we subjected it to a surface chemical treatment procedure (Chapter 5). For this particular experiment, we had chosen to use propyne as the reagent gas. The procedure generally results in a reduction of intrinsic friction at 4K by a factor of 2-5, depending on the recipe used and the air exposure time between preparation and the start of vacuum pumping. Please consult the relevant section for details of the procedure (A.1.3).

### E.2 Micromasking

To test whether the spontaneous appearance of diamond pillars during ICP etching could have been caused by the presence of masking impurities, we performed an...
Figure E-3: Method for Performing Liquid-Phase Reaction on Nanowire Sample Platforms (A) A nanowire tip before liquid-phase reaction. (B) A capillary containing reagent solution is brought close and used to immerse the cantilever tip inside. (C) the capillary was retracted after the dipping.

experiment by covering part of a diamond sample using microscope glass cover slip that was 180 $\mu$m in thickness. A density gradient of pillars is clearly visible, as indicated in Fig. E-2A-B. As a result, the micromask could be silicon dioxide from the quartz carrier wafer, which is a good hardmask material for diamond etching in oxygen plasma. We also notice that at the immediate vicinity of where the glass mask had been, there is a depletion of pillar density. This is despite the fact that diamond etching at this location had taken place at the same rate as at other exposed locations. We attribute the result to the existence of a certain trajectory of micromask falling from on top of the glass cover slip. The macroscopic analogue would be for people to run for cover toward the edge of a cliff during an earthquake, so that falling boulders had smaller chances of hitting them.

E.3 Strategy for Future Attachment of Biological Samples onto Diamond Nanowire tip

We developed a controllable method to conduct conventional solution-phase chemistry on nanowires tips attached to silicon cantilevers. The method consist of using glass capillary as a ‘micro-beaker’ that can be precisely positioned in 3D (Fig. E-3). The $z$ height difference was judged via focus. We have tested that aqueous and alcoholic solutions of proteins and silanes can be applied this way.
E.4 Measurement of Noncontact Friction

Mechanical properties of DNW-tipped Si cantilever and its interaction with a gold surface were measured in a custom-built scanning force microscope designed for magnetic resonance force microscopy [69]. After surface treatment for intrinsic friction reduction, cantilevers were equipped with DNW under ambient conditions and then mounted in a high-vacuum chamber (< $10^{-6}$ mbar) at the bottom of a dilution refrigerator (≈ 65 mK – 300 K). The distance between the cantilever tip and a gold surface mounted on a 3D piezo walker-scanner (Attocube) was decreased to within 10 μm by monitoring through a stereo microscope. The high-vacuum chamber was closed and evacuated to < $10^{-6}$ mbar.

When vacuum was sufficiently deep to allow for coherence vibration of the cantilever, its motion was detected using a low-power fiber-optic interferometer [115] operating at a wavelength of 1550 nm and producing less than 10 nW of laser light incident at the cantilever. Cantilever was actuated by a piezo actuator and its motion was controlled by a custom self-oscillation control loop implemented in Labview FPGA (National Instruments). We oscillated the cantilever at a constant oscillation amplitude of 5 nm while further decreasing the distance between the tip and the surface. Physical contact between the two led to the disappearance of the mechanical peak (7 kHz) from the spectrum. Concurrently, there was the appearance of another peak (≈ 20 kHz) in the spectrum, likely due to the cantilever oscillating as a doubly-clamped device when the tip is fixed by the tip-surface contact point. The point of contact could be reproducibly determined for each (x, y) location, as detailed in Section E.5.

Resonator frequency $f_c$ and quality factor $Q$ were measured using the ring-down method [13], and the spring constant $k_c$ calibrated via a thermomechanical noise measurement at room temperature [222]. To exclude cavity effects, it was verified that the same $Q$ factor was obtained whether the measurement was done on the positive or negative (red- or blue-shifted) side of the interferometer fringe.
Figure E-4: Determination of the Reliability of the \( z = 0 \) Point The cantilever was repeatedly approach to the surface until physical contact. The \( y \) axis is \( z \) piezo extension needed to induce the touching. The results shows that the standard deviation was below 1 nm.

E.5 Reproducibility of \( z = 0 \) point calibration

In order to determine the reliability of the \( x \) axes in Fig. 10-4, we performed repeated touch down at the same \( (x, y) \) location in 2-Å steps. We find that the there is a spread in the actually obtained value. Standard deviation was measured to be 0.54 nm. This value is small enough for us to be confident of the main conclusions of the study that no measurable noncontact friction was observed above 10 nm.
Bibliography


262


266


*Atomic-Scale Mechanistic Study of Iodine/Alcohol Passivated Si(100)*, October 1999.


Curriculum Vitae

08/14/1985 Born in Qu Jin, China

1992-1997 Elementary School in Kunming, China

1997-1999 Middle School in Syracuse, NY, USA

1999-2002 Secondary School in Montreal, Canada

Classical Music Concentration Program
Ecole Secondaire Pierre-Laporte

2002-2005 CEGEP in Montreal, Canada

Natural Sciences and Music
Marianopolis College and McGill University

2004 Gold Medallist

The 36th International Chemistry Olympiad
Kiel, Germany

2005 Summer Research Assistant with Prof. Louis Cuccia

Mechanism of Crystal Chiral Symmetry Breaking
Concordia University

2005-2009 Undergraduate Education in Cambridge, MA, USA

Chemistry and Biochemical Sciences
Harvard University

2006 Summer Research Assistant with Prof. Olof Ramström

Reactivity and Properties of a Resorcinol-Derived Zwitterion
KTH Royal Institute of Technology

2005-2009 Research Assistant with Prof. Eric Jacobsen

Mechanism of Enantioselective Catalysis
Harvard University

282
2009  Research Assistant with Prof. Victoria D’Souza

Structure and Mechanism of Ribosomal Frameshifting
in SARS coronavirus
Harvard University

2009  Bachelor thesis:

Molecular Dipoles in Non-polar Solvent:
A Mechanistic Investigation of complexation Phenomena and
Selectivity in Asymmetric Urea-Super Acid Cocatalysis

Thomas Temple Hoopes Prize (Outstanding Thesis)
Christiensen Prize (Outstanding Research Achievement)

2009-2011  Graduate Education in Cambridge, MA, USA
Research Assistant with Prof. Christian Degen

Physical Chemistry
MIT

2011-2015  Research Assistant with Prof. Christian Degen

Physical Chemistry and Solid-State Physics
MIT and ETH Zurich

July 2015  Ph.D. thesis at MIT (this work)
List of Publications


