Control of Morphology for Enhanced Electronic Transport in PECVD-grown a-Si:H Thin Films

by

Sebastián Castro Galnares

S.B. in Mechanical Engineering, Massachusetts Institute of Technology (2008)
S.B. in Mathematics, Massachusetts Institute of Technology (2008)

Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

September 2010

© Massachusetts Institute of Technology 2010. All rights reserved.
Abstract

Solar cells have become an increasingly viable alternative to traditional, pollution causing power generation methods. Although crystalline silicon (c-Si) modules make up most of the market, thin films such as hydrogenated amorphous silicon (a-Si:H) are attractive for use in solar cell modules because of the capacity to fabricate cells with much less material. However, several challenges exist in making this material a more practical alternative to c-Si; despite having superior optical absorption properties, a-Si:H suffers in electronic transport, having a hole mobility 3–7 orders of magnitude less than that of c-Si.

In the MOSFET transistor industry, carrier speeds and thus mobilities of c-Si were improved through the application of stress in the material. This work hypothesizes that a similar application of stress on a-Si:H thin films can enhance this material's hole mobility. A comprehensive study of the parameter space for a plasma enhanced chemical vapor deposition technique used to produce a-Si:H is performed. This enables the control of stress within the deposited film, from compressive to tensile; the mechanical limits of the material resulting in buckling and delamination failure are observed.

Further characterization of a-Si:H thin films with different levels of engineered stress was performed; an analysis of the films' surface using AFM measurements to calculate a fractal dimension for each did not result in a significant descriptor of the surfaces' domain distribution.

This work includes a detailed analysis of the theory of time-of-flight for measuring carrier mobility in thin film materials, and the system requirements needed to perform them.

Thesis Supervisor: Tonio Buonassisi
Title: Assistant Professor of Mechanical Engineering
Acknowledgements

Quiero agradecer de todo corazón a mi familia. Pa, tu fuerza y tu sabiduría siempre han sido y seguirán siendo mi inspiración. Ma, tu elegancia y pasión por la vida me han formado de una manera muy poderosa, y espero algún día poder tener aunque sea un poquito de tu espíritu. Nikki, eres única. Eres la persona que más admiro en este mundo; me iluminas, en todo el sentido de esa palabra. Sin mi familia no tengo nada, y los quiero mucho más de lo que se pueden imaginar.

Tonio, obrigado por ter acreditado em mim, mesmo nos momentos quando eu tinha deixado de acreditar em mim mesmo. Foi uma honra trabalhar com você, e posso dizer com orgulho que eu aprendi ao lado de alguém que vai mudar o mundo. Não tenho dúvidas de que algum dia, nossos caminhos se cruzarão novamente.

To all of my colleagues in the Laboratory for Photovoltaic Research, I thank you immensely for these two years; through our research, but most importantly through your character and friendship, I have taken a small step towards bettering myself, both professionally and as a person.

Mariana, gracias por haberme cuidado y por brindarme una amistad tan bonita. Tu apoyo ha sido imprescindible en mi éxito, y no sé que hubiese sido de mí sin tu ayuda.

Finally, I would like to thank all of my collaborators at King Fahd University of Petroleum and Minerals. Your enthusiasm and knowledge for our project has been remarkable; your generosity, hospitality, and friendship a blessing. I am sure that this collaboration will only continue to grow and produce outstanding results.
This page intentionally left blank
# Contents

Abstract ................................................................. 3

Acknowledgements ......................................................... 5

List of Figures ............................................................ 13

List of Tables ............................................................... 15

1 Introduction .............................................................. 17
  1.1 Energy consumption in the 21st century .......................... 17
  1.2 Solar power .......................................................... 19
    1.2.1 Solar resources ................................................. 19
    1.2.2 Photovoltaic technology ...................................... 20
  1.3 The economics of PV ................................................ 21
    1.3.1 The Levelized Cost of Electricity ........................... 23
  1.4 Basic photovoltaic conversion theory ............................ 24
    1.4.1 Diffusion length ............................................... 25
    1.4.2 Mobility ....................................................... 26
  1.5 Amorphous silicon ................................................ 26
    1.5.1 Growth modes .................................................. 27
    1.5.2 Plasma Enhanced Chemical Vapor Deposition technology ... 29
    1.5.3 Substrate selection and cleaning procedures ................. 30
    1.5.4 Experimental design and sample deposition .................. 31
2 Stress in Thin Films

2.1 Types of stresses in thin films

2.1.1 Thermal stresses

2.1.2 Intrinsic stresses

2.1.3 Epitaxial stress (lattice mismatch)

2.1.4 Surface stress

2.1.5 Coalescence stress

2.1.6 Grain growth stress

2.2 Stoney's formula (Stress in a thin film)

2.3 Substrate curvature change measurements

2.4 Results of stress measurements on thin films for varying deposition conditions

3 Fractal Dimension in Thin Films as a Proxy for Nanostructure

3.1 Introduction to fractals and fractals in nature

3.1.1 Defining fractals

3.2 Fractal dimension in a-Si:H as a proxy for nanostructure

3.2.1 Defining fractals on a thin film

3.2.2 Power Spectral Density (PSD) analysis

3.2.3 AFM imaging, data acquisition, and power spectra analysis

3.2.4 Results of fractal studies on thin films for varying deposition conditions

4 Thin Film Spectroscopy for Thickness, Index of Refraction, and Density Determination

4.1 Spectral reflectance measurements

4.1.1 Basic spectral reflectometry theory

4.1.2 Thickness and index of refraction mathematical modeling with Kramers-Kronig relationship

4.2 Film density calculation
4.2.1 Theory of film density calculation through Clausius-Mosotti model ........................................... 67
4.2.2 FTIR for determination of thin film hydrogen content ........................................... 68
4.3 Results of film microstructure as a function of stress and deposition conditions ........................................... 68
5 Time-of-Flight for Mobility Measurements in an a-Si:H Thin Film ........................................... 71
  5.1 Basic theory of Time-of-Flight ................................................................................................. 71
  5.2 System design .......................................................................................................................... 74
    5.2.1 RC-time constraints for a lumped-parameter TOF system model ................................... 75
    5.2.2 Swept-charge physics and bias constraints from Hecht’s Law ........................................ 77
    5.2.3 Optical excitation constraints and ablation avoidance .................................................... 79
6 Conclusions and Future Work ........................................................................................................... 81
  6.1 Conclusions ................................................................................................................................ 81
    6.1.1 Stress modification through PECVD parameter variation ............................................. 81
    6.1.2 Morphology characterization through AFM and applications of fractal dimension .............. 81
    6.1.3 Film densification and microstructure enhancement through the application of stress ............. 82
  6.2 Future work ................................................................................................................................ 82
    6.2.1 Time-of-Flight measurements of hole mobility in a-Si:H ................................................ 82
Bibliography ........................................................................................................................................ 84
List of Figures

Fig. 1-1  CO₂ concentration in the atmosphere over the past millenium, measured from air trapped in ice cores up to 1977 and then directly in Hawaii from 1958 onwards. The year 1769 is marked, as it saw the patenting of James Watt’s steam engine. Note the exponential increase after this date; from [1] ................................. 18

Fig. 1-2  Historical and projected CO₂ emissions through 2030; from [2] 18

Fig. 1-3  Present and projected energy consumption in Quadrillion BTUs; from [3] ................................. 19

Fig. 1-4  Schematic illustrating the power generating capacity of several resources versus current generation need; from [4] ................................. 20

Fig. 1-5  Diagram of a typical PV setup; from [5] ................................. 21

Fig. 1-6  Summary of the economics of a 1 MW_p commercial installation in average irradiance fo 5 kW/m²/day. Shows Compounded Annual Growth Rates (CAGR) of average grid retail price and average grid price for several PV technologies. Note that grid parity is achieved between 2014 and 2015; from [6] ................................. 22

Fig. 1-7  Schematic of electron-hole pair generation and charge separation in a semiconductor pn junction; from [7] ................................. 24

Fig. 1-8  Comparison of absorption coefficients for various materials; from [8] 27

Fig. 1-9  Visual summary of thin film growth modes; (a) Volmer-Weber island formation, (b) Frank-van der Merwe layer-by-layer and (c) Stranski-Krastanov layer-plus-island. Θ denotes amount of surface coverage; from [9] ................................. 28
Fig. 1-10  Simplified schematic of a PECVD system; from [10] ........................................ 29

Fig. 2-1  Thermally induced stress calculation for a-Si:H film on c-Si substrate .......................... 34
Fig. 2-2  Diagram of film stress arising from lattice mismatch; gold material is film while blue is substrate, redrawn from work [11] ......................................................... 36
Fig. 2-3  Thin film crystallite (gold) of thickness $t$ and radius $r$ deposited on substrate (blue) ......................... 37
Fig. 2-4  Wolmer-Weber growth islands coalescing. Stress is determined by a characteristic island radius ......................................................... 38
Fig. 2-5  Deposition process with surface adatoms filling a grain boundary and inducing a compressive stress $\sigma$. The chemical potential of the free surface $\mu_s$ is greater than that of the grain boundary, $\mu_{gb}$. $l(t)$ is the current film thickness as a function of time; from [12] ......................... 39
Fig. 2-6  Substrate with film applying a distributed line force $f$; detail shows a unit element being stressed in the radial and angular directions; from [13] ......................................................... 41
Fig. 2-7  Toho FLX system for substrate curvature measurement, right image shows sample on test bed ......................................................... 44
Fig. 2-8  Micrograph of film that failed from delamination ......................................................... 46
Fig. 2-9  Micrograph of films that failed from buckling ......................................................... 47
Fig. 2-10 Stress as a function of process pressure for the entire sample set ......................................................... 48

Fig. 3-1  Object $M$ covered in $N(\epsilon)$ cubes. The size of points comprising $M$ and cubes are varied in the figure to suggest depth, though they in fact remain a constant size. Note that cubes can envelop multiple points ......................................................... 50
Fig. 3-2  Visual depiction of the Cantor set. Note that the structure is scale-invariant ......................................................... 51
Fig. 3-3  Visualization of two surfaces with different morphological distributions, yet identical root-mean-square roughness $R = A$ ......................................................... 53
Fig. 3-4  Typical 2 $\mu$m x 2 $\mu$m AFM scan; this film deposited at 600 mTorr and 20W, 200 nm thick ......................................................... 56
Fig. 3-5  PSD for a-Si:H AFM data with $k$-correlation fit; $A = 1.5 \times 10^{-9}$, $B = 8.33$, $C = 4.21$ Note signal rise at high frequencies ............................... 57

Fig. 3-6  Fractal dimension as a function of process pressure ........................................ 59

Fig. 3-7  Fractal dimension as a function of power ....................................................... 60

Fig. 3-8  Fractal dimension as a function of measured film stress ................................. 61

Fig. 4-1  Schematic of basic spectral reflectance measurement ...................................... 64

Fig. 4-2  Measured spectra for an a-Si:H thin film sample; Blue traces are the actual measurement and the initial guess for values of the index of refraction $n$, while red traces are the model fit for the spectra and index of refraction based on the Kramers-Kronig relation and user defined inputs ................................................................. 66

Fig. 4-3  Measured index of refraction $n$ as a function of measured stress ..................... 69

Fig. 4-4  Measured stress as a function of $C \times \rho$, where $C$ encompasses constants from the Clausius-Mosotti relation and the material’s polarizability. The grey lines are meant as a guide for the eye, showing first a linear decrease and then a constant value for stress over the range of the abscissa ................................................................. 70

Fig. 5-1  Typical a-Si:H sample architecture for hole mobility TOF ............................... 72

Fig. 5-2  System schematic of typical TOF setup ........................................................... 75

Fig. 5-3  Required time resolution curves for TOF mobility measurement .................... 76

Fig. 5-4  Percentage of swept charge for TOF setup as a function of applied voltage ................................................................. 78

Fig. 5-5  Absorption depth to typical depth ratio for various thin film materials[14–16] ........ 80
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1.1</td>
<td>RCA clean summary indicating ratio of parts of each species for each step</td>
<td>30</td>
</tr>
<tr>
<td>Table 1.2</td>
<td>Summary of base line PECVD recipe used to produce a-Si:H thin film samples</td>
<td>31</td>
</tr>
<tr>
<td>Table 2.1</td>
<td>Stress data summary</td>
<td>46</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>Morphology and fractal dimension data</td>
<td>58</td>
</tr>
</tbody>
</table>
This page intentionally left blank
Chapter 1

Introduction

1.1 Energy consumption in the 21st century

Although many still dispute the impact of humanity’s industrial activity on the Earth’s resources and health, the available science has unequivocally demonstrated otherwise. Human energy consumption has become an issue of vital importance in assuring the continued availability of natural resources, and the minimization of human-caused pollution that in turn impacts society’s well being. Consider the growth of the greenhouse gas CO$_2$ over the past millenium in Figure 1-1,

It should not strike anyone as a coincidence that the 1800s, seeing the birth of the Industrial Revolution, was the time period in which a marked increase in CO$_2$ emissions and atmospheric concentration was noted. But given the complexity of simulating the flow of greenhouse gases to and from the atmosphere, the research literature shows a certain disparity in what future emissions will be. However, there is widespread agreement that it will continue increasing, with some projections, such as the one shown in Figure 1-2 nearly doubling CO$_2$ emissions for the year 2030 from 2000 levels, if no concrete steps are taken towards abating emissions levels [2].

This rise in pollution is not surprising when considering the amounts of energy that humans use. Figure 1-3 shows present energy consumption and projected consumption through 2030. Despite a somewhat leveling off of energy demand from OECD (mostly developed) nations, the projected use from non-OECD nations, which include
Figure 1-1: CO₂ concentration in the atmosphere over the past millennium, measured from air trapped in ice cores up to 1977 and then directly in Hawaii from 1958 onwards. The year 1769 is marked, as it saw the patenting of James Watt’s steam engine. Note the exponential increase after this date; from [1]

Figure 1-2: Historical and projected CO₂ emissions through 2030; from [2]
rapidly developing countries such as China and India, will rise substantially.

Figure 1-3: Present and projected energy consumption in Quadrillion BTUs; from [3]

1.2 Solar power

The sun’s radiation provides a vast energy source for human consumption. There are several available and developing technologies which allow for the conversion of solar energy to other forms of energy. Solar thermal technologies use the sun’s radiation to directly heat water or other liquid energy storage mediums, for either direct consumption or the generation of electricity through the production of steam. Solar hydrolysis and Solar biodiesel use the sun’s energy for the production of liquid and/or compressed fuels, H₂ and methylated hydrocarbons, respectively. Photovoltaics convert sun light directly into electricity, through the use of semiconductors.

1.2.1 Solar resources

The total amount of solar energy that is incident on the Earth is very large compared to most other resources. Consider below Fig. 1-4 detailing the availability of energy from different sources,
Although much of the sun’s solar resource cannot be directly harvested, it is still by far the largest available source on Earth, and is abundant enough to fulfill current and future power generation needs, many times over. This provides a strong, practical incentive to research photovoltaic and other solar energy harvesting technologies, such that they might be widely available and at an economically feasible price. By contributing no direct emissions, and requiring on average only a two year "payback" period on producing the amount of energy that was required to make it, photovoltaics could lead the way into a future where a significant amount of the world’s energy needs are met by renewable sources, and the harm caused by human’s reckless contamination and use of resources can be reversed.

1.2.2 Photovoltaic technology

Although two broader varieties of photovoltaics, crystalline silicon and thin films, exist, the basic concept behind all photovoltaic technologies is identical. The diagram below in Fig. 1-5 illustrates a typical PV setup.
Sunlight impinging on a PV array is converted into electricity (see details of conversion in Section 1.4). The DC electricity generated is diverted to a charge controller which meters out the electricity to the various subsystems that are connected to the array. The charge controller also ensures that the power output is appropriately matched to all of the loads connected to the array. Some PV systems are connected to batteries which can store the generated energy for later use; however they are not necessary for the system to operate. Most PV systems also have an inverter; particularly for systems installed downstream where the generated electricity will be used in residential or commercial applications, an inverter is necessary to convert the electricity from the DC to AC.

1.3 The economics of PV

The simplicity of use and environmental friendliness of PV systems have made these systems popular since their inception; however, the historically high cost of the energy produced with a photovoltaic array has until recently prevented it from becoming a substantial percentage of both the national and global energy portfolio (usually expressed in \textit{cost per kilowatt hour}, or \$/kW·hr). Higher demand, better manufac-
turing techniques, as well as government subsidies, tax breaks, and incentives have all driven the price of photovoltaics down, to where in many markets it has already reached the average price of electricity in that market. This price equilibrium is called grid parity. The last five years in particular have seen an average 60% growth rate in the demand and sale of photovoltaics [17], despite a slowing-down of the market in 2009 from the world wide financial crisis and recession. Consider the below summary of the photovoltaic electricity market in Fig. 1-6.

Figure 1-6: Summary of the economics of a 1 MWp commercial installation in average irradiance fo 5 kW/m²/day. Shows Compounded Annual Growth Rates (CAGR) of average grid retail price and average grid price for several PV technologies. Note that grid parity is achieved between 2014 and 2015; from [6]

Despite the recession in 2008-2009 and the removal of subsidies in large PV markets such as Spain, the price of PV-generated electricity has continued to fall. Notwithstanding an approximately 20%-30% difference in generated electricity cost between crystalline silicon and thin-film technologies, it is likely that large-scale photovoltaic arrays will be able to achieve average-price grid parity between 2014 and 2015 in the U.S. and other developed nations [6]. In order to appropriately analyze the cost-benefit of a particular photovoltaic installation, the calculation of the levelized cost of electricity gives the investor a simple estimate of how modifying one or several of the parameters in a photovoltaic array investment can impact the profitability of the
project.

1.3.1 The Levelized Cost of Electricity

An LCOE calculation allows for an investor to make generalized yet effective estimates as to the overall cost and profitability of a photovoltaic installation. In the simplest of terms for any energy-generating project, LCOE can be expressed as [18],

$$LCOE = \frac{\text{Total Life Cycle Cost}}{\text{Total Lifetime Energy Production}}$$  \hspace{1cm} (1.1)

For the solar industry specifically, this can further be refined to,

$$LCOE = \frac{\text{Initial Investment} - \sum_{n=1}^{N} \frac{DR^n}{(1 + r)^n} \times (TR) + \sum_{n=1}^{N} \frac{AC^n}{(1 + r)^n} \times (1 - TR) - \frac{RV}{(1 + r)^n}}{\sum_{n=1}^{N} \frac{\text{Initial} \frac{kW.h}{kW_p} \times (1 - SDR)^n}{(1 + r)^n}}$$  \hspace{1cm} (1.2)

Where $r$ is the discount rate, $DR$ is the depreciation rate, $AC$ are the annual costs, $TR$ is the tax rate, $RV$ is the residual value and $SDR$ is the system degradation rate. The indices $n$ and $N$ indicate a given year and the final year of a project, respectively [18]. Note that by final year this analysis refers to the final year of financing; the useful lifetime of photovoltaic systems are usually much longer than their financing periods (35-45 years versus 20-25 years respectively), making parameters such as the residual value and the system degradation rate very important in ensuring a low LCOE. The technology innovation and geographical solar resource components of a systems cost are reflected in the Initial $\frac{kW.h}{kW_p}$ term. Thus the equation reflects a clear aggregated benefit from research that both maximizes the useful energy produced by a solar array, and minimizes the cost of producing it.

In general, this simple LCOE model for the pricing of solar generated electricity can exemplify the sensitivity of price based on small changes in the input parameters of the photovoltaic system being designed. Although minimization of costs and maximization of energy production are in the broadest terms the best way to minimize the cost of PV generated electricity, the LCOE highlights the importance of
sound strategic financing when designing a system for the cheapest possible energy production.

1.4 Basic photovoltaic conversion theory

Photovoltaic conversion begins with the interaction of a photon with a semiconductor material. Semiconductors (and in reality all materials) possess a property called the band gap. The band gap is the amount of energy required to excite an electron from the valence band to the conduction band. Consider the schematic of a photovoltaic process in Fig. 1-7 below, with band gap $E_g$.

![Figure 1-7: Schematic of electron-hole pair generation and charge separation in a semiconductor pn junction; from [7]](image)

If an incident photon of energy $h\nu$ has greater energy than the band gap, an electron-hole pair is generated in the material. In order to separate the charges and have them contribute to the current through the device, a potential drop must be created within the device. To achieve this, photovoltaic devices are $n$-doped and $p$-doped, creating regions with excess electrons and holes respectively. The gradient in charge across the length of the device allows for charge separation; in particular the region between the doped layers, called the depletion region, acts to sweep the charges through the load connected to the device.
The transport properties of the material measure the facility with which carriers move through a semiconductor material. Note that depending on the doping of the material, it can have either excess electrons or excess holes; the carrier in excess is denoted the majority carrier, while the other is the minority carrier. Most transport properties can be measured for both, although the performance of a pn-junction-based solar cell is dictated by minority carrier transport properties. In some cases different techniques must be used to isolate the majority measurement from the minority measurement.

1.4.1 Diffusion length

The diffusion length of a carrier is defined as the distance that it travels before recombining. Diffusion length must be maximized in order to ensure that the generated carriers reach the depletion layer of the PV device and thus being swept through the circuit and being harvested as useful energy. The diffusion length is written as,

$$ L_d = \sqrt{D\tau} \quad (1.3) $$

where $D$ is the carrier’s diffusivity in the material, and $\tau$ is the carrier’s lifetime. Lifetime is simply the amount of time that a carrier exists in the material before it recombines. Thusly by maximizing lifetime the distance the carrier is able to travel without recombining is maximized as well, allowing it to reach the depletion layer. A related concept is that of time-of-flight. Time-of-flight is the amount of time that it takes a carrier to traverse a certain distance within a device; in this work, that distance is from near one contact of a sample (where carriers are being generated) to the other, where they are swept through the circuit. Measuring the time-of-flight enables the calculation of another important transport property particularly important to the body of this work: carrier mobility.
1.4.2 Mobility

A carrier's mobility is a measure of how quickly it moves through a device with an applied electric field $\xi$, such as those found in a photovoltaic device. The mobility $\mu$ is defined as,

$$\mu = \frac{v_d}{\xi}$$  \hspace{1cm} (1.4)

where $v_d$ is the carrier's drift velocity in the electric field. The current densities from electrons and holes $J_e$ and $J_h$ can be estimated from the carrier mobilities through,

$$J_e = q\mu_e n\xi$$  \hspace{1cm} (1.5)

$$J_h = q\mu_h p\xi$$  \hspace{1cm} (1.6)

where $n$ and $p$ are the electron and hole densities in the conduction and valence bands, respectively. Mobility is affected by device parameters such as temperature, dopant species and concentration, and defect concentrations. In amorphous materials this last measure is particularly important, as the lack of an organized lattice provides a wealth of inherent scattering centers in the material. This both hampers the mobility by increasing the likelihood of carriers colliding with atoms or defects, as well as that of a recombination event which prevents the carrier from contributing to the device's circuit.

1.5 Amorphous silicon

There are several advantages to using amorphous silicon (a-Si) thin film solar cells as compared to crystalline silicon ones. In the visible spectra, a-Si is a much stronger absorber than c-Si. Below in Fig. 1-8 a comparison of the absorption coefficient for various thin film materials and c-Si.

The increased absorption allows for up to 100x less material to be used in an a-Si
Figure 1-8: Comparison of absorption coefficients for various materials; from [8]

device as compared to a c-Si one. The relatively low deposition temperature and this
smaller energy inputs for a-Si fabrication as compared to c-Si also makes it attractive
for use in lower cost photovoltaic devices.

Unfortunately, the defect-intense nature of a-Si gives it poor electrical transport
properties. The mobility of carriers in a-Si, and in particular holes, is several orders
of magnitude worse than that in c-Si; they can be as low as $1 \times 10^{-3}$ $\text{cm}^2\text{V}^{-1}\text{s}$ [19]. As a
result, a-Si devices exhibit much lower overall efficiencies than their c-Si counterparts,
with a record efficiency of $9.5 \pm 0.3\%$ for a monojunction a-Si device [20].

1.5.1 Growth modes

Amorphous silicon, along with other semiconductor, metal, and non-metal thin films,
are usually deposited onto a substrate through some kind of chemical vapor deposition
technique, in which a target material is either vaporized or already in gaseous form, and made to flow over a substrate. The material adatoms then attach to the substrate and eventually among themselves, build islands and layers. Most thin film growth can be characterized by three different growth modes. In Fig. 1-9 a visual summary of these modes is shown.

![Diagram of thin film growth modes](image)

Figure 1-9: Visual summary of thin film growth modes; (a) Volmer-Weber island formation, (b) Frank-van der Merwe layer-by-layer and (c) Stranski-Krastanov layer-plus-island. Θ denotes amount of surface coverage; from [9]

Volmer-Weber growth results in the formation of island structures scattered about the substrate surface. Most extremely thin films (thickness < 1 nm) usually exhibit Volmer-Weber growth to some extent. For films that have a very high surface energy with respect to the substrate that they are being deposited on, Volmer-Weber growth is usually the dominating growth mechanism.

In Frank-van der Merwe growth, smooth layers are built up one on top of the other. This growth mechanism is prevalent in film species with high self-affinity, and is characteristic of epitaxial growth techniques such as molecular beam epitaxy.

Stranski-Krastanov growth involves elements of both Volmer-Weber and Frank-van der Merwe. Films that grow in this mode usually begin with several layers, and then begin to generate islands on top. Subsequent growth might continue islanding, but “filling-in” of the islands and observing subsequent layer-by-layer growth has been observed. Most real film deposition processes are more accurately portrayed by
Stranski-Krastanov growth than the other two growth modes.

### 1.5.2 Plasma Enhanced Chemical Vapor Deposition technology

Most chemical vapor deposition techniques involve the vaporization or plasmification of a species to generate adatoms on the substrate surface. These adatoms then adhere to the surface and each other, forming the actual material of the film. This study focuses on the use of *Plasma Enhanced Chemical Vapor Deposition* for the deposition of hydrogenated amorphous silicon samples (a-Si:H). Below in Fig. 1-10 a simple schematic of a PECVD system is shown.

![Figure 1-10: Simplified schematic of a PECVD system; from [10]](image)

In a PECVD process, a gas or combination of gases is flowed into a process chamber over a substrate. The substrate sits on the bottom of an electrode, and another electrode hovers over the top of the sample. As the gas flows through the resultant space between the electrodes, and AC current or RF signal is used to generate a plasma of the gas mixture. In the plasma, several radical species form, of which some are adsorbed onto the substrate surface and become adatoms. Most PECVD tools have the ability to deposit at low frequencies (100s of kHz), high frequencies (13.56 MHz), or a mixture of both. Increasingly PECVD tools are the preferred choice for both research and industrial chemical vapor deposition: flow gases are easier to install than targets or hot wires, plasma enhancement allows for a much lower deposition
temperature and thus reduce the energy input into the system, and the ability to mix deposition frequencies allows for the control of stress and other film properties. This work uses a *Surface Technology Systems* PECVD for the deposition of a-Si:H.

### 1.5.3 Substrate selection and cleaning procedures

For this work, all samples were deposited on p-doped, 3" crystalline silicon substrates. The circular substrates allow for easy curvature change measurements, permitting the calculation of stress of films deposited on the surface. It was also chosen for flexibility in contacting; when a certain characterization technique required a direct contact, it can be evaporated directly on the c-Si surface prior to the deposition of the a-Si:H layer. Alternatively, if electric insulation is required, it is simple to deposit an oxide layer in between the substrate and the a-Si:H layer to accomplish this.

Substrate cleaning and preparation was accomplished through a typical *RCA clean*, summarized below in Table 1.1,

<table>
<thead>
<tr>
<th>Step name</th>
<th>H$_2$O$_2$</th>
<th>NH$_4$OH</th>
<th>Deionized H$_2$O</th>
<th>H$_2$SO$_4$</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCA-1</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Oxide strip</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>To necessary dilution</td>
<td>1</td>
</tr>
<tr>
<td>RCA-2</td>
<td>1</td>
<td>0</td>
<td>5</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 1.1: RCA clean summary indicating ratio of parts of each species for each step

The above table shows the composition of chemicals used for each of the necessary steps. RCA-1 and RCA-2 are used to remove organic and metallic contaminants respectively; the samples should in these steps be placed into the mixture, at 75 °C for 10 minutes. It is recommended that the hot plate used should first be elevated to the necessary temperature, and to then pour in the necessary chemicals: failure to do so can result in an unwanted exothermic reaction, with vigorous bubbling spilling out of the chemical bath. RCA-2 is a particularly important step, as beyond its cleaning function, it also changes the surface states favorably for the deposition of a-Si:H and other thin films.

The oxide strip is used to remove the built up native oxide layer, and any contaminants within it. It is performed at room temperature, and a dipping time of one minute or
less is adequate with a sufficiently high percentage HF. Depending on the nature of
the particular cleaning procedure desired, 10%-50% HF can be used
Between all steps, including after the RCA-2 step, the samples are placed in a *quick rinse* of deionized water, and are submitted to at least 3 cycles, ensuring complete removal of the chemicals used prior.

1.5.4 Experimental design and sample deposition

This work examines the modification of a-Si:H film properties through the induction of stress in the film. In particular, it is hypothesized that a-Si:H films' transport properties can be modified through the use of stress, similar to how the stressing of c-Si MOSFETs has augmented carrier mobility through the material, and thus allowing for faster transistor switching speeds [21].

To determine the effect that modifying the process conditions on a PECVD deposition of a-Si:H has on the level of film stress, and in turn how this stress affects film transport properties, a sample set of films was deposited on top of c-Si substrates. For the purpose of electrically isolating the film from the substrate, all samples had a 200 nm layer of silicon oxide deposited on its surface prior to a-Si:H deposition. Shown below in Table 1.2 is the base process recipe used for the generation of the films,

<table>
<thead>
<tr>
<th>Basic a-Si:H PECVD recipe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Flow rate SiH₄</td>
</tr>
<tr>
<td>Flow rate Ar</td>
</tr>
<tr>
<td>Process pressure</td>
</tr>
<tr>
<td>Power</td>
</tr>
</tbody>
</table>

Table 1.2: Summary of base line PECVD recipe used to produce a-Si:H thin film samples

From this basic recipe, several samples were deposited testing the extremes of each process condition, ensuring that for each, the film adhered to the substrate surface. Note that this does not necessarily imply that the films did not mechanically fail; part of this study characterizes the stress at which the films fail.
For the characterized batch of films, only process pressure and power were varied; large variations in these parameters still produced consistently wetted films, while still exhibiting variation in stress and other characterized properties. In the following sections, the range of variation in process pressure and power is discussed in more detail.
Chapter 2

Stress in Thin Films

2.1 Types of stresses in thin films

Mechanical stress in thin films arises from a modification in atomic positioning during film growth. By controlling the average distance from equilibrium that atomic position is changed, tensile and compressive stresses can be engineered into films [22]. Thus the stress in a film can be controlled, as well as its density. This work attempts to quantify the possible stress variation in a-Si:H films. The process conditions in the PECVD chamber used to deposit the films are systematically altered (See section 1.5.2-1.5.4 for detail). The process variables are temperature, process pressure, power, and film thickness. The stress conditions generated take the material through the extremes of possible stress states: from buckling failure, to compressive stress, to tensile stress and finally to delamination. Knowing the mechanical limits and the range of stresses which can be engineered into the films could be used to control the transport properties of the material.

2.1.1 Thermal stresses

Thermal stresses arise from the temperature differential the film experiences during growth and processing. A difference in the coefficient of thermal expansion (CTE) between the film and the substrate results in a larger contraction (or expansion) of
one material over the other, and thus inducing a stress. In Fig. 2-1, a calculation using published values for the CTE of a-Si:H [23] at different temperatures is used to estimate the amount of thermally induced stress for an a-Si:H film on a c-Si substrate.

\[ \sigma_t = \epsilon_t M_f \]  
\[ \epsilon_t = (\alpha_s - \alpha_f) \Delta T \]  

Figure 2-1: Thermally induced stress calculation for a-Si:H film on c-Si substrate

The stress \( \sigma_t \), as shown on the y-axis of Fig. 2-1, is calculated through,

where \( \epsilon_t \) is the film strain, \( M_f \) is the film modulus, \( \alpha_s \) and \( \alpha_f \) are the CTEs of the substrate and film, and \( \Delta T \) is the temperature differential. The calculation reveals that in comparison to the intrinsic stresses locked into the film during growth (see data summary of intrinsic stresses for this study’s samples in Table 2.1), the
thermal stresses do not contribute significantly for an a-Si:H thin film grown on a 
c-Si substrate. This is caused by the similarity of CTE for amorphous and crystalline 
silicon.

2.1.2 Intrinsic stresses

Intrinsic stresses is the general name for stresses that develop in a film during the 
growth stage. They can arise from a variety of mechanisms, of which the most 
important ones will be discussed in the following sections.

2.1.3 Epitaxial stress (lattice mismatch)

Epitaxial stresses arise from a lattice mismatch between the deposited film, and the 
substrate underneath. If the growth conditions are such that the creation of a per-
fectly coherent interface \([11]\) is possible, the film's lattice will align with that of the 
substrate; the larger the difference, the larger the stress. Figure 2-2 illustrates a 
typical lattice mismatch setup.

For a perfectly symmetrical case, the epitaxial stress \(\sigma_e\) can be calculated by,

\[
\sigma_e = \epsilon_e M_f
\]

\[
\epsilon_e = \frac{a_s - a_f}{a_f}
\]

where \(a_s\) and \(a_f\) are the substrate and film lattice constants, respectively.

2.1.4 Surface stress

Surface stresses arise from the amount of reversible work required to create a surface 
area \(A\). The total amount of work needed to create a surface is given by,

\[
dw = \gamma dA
\]
where $\gamma$ is the surface energy of the material. Surface stresses are the predominant contributor of intrinsic stress for films that have at least one dimension less than 10 nm [24]. Consider a schematic of a thin film crystallite under surface stresses, in Figure 2-3.

With a small island-like structure such as the one depicted in Fig. 2-3, the surface stresses on the top, side walls, and interface with the substrate can be used to express the total strain $\varepsilon_r$ the element experiences under equilibrium[11],

$$\varepsilon_r = \frac{1}{M_f} \left[ \frac{f + h}{t} + \frac{g}{r} \right]$$

(2.6)

where $f$, $g$, and $h$ are the surface stresses of the top, sidewall, and interface stresses respectively, $t$ is the film’s thickness, and $r$ is the radius of the feature.
2.1.5 Coalescence stress

Recall from section 1.5.1 the Volmer-Weber mechanism of film growth: adatoms on the substrate surface agglomerate to form islands of material distributed over the substrate surface. Once islands begin to impinge on each other (called the percolation point), they coalesce into grains and grain boundaries, and stresses arise from the input of material into the now closed space between these islands.

Consider below in Fig. 2-4 a network of film islands transitioning into coalescence. Note that though the islands here are shown as spherical caps (and are a good approximation of morphology observed for a-Si:H thin films), films can exhibit a variety of Volmer-Weber island shapes.

Following the analysis of [13], for a characteristic island of radius $R$, the average stress that develops from coalescing islands on a substrate surface is given by,

$$
\sigma_{ave} = 0.44 \frac{E^{\frac{1}{3}} \gamma^{\frac{2}{3}}}{R^{\frac{2}{3}}} \tag{2.7}
$$

Coalescence stresses are often related to the deposition rate of a given deposition con-
Figure 2-4: Wolmer-Weber growth islands coalescing. Stress is determined by a characteristic island radius.

Slower depositions tend to form larger crystallite islands before reaching the percolation point, and thus result in lower coalescence stresses.

2.1.6 Grain growth stress

Stresses can develop in a film with the development of grain boundaries, and in particular when they are incorporated in the material bulk [11]. In general, grain boundaries are less dense than the bulk material, meaning that their annihilation leads to increased film density and thus film stress. There are several mechanisms for stress changes associated with grain boundary modification, which can lead to both tensile and compressive stresses.

Consider a film with average grain size $L_0$ and an excess volume per unit of grain boundary $\Delta a$. If the film grains are allowed to grow to a size $L$ (for example through an annealing procedure), the volumetric strain is given as,

$$\Delta V = 3\Delta a \left( \frac{1}{L} - \frac{1}{L_0} \right)$$ \hspace{1cm} (2.8)

This results in in-plane strains given by,

$$\epsilon_g = \Delta a \left( \frac{1}{L_0} - \frac{1}{L} \right)$$ \hspace{1cm} (2.9)

Thus the stress from grain size enhancement (and thus grain boundary annihilation)
Another important mechanism for stress arising from the growth of grains is the filling of grain apertures with flux adatoms from the PECVD or sputtering procedure [12]. Consider a film/substrate system such as the one below in Fig. 2-5, where \( u(y) \) is the width of the layer of material at a particular point \( y \) along the axis of the grain boundary.

![Figure 2-5: Deposition process with surface adatoms filling a grain boundary and inducing a compressive stress \( \sigma \). The chemical potential of the free surface \( \mu_s \) is greater than that of the grain boundary, \( \mu_{gb} \). \( l(t) \) is the current film thickness as a function of time; from [12]](image_url)

A simple linear spring model for the stress developed in a grain boundary crack is given by,

\[
\frac{u(y)}{w} = -\frac{\sigma_{gb}(y)}{M_f}
\]  

(2.11)

where \( w \) is the grain width and \( M_f \) is the film elastic modulus. A gradient in the chemical potential \( \mu_s \) and \( \mu_{gb} \), of the surface and grain boundary respectively, causes the adatoms concentrated on the surface to fill in the gap of the grain boundary. If \( \Gamma \) is the jump rate of adatoms into the grain boundary, and is a function of an activation
barrier \( \Delta G^* \) for incorporating the adatom into the grain boundary wall's material, the evolution of the stress in the grain boundary can be written as,

\[
\frac{\partial \sigma}{\partial y}(l, t) = \frac{2C_s \Gamma \Omega^{2/3}}{\delta D} \left[ \sigma_s - \sigma(l, t) \right]
\]

where \( C_s \) is the concentration of adatoms on the surface, \( \Omega \) is the atomic volume, \( D \) is the grain boundary diffusivity, and \( \delta \) is the thickness of a layer in which interface diffusion is supposed to take place. The quantity \( \sigma_s \) is a constant representing the steady-state grain boundary stress if the grain boundary and free surface reached equilibrium during deposition [12]. Note that this description of stress is strictly the normal, localized stress at the point \( y \) on the grain boundary. A further relation is needed to relate this quantity to the overall stress of the film. If the average grain boundary stress is given by \( \sigma_{\text{ave}} \), the change in the product of stress and thickness (also called the line force) given in several experimental results can be written as,

\[
\Delta(\sigma l)_{\text{exp}} = \Delta \left[ \sigma_{\text{ave}}(4l/w) \tanh(w/4l) \right]
\]

### 2.2 Stoney’s formula (Stress in a thin film)

Because thin films are usually several orders of magnitude thinner than the substrates that they are deposited on, stresses induced by thin film deposition are usually considered to be constant throughout the entire thickness of the thin film. The observed curvature change after film deposition can be used with Stoney’s formula to calculate the stress in the film. The following derivation is based on work presented in [13] and the substrate-film system used for the derivation is shown in Fig. 2-6.

Several assumptions are needed for the proper derivation of the formula. First, the distributed line force and the deformation it induces are assumed to be axially symmetric, implying that all stress states are independent of \( \theta \) in the selected coordinate system. Second, the distributed line force \( f \) induces a plane stress state, and any nonlinear effects towards the edges of the bi-layer are ignored. Finally, the substrate’s midplane is assumed to deform through an isotropic strain, and its curvature is uni-
The complete stress state of the deformation can be expressed as a function of the Lamé constants with the following tensor:

$$
\begin{bmatrix}
\sigma_{rr} \\
\sigma_{\theta\theta} \\
0
\end{bmatrix} =
\begin{bmatrix}
2\mu + \lambda & \lambda & \lambda \\
\lambda & 2\mu + \lambda & \lambda \\
\lambda & \lambda & 2\mu + \lambda
\end{bmatrix}
\begin{bmatrix}
\varepsilon_{rr} \\
\varepsilon_{\theta\theta} \\
\varepsilon_{zz}
\end{bmatrix}
\tag{2.17}
$$

The Lamé constants $\mu$ and $\lambda$ are functions of the Young’s Modulus $E$ (sometimes denoted Elastic Modulus) and the Poisson’s ratio $\nu$ of the substrate material,

$$
\mu = \frac{E}{2(1-2\nu)}
\tag{2.18}
$$

$$
\lambda = \frac{\nu E}{(\nu + 1)(1-2\nu)}
\tag{2.19}
$$
The stress induced by a deposition process in the thin film can be derived from the overall energy that is derived from this process in deflecting the substrate. The following expression describes the total energy density of the substrate, in terms of the perceived stresses and strains in each of the coordinate directions, and the appropriate material properties:

\[ p = \sum \frac{1}{2} \sigma_{ij} \varepsilon_{ij} = \frac{E}{2(1 + \nu)(1 - \nu)} \left[ \varepsilon_{rr}^2 + \varepsilon_{\theta\theta}^2 + 2\nu \varepsilon_{rr} \varepsilon_{\theta\theta} \right] \]

(2.20)

Note that strains can be written in terms of unit cell displacements in the coordinate directions. Let \( u, v, \) and \( w \) represent displacements in the \( r, \theta, \) and \( z \) directions respectively. The non-zero strains in the deformed substrate can be written in terms of these displacements and their derivatives as follows:

\[ \varepsilon_{rr}(r, z) = \dot{u}(r) - z\ddot{w}(r) \quad (2.21) \]

\[ \varepsilon_{\theta\theta}(r, z) = \frac{u(r)}{r} - \frac{z}{r} \dot{w}(r) \quad (2.22) \]

The displacements in turn, can be written parametrically such that the expression for the displacement of the material is expressed only in terms of the material’s mechanical properties, the induced isotropic strain and constant curvature \( \epsilon_0 \) and \( \kappa \) respectively, and the coordinate \( r \), namely:

\[ u(r) = \epsilon_0 r \quad (2.23) \]

\[ w(r) = \frac{1}{2} \kappa r^2 \quad (2.24) \]

If we input these parametric expressions and their derivatives into the equations for strain, we can re-write the energy density of the deflected substrate as,

\[ p = M_s(\epsilon_0 - \kappa z)^2 \quad (2.25) \]
where $M_s$ is the substrate's biaxial elastic modulus, defined as,

$$M_s = \frac{E}{1 - \nu} \quad (2.26)$$

The total potential energy in the deformed substrate is the sum of energies contributed from the intrinsic deformation of the substrate and that contributed by the deposition induced distributed line force $f$. If we consider a substrate with radius $0$ to $R$ on the $r$ axis, angular rotation of $0$ to $2\pi$ on the $\theta$ axis, and extension $-h_s/2$ to $h_s/2$ on the $z$ axis (with the magnitude $h_s$ defining the total thickness of the substrate), the expression for the total potential energy is as follows:

$$V(\epsilon_0, \kappa) = 2\pi \int_0^R \int_{-h_s/2}^{h_s/2} p(r, z) \cdot r \cdot dz \, dr + 2\pi R^2 f \cdot p(R, h_s)$$

$$= \pi R^2 M_s h_s \left( \epsilon_0^2 + \frac{1}{12} \kappa^2 h_s^2 \right) + 2\pi R^2 f \left( \epsilon_0 - \frac{1}{2} \kappa h_s \right) \quad (2.27)$$

Once a film has been deposited on the substrate, determining the stress in the film through the total potential energy is a matter of considering the parameters that make the total potential energy stationary, vis-à-vis,

$$\frac{\partial V}{\partial \epsilon_0} = \frac{\partial V}{\partial \kappa} = 0 \quad (2.28)$$

At a stationary total potential energy, the above can be solved to yield the midplane strain $\epsilon_0$ and the curvature $\kappa$,

$$\epsilon_0 = \frac{f}{M_s h_s} \quad (2.29)$$

$$\kappa = \frac{6f}{M_s h_s^2} \quad (2.30)$$

Referring back to the key assumption of the film being much thinner than the substrates they are deposited on, the induced stress in the thin film is constant throughout its thickness, thus a mean stress can be determined with,
\[ \sigma_m = \frac{f}{h_f} \]  

where \( h_f \) is the thickness of the deposited film. Finally, inputting the appropriate expression for \( f \) from the curvature \( \kappa \) yields Stoney's formula,

\[ \sigma_m = \frac{M_s h_f^2 \kappa}{6h_f} \]  

(2.32)

### 2.3 Substrate curvature change measurements

The stress of the sample set described in Section 1.5.4 was measured through changes in substrate curvature before and after thin film deposition, as described previously through Stoney’s formula. The measurement was performed in a Toho FLX-2320-S thin film stress measurement system. The system is shown in Fig. 2-7, together with a sample on the instrument’s test bed.

![Toho FLX system for substrate curvature measurement, right image shows sample on test bed](image)

The measurement is performed by rastering a laser over an axis on the sample’s surface; an optical detector receives the reflected laser beam and interpolates changes in angle as the shape of the substrate surface. The software then calculates a radius of curvature based on the detected profile. For best results with the tool, it is recommended to exclude the edges of the samples; for the 76.2 mm c-Si substrates
being used, only the inner 60 mm of each were measured. A measurement is taken before the film is deposited, and one is taken after. With these two measurements, the change in curvature \( \kappa \) can be calculated through,

\[
\kappa = \frac{1}{R} - \frac{1}{R_0}
\]

where \( R \) is the substrate's post-deposition radius of curvature, and \( R_0 \) is the radius of curvature before deposition. It should be noted that although it was not used for this study, this system is capable of temperature dependent measurement in the range of \(-65 ^\circ C\) to \(500 ^\circ C\); this allows for the calculation of biaxial modulus and coefficient of thermal expansion for novel materials.

### 2.4 Results of stress measurements on thin films for varying deposition conditions

Stress was measured for a sample set which included films deposited at different power and pressure. Different thickness films were also deposited; for the submicron thickness range, thickness variation did not significantly impact stress, and is further discussed in Chapter 4. Stress data for the sample set is shown in Table 2.1. Note that several other films are not listed because they exhibited some failure mechanism, invalidating any curvature change measurement for the calculation of stress.

The objective of this study was to investigate the effect of changes in the PECVD chamber conditions on stress; in particular process pressure and power. Both tensile and compressive stresses were engineered and the parameter space was studied until the a-Si:H films reached mechanical failure. Shown in Figs. 2-8 and 2-9 are micrographs of the films in tensile and compressive failure modes, denoted delamination and buckling, respectively.

The a-Si:H samples were engineered to stresses that ranged from about \(-1000\) MPa to \(400\) MPa. By extrapolating to the stress measured in the process conditions closest to where films were found to fail, the buckling stress and delamination stress were
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Power [W]</th>
<th>Process pressure [mTorr]</th>
<th>Stress [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>W01</td>
<td>30</td>
<td>100</td>
<td>-910.6</td>
</tr>
<tr>
<td>W03</td>
<td>30</td>
<td>100</td>
<td>-983.4</td>
</tr>
<tr>
<td>W12</td>
<td>20</td>
<td>600</td>
<td>340.5</td>
</tr>
<tr>
<td>W13</td>
<td>30</td>
<td>600</td>
<td>343.2</td>
</tr>
<tr>
<td>W14</td>
<td>35</td>
<td>200</td>
<td>-605.5</td>
</tr>
<tr>
<td>W15</td>
<td>35</td>
<td>600</td>
<td>343.1</td>
</tr>
<tr>
<td>W16</td>
<td>20</td>
<td>600</td>
<td>324.1</td>
</tr>
<tr>
<td>W17</td>
<td>30</td>
<td>600</td>
<td>377.1</td>
</tr>
<tr>
<td>W18</td>
<td>20</td>
<td>200</td>
<td>-422.1</td>
</tr>
<tr>
<td>W19</td>
<td>30</td>
<td>200</td>
<td>-563.9</td>
</tr>
<tr>
<td>W20</td>
<td>30</td>
<td>200</td>
<td>-462.3</td>
</tr>
<tr>
<td>W21</td>
<td>35</td>
<td>200</td>
<td>-605.4</td>
</tr>
<tr>
<td>W22</td>
<td>20</td>
<td>200</td>
<td>-406.1</td>
</tr>
<tr>
<td>W23</td>
<td>30</td>
<td>400</td>
<td>168.0</td>
</tr>
<tr>
<td>W24</td>
<td>30</td>
<td>800</td>
<td>387.4</td>
</tr>
<tr>
<td>W25</td>
<td>35</td>
<td>600</td>
<td>355.1</td>
</tr>
</tbody>
</table>

Table 2.1: Stress data summary

Figure 2-8: Micrograph of film that failed from delamination

estimated to be $-1200$ MPa and 450 MPa, respectively.

Power was found to not have a significant effect on the stress; at identical power conditions, stress varied on average only by 10.5%, which was consistent with the
measurement error in curvature over all samples.

Pressure was found to be a powerful method of adjusting the stresses in the deposited film. The compressive values are consistent with what has been reported in the literature previously [25]. This study is novel in that it used a large pressure range of 100 - 1000 mTorr to show a transition from compressive to tensile stresses in a-Si:H. Figure 2-10 shows the evolution of stress in a-Si:H over this range. Note that data points for 1000 mTorr are not shown because all of the films deposited at this pressure failed and delaminated.

Increase of process pressure in other studies has been shown to exhibit changes in stress from compressive to tensile regimes [16], much like that observed in this study. This phenomenon is thought to arise from the increased collisions between plasma and gas molecules under increased pressure; this results in less plasma molecules impinging on the surface of the substrate and densifying into a film [16]. Less dense films are thus composed of atoms that are more spread out in their amorphous matrix, and farther away from an equilibrium position. Note that the 800 mTorr films show roughly the same amount of stress as the 600 mTorr and 1000 mTorr films; however,
Figure 2-10: Stress as a function of process pressure for the entire sample set

Unlike the 1000 mTorr films, these did not fail.
Chapter 3

Fractal Dimension in Thin Films as a Proxy for Nanostructure

3.1 Introduction to fractals and fractals in nature

First described formally in Benoît Mandelbrot’s seminal work in 1975 [26], fractals are geometric shapes exhibiting complex branch-like structures which are difficult to describe with regular Euclidean geometry, and that have the non-intuitive property of being characterized by a dimension that is usually non-integer. What sets fractal structures apart from other families of irregular or fragmented structures is that they exhibit the property of self similarity. Self similar objects are those that resemble themselves at varying scales of magnification. These can further be divided into scale-invariant objects and self-affine ones. Scale invariance describes objects that resemble themselves exactly in all spatial directions for which the object is defined and can be either statistically invariant or exactly invariant, the former denoting invariance over a range of scales and the latter that the object resembles itself over all scales. Self-affine objects are those whose similarity is scaled by different amounts in different spatial directions. Although typically associated with mathematical abstraction (and many famous fractal structures, such as the Burning ship fractal, are defined mathematically), fractals can be appreciated in all sorts of natural systems, such as clouds, mountains, and coastlines. There is a wealth of research into the use of frac-
tional descriptions in natural systems, much of it suggesting that non-integer dimensions offer a more complete intuition into their workings [27]. Although fractal dimension has been used in the past to describe thin films [28], concrete methods of using it as a proxy for surface roughness and other measures of thin film surface nanostructure have remained elusive. This chapter attempts to find a correlation between the stress induced in a film and the resulting fractal morphology on its surface.

3.1.1 Defining fractals

The subsequent fractal definition follows mostly from [29], and defines a fractal as an object in strictly mathematical terms. Subsequent sections will quantify fractals for use in measurable systems, such as data describing the surface of a thin film.

Consider a sequence of points or object, $M$ in a $p$-dimensional space. Figure 3-1 shows such an object; note that for most physical setups $p = 3$. A minimum number $N$ of cubes of linear dimension $\epsilon$ are used to cover the object.

![Figure 3-1: Object $M$ covered in $N(\epsilon)$ cubes.](image)

This leads to the following relation for the amount of cubes needed to cover $M$,

$$N(\epsilon) = C\epsilon^{-d}$$  \hspace{1cm} (3.1)

where $d$ is the fractal dimension (sometimes called the Hausdorff dimension), and $C$
is a constant. If we solve for $d$ this yields,

$$d = \frac{\ln N(\varepsilon) - \ln C}{\ln(1/\varepsilon)}$$

(3.2)

In the limit that $\varepsilon$ is taken to 0, we obtain the formal definition of the fractal,

$$d = \lim_{\varepsilon \to 0} \frac{\ln N(\varepsilon)}{\ln(1/\varepsilon)}$$

(3.3)

Consider the preceding abstraction in the following examples. If the object $M$ is a line of length $L$, the required amount of cubes to cover $M$ is simply,

$$N(\varepsilon) = L\varepsilon^{-1}$$

(3.4)

It follows that $d = 1$, which concurs with $M$ as being defined as a line. Now consider defining $M$ as a surface, with area $A$. As before, it follows that,

$$N(\varepsilon) = A\varepsilon^{-2}$$

(3.5)

and hence that $d = 2$. Now define $M$ with the following construct: a unit line segment has its middle third removed; the remaining pieces have their middle thirds removed, and those pieces have their middle third removed, etc *ad infinitum*. This object is called the Cantor set, and is depicted below visually in Fig 3-2.

![Cantor set diagram](image)

Figure 3-2: Visual depiction of the Cantor set. Note that the structure is scale-invariant.

To calculate the fractal dimension of the Cantor set, consider the number of cubes needed to cover subsequent iterations of the object:
Thus it can be seen that in the generalization of $m$ iterations,

$$N(\epsilon = 1/3^m) = 2^m$$  \hspace{1cm} (3.6)$$

By plugging equation (3.7) into the formal definition for fractal dimension (3.3), we obtain a non-integer dimension for the Cantor set, as given by,

$$d_{Cantor} = \lim_{m \to \infty} \frac{\ln 2^m}{\ln 3^m} = \frac{\ln 2}{\ln 3} \approx 0.63$$  \hspace{1cm} (3.7)$$

### 3.2 Fractal dimension in a-Si:H as a proxy for nanos-structure

Typical morphological descriptions of thin films can often be misleading in their ability to accurately describe a film. Consider as an example, the definition of root-mean-square roughness $R$ for a film surface,

$$R = \sqrt{\frac{1}{n} \sum_{i=1}^{n} z_i^2}$$  \hspace{1cm} (3.8)$$

where $n$ is the number of data points taken on the film surface, and $z$ is the measured height of the surface at the point $i$. Such a definition for roughness can encompass film’s whose peaks and distribution are radically different. A visualization of this is shown below in Fig. 3-3.

#### 3.2.1 Defining fractals on a thin film

Applying fractal dimension concepts to surfaces allows for a more robust description than traditional parameters. Fractal dimension gives a measure of the complexity of
a film, the distribution of its features, as well as its roughness. For the surfaces of thin films, the fractal dimension will be a real number between 2 and 3, with 2 denoting a perfectly flat surface (also called the marginal fractal), and 3 one whose structure reaches out in all possible directions (also referred to as the extreme fractal) [30].

The Hausdorff dimension described in the preceding section is one of several metrics which can be applied to fractal surface system. Other metrics, such as packing dimension, Minkowski-Bouligand dimension, and correlation dimension exist; mathematically they usually reduce to the same description of the fractal, and only the implementation of different counting structures and their position over the points in the vector space differ. A typical method to perform the calculation of equation (3.3) for a surface involves drawing a log-log plot of $N(\epsilon)$ and $1/\epsilon$. The slope of the linear region of such a plot can easily be related to the fractal dimension. Note that saturation will occur for low values of $1/\epsilon$ as the cube size becomes large enough to envelop the entire structure. Likewise, large values of $1/\epsilon$ will approach a lower bound as the increasingly small cube sizes mostly fail to envelop the points on the structure. It should be noted that most "box counting" methods of this sort are usually highly dependent on the specific algorithm that is used to calculate them, and the litera-
ture shows that the calculated fractal dimension can vary substantially depending on algorithm choice; variation method box counting algorithms give the most accurate fractal dimension calculations, when tested with computer-generated surfaces with known fractal dimension [31]. Other methods to investigate the fractal dimension of a film and its broader context among other film structures involves the calculation of a film power spectral density.

3.2.2 Power Spectral Density (PSD) analysis

Much like power spectra is calculated for signals, it can be similarly calculated for film surfaces. These PSD can then be used to fit several types of spatial-frequency based models which can reveal roughness parameters, fractal dimension, and other metrics. Consider a film whose measured height at the point \((m, n)\) is \(Z_{mn}\). The fast Fourier transfer (FFT) PSD of such a film is given by,

\[
P(f_x, f_y) = \frac{1}{L^2} \left[ \sum_{m=1}^{N} \sum_{n=1}^{N} Z_{mn} e^{-2\pi i \Delta L(f_x m + f_y n) (\Delta L)^2} \right]^2
\]

(3.9)

where \(f_x\) and \(f_y\) are the spatial frequencies in the \(x\) and \(y\) directions, \(L^2\) is the total area being analyzed, \(N\) is the total number of data points in a given direction, and \(\Delta L = L/N\) is the sampling distance. Frequently it is more useful to plot and analyze PSD as functions of only one spatial frequency instead of the two presented above; in these cases, a transform of the data is performed converting it into polar coordinates, and the PSD are expressed as a function of the radial component.

Most films exhibit some sort of fractal behavior. A purely fractal model for a film [30] is given by,

\[
P_{\text{fractal}}(f) = \frac{K}{f^{\nu+1}}
\]

(3.10)

where \(K\) is denoted the spectral strength and \(\nu\) is the spectral index. From a log-log plot of \(P\) and \(1/f\) the spectral index can be calculated. It can be shown that the spectral index is related to the fractal dimension by,
\[ d = \frac{6 - \nu}{2} \]  

(3.11)

Another powerful model used in PSD analysis is the $k$-correlation, or $ABC$ model[32]. This model fits three parameters, and accounts for the saturation effect seen at low spatial frequencies.

\[ P_{ABC} = \frac{A}{(1 + B^2 f^2)^{(C+1)/2}} \]  

(3.12)

The parameter $A$ determines the constant value of the PSD at low spatial frequencies. The parameter $B$ is used to determine the correlation length of the PSD, which indicates the lower limit where a spectra goes from saturated to fractal. The parameter $C$ determines the fall-off of the PSD in the fractal regime, which is characterized by a negative linear slope. Additional models that attempt to explain other features in a PSD can be found in the literature [30]. It is common in modeling to assume linear superposition of several model types to account spectra features.

### 3.2.3 AFM imaging, data acquisition, and power spectra analysis

The deposited films in section 1.4.3 were analyzed using atomic force microscopy (AFM). Scans were performed on a 2 $\mu$m x 2 $\mu$m area, with a scan size of 512 x 512 data points. Scans were taken near the center of the wafer, and placed to avoid extraneous particles or flakes that sometimes were present on the film surfaces. Silicon cantilevers with a diamond like carbon coating (purchased from Ted Pella), and an average resonance of 190 kHz were used in all scans. Figure 3-4 shows a typical film scan.

Films exhibited evenly spaced, rounded hill-like features. Smaller granular features were often present in the space between hills. In general, overall morphology observed was qualitatively similar to other a-Si:H thin films found in the literature [33].

Typical film parameters average and root-mean-square roughness were calculated for
all films; little variation was noted. Average film roughness was $1.49 \pm 0.34$ nm, and average root-mean-square roughness was $2.02 \pm 0.54$ nm.

Spectral data was processed in MatLab using a modified power spectral analysis script based on [34] for generating the radially averaged 2D PSD. A typical film PSD is shown below in Figure 3-5.

All obtained spectra were well-fitted with the k-correlation model, but displayed deviations from linearity at high spatial frequencies. Although the prevalent granular structure at the nanometer level can partially account for this, it is likely that tool noise is mostly responsible [35]. Spectra did not exhibit any local maxima associated with super-structures or other features commonly found in non-metal thin film depositions.

The SPIP 5.1.1 software suite for AFM data processing was used to evaluate the film’s fractal dimension. The fractal dimension calculation uses a box count algorithm similar to the one described in 3.2.1. The subsequent section details the findings of
Figure 3-5: PSD for a-Si:H AFM data with $k$-correlation fit; $A = 1.5 \times 10^{-9}$, $B = 8.33$, $C = 4.21$ Note signal rise at high frequencies

3.2.4 Results of fractal studies on thin films for varying deposition conditions

Fractal dynamics and their expression in nature have long been associated with material behavior, and thin films in particular. The concept of a fractal stress and strain has been explored before within the context of material mechanics; in particular, it has been observed that certain solids exhibit deformation patterns and stress distributions akin to fractal patterns [36]. AFM analyses on thin films, both metals and non-metals, have shown a breadth of self-similar structures which instantly remind mathematicians of their theoretically defined analogues. This work hypothe-
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Average roughness [nm]</th>
<th>RMS roughness [nm]</th>
<th>Fractal dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>W01</td>
<td>1.78421</td>
<td>2.24902</td>
<td>2.06576</td>
</tr>
<tr>
<td>W03</td>
<td>1.30439</td>
<td>1.64426</td>
<td>2.20894</td>
</tr>
<tr>
<td>W12</td>
<td>1.19074</td>
<td>1.85509</td>
<td>2.17595</td>
</tr>
<tr>
<td>W13</td>
<td>1.26535</td>
<td>1.77438</td>
<td>2.19215</td>
</tr>
<tr>
<td>W14</td>
<td>2.05016</td>
<td>2.85187</td>
<td>2.17408</td>
</tr>
<tr>
<td>W15</td>
<td>1.53611</td>
<td>2.66337</td>
<td>2.17453</td>
</tr>
<tr>
<td>W16</td>
<td>1.94752</td>
<td>3.15344</td>
<td>2.04701</td>
</tr>
<tr>
<td>W17</td>
<td>1.93800</td>
<td>2.69108</td>
<td>2.21056</td>
</tr>
<tr>
<td>W18</td>
<td>1.29431</td>
<td>1.62624</td>
<td>2.29462</td>
</tr>
<tr>
<td>W19</td>
<td>1.25399</td>
<td>1.57093</td>
<td>2.29731</td>
</tr>
<tr>
<td>W20</td>
<td>2.24429</td>
<td>2.83488</td>
<td>2.04055</td>
</tr>
<tr>
<td>W21</td>
<td>1.26304</td>
<td>1.58394</td>
<td>2.27211</td>
</tr>
<tr>
<td>W22</td>
<td>1.61059</td>
<td>2.02535</td>
<td>2.22963</td>
</tr>
<tr>
<td>W23</td>
<td>1.33660</td>
<td>1.70049</td>
<td>2.14026</td>
</tr>
<tr>
<td>W24</td>
<td>0.94192</td>
<td>1.28583</td>
<td>2.12070</td>
</tr>
<tr>
<td>W25</td>
<td>1.70887</td>
<td>2.34995</td>
<td>2.23208</td>
</tr>
</tbody>
</table>

Table 3.1: Morphology and fractal dimension data

sizes a novel insight: the fractal morphology of a thin film surface is a function of the growth-induced stresses in the film. Thus an appropriately defined fractal dimension could be used as a concrete proxy for nanostructure, not only in superseding typical morphological parameters as a more adequate description of the film, but also allowing for the engineering of specific stress/morphology combinations. In photovoltaic applications and particularly those related to the creation of a-Si:H devices, this could allow for the creation of films that minimize hole traps through an adequate application of stress [37], at the same time that their domain structure is such that it enhances hole mobility [38]. The fractal dimension of all films described in 1.4.3 were calculated using the previously described procedure for AFM data. As was with the stress data in chapter 2, consider first the manipulation of fractal dimension through the variation of growth conditions, namely process pressure and power. The obtained results are summarized in Table 3.1, and Figs. 3-6 and 3-7.

The obtained data do not suggest any clear correlation between process conditions and the resulting fractal morphology. An average fractal dimension of $2.18 \pm 0.07$ was found, indicating that films were marginally fractal. A weak, linearly decreasing correlation can be observed with increasing process pressure. As previously described
in 2.4, an increase in pressure results in an increased inter-gaseous impact probability; the increased deposition rate could result in a sparser matrix, making the growth kinetics of a relatively flat surface more likely. However, the spread of this same data is very large, particularly when accounting for films deposited at different power levels. Consider next the fractal data in terms of the measured stresses for each of the films, summarized below in Figure 3-8.

Similarly, no correlation was found between the measured stress in the film and the fractal dimension. Although changes in domain structure have been noted [reference] for films deposited over larger thickness ranges than the ones presented (well in excess of one micron), the sub-micron range does not exhibit significant changes in morphology, despite a variation in stress of almost 1 GPa, as noted earlier.
Figure 3-7: Fractal dimension as a function of power
Figure 3-8: Fractal dimension as a function of measured film stress
This page intentionally left blank
Chapter 4

Thin Film Spectroscopy for Thickness, Index of Refraction, and Density Determination

4.1 Spectral reflectance measurements

Spectroscopy measurements determine the amount of light reflected from a sample at different wavelengths. By taking this measurement over a range of wavelengths (typically starting near the ultraviolet), a wealth of information can be determined, including film thicknesses and indices of refraction. This can be done even for samples with multiple layers. More sophisticated data processing can take the measured indices of refraction and determine the density of a film, thus allowing for an optical measurement of film microstructure.

4.1.1 Basic spectral reflectometry theory

Consider below in Fig. 4-1 a simplified schematic of a spectral reflectance measurement; incident and reflected light showed at a non-normal angle for simplicity.

An incident light beam is directed at a sample. Some of that light is transmitted through the sample; some of it gets absorbed by the sample material. This dual
nature of a material’s ability to both transmit and absorb light is reflected in the definition of its complex index of refraction, \( N = n - ik \). The index of refraction \( n \) is the ratio of the speed of the propagating light in vacuum to that in the medium; the extinction coefficient \( k \) is a measure of how much light gets absorbed by the medium.

The spectral reflectance measurement uses an optical detector to determine the fraction of light that was reflected off of the sample’s surface. Note that although Fig. 4-1 shows the light at a non-normal angle, the actual measurement directs the light (and detects its reflection) at a normal angle to the sample.

Consider a simple film monolayer whose \( n \) and \( k \) do not depend on the wavelength of light being directed at the material. Reflectivity \( R \) of a film in air with \( n_{air} = 1 \) can be used to calculate \( n \) and \( k \) of the film through,

\[
R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}
\]  

(4.1)

\( Cauchy’s \ equation \) is an empirical formula that relates \( n \) to the wavelength of light, and is also a useful tool for calculating indices of refraction for well-known materials in monolayer configurations,

\[
n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + ... 
\]  

(4.2)

Here the coefficients \( A, B, \) and \( C \) can be determined by fitting. Note that Cauchy’s
The equation is usually only valid in the visible wavelength region. To determine a material's index of refraction over a wider range of wavelengths and with the presence of multiple interface dispersion, the mathematical tool of the Kramers-Kronig relationship must be used to relate the complex reflectance spectra for such a system.

### 4.1.2 Thickness and index of refraction mathematical modeling with Kramers-Kronig relationship

The Kramers-Kronig relationship is a set of mathematical precepts that allows for the building of a domain from an incomplete response [39]. Consider a complex function \( \chi(\omega) = \chi_1(\omega) + \chi_2(\omega) \). If the function is analytic in the upper half plane of the variable \( \omega \) and vanishes faster than \( 1/|\omega| \) as \( |\omega| \to \infty \), they are expressed as,

\[
\begin{align*}
\chi_1(\omega) &= \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\chi_2(\omega')}{(\omega' - \omega)} d\omega' \quad (4.3) \\
\chi_2(\omega) &= -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\chi_1(\omega')}{(\omega' - \omega)} d\omega' \quad (4.4)
\end{align*}
\]

where \( P \) is the residue, or Cauchy principal value. To illustrate the application of the Kramers-Kronig relationship to a thin film measurement, consider the following model for the imaginary part of an amorphous material's complex permittivity \( \varepsilon_2(E) \) [40],

\[
\varepsilon_2(E) = 2nk = \sum_{j=1,2,3} A_j C_i E_{0k} (E - E_{0j})^2 \frac{1}{(E^2 - E_{0j}^2) + C_i^2 E^2} \cdot \frac{1}{E} \quad (4.5)
\]

The coefficients presented are all fitting parameters, and \( E \) is the energy of the particular wavelength being considered. Applying this definition to Kramers-Kronig, the real part of the complex permittivity \( \varepsilon_1(E) \) can be determined as,

\[
\varepsilon_1(E) = n^2 - k^2 = \varepsilon_1(\infty) + \frac{2P}{\pi} \int_0^{\infty} \frac{s \varepsilon_2(s)}{s^2 - E^2} ds \quad (4.6)
\]

Note that with the large amount of fitting parameters, specialized software is required.
to perform these calculations. None the less, the Kramers-Kronig relationship is a simple way of determining thickness and index of refraction attributes of a multi-interface system from spectral reflectance measurements. For this study, a Filmetrics F40-EXR spectroscopy tool and software was used for the acquisition of spectra and calculation of thicknesses and indices of refraction. Below in Figure 4-2 is a sample spectra from an a-Si:H film of 191.6 nm thickness.

Figure 4-2: Measured spectra for an a-Si:H thin film sample; Blue traces are the actual measurement and the initial guess for values of the index of refraction $n$, while red traces are the model fit for the spectra and index of refraction based on the Kramers-Kronig relation and user defined inputs

### 4.2 Film density calculation

Film density calculation through optical measurements is a nondestructive and straightforward way of determining film microstructure. It is possible because of the way that an electric field affects the charge distribution of an atom, and how that charge distri-
bution affects the passage of electromagnetic radiation. The electronic polarizability $\alpha$ of an atom or molecule is defined as,

$$\alpha = \frac{p}{E} \quad (4.7)$$

where $p$ is the induced dipole moment of the atom or molecule, and $E$ is the electric field. Once the polarizability of a film is known, the Clausius-Mosotti relation can be used to determine the density of any material whose optical constants can be measured.

### 4.2.1 Theory of film density calculation through Clausius-Mosotti model

In its simplest form, the Clausius-Mosotti model gives the following relation between index of refraction $n$ and film density $\rho$ [41],

$$\frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} = \frac{4\pi}{3} N\alpha \quad (4.8)$$

where $M$ is the atomic or molecular weight, $N$ is Avogadro’s number, and $\alpha$ is the aforementioned polarizability of the atom or molecule. For a material such as a-Si:H, the contributions to polarizability of the Si, H, and dangling bonds must be considered [42]. The modified Clausius-Mosotti for this system becomes,

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi \rho}{3M_{Si}} \left( 2\alpha_1 + \frac{c_H}{1 - c_H} (\alpha_2 - 2\alpha_1) \right) \quad (4.9)$$

where $M_{Si}$ is the mass of Si and $c_H$ is the concentration of bonded hydrogen. The polarizability of the Si-Si bonds in the amorphous phase and Si-H bond are $\alpha_1 = 1.87 \times 10^{-24} \text{ cm}^3$ and $\alpha_2 = 1.36 \times 10^{-24} \text{ cm}^3$, respectively [42]. Thus to enable the measurement of density it becomes necessary to establish the hydrogen content of the film; this can be done with Fourier transform infrared spectroscopy.
4.2.2 FTIR for determination of thin film hydrogen content

Fourier Transform Infrared Spectroscopy (FTIR) is a similar technique to spectral reflectometry in that it provides a measure of how much light of a certain wavelength is transmitted through a sample. It differs in two principal points. First, an FTIR measurement scans all frequencies (or wavenumbers) at once, producing an *interfogram* which is deconvolved into each frequency’s contribution through a Fourier transform. This allows for a higher resolution in frequency (or wavelength) space than a reflectance measurement, which measures each frequency’s contribution individually through a selective grating. The second advantage is the range in which FTIR measures: as the name suggests, it measures well into the infrared, which allows for the detection of resonance peaks from different types of bonds in the sample. By comparing empirical data relating the width and location of these peaks in the spectra, the amount of hydrogen in an a-Si:H sample can be tabulated.

There are three principal spectral bands associated with Si-H bonds in a-Si:H. The first is located at ~2000 cm\(^{-1}\) and is associated with stretch-type Si-H bonds. The second is at ~900 cm\(^{-1}\) and is associated with bending-type bonds. Finally, the peak at ~640 cm\(^{-1}\) is associated with the wagging mode of the Si-H bond. All three can be used empirically to determine the amount of hydrogen in an a-Si:H film [43].

4.3 Results of film microstructure as a function of stress and deposition conditions

This work studied the effect of stress on index of refraction in a-Si:H films, and how this in turn affects the density of the film. The index of refraction is shown below as a function of stress in Fig. 4-3. Using the Clausius-Mosotti relation, the below data in Fig. 4-4 shows the stress of the films as a function of the Clausius-Mosotti measure, \(\frac{n^2 - 1}{n^2 + 2}\).

Although further measurements would need to be taken (FTIR to deconvolve the hydrogen content contribution to polarizability), the data shown in Fig. 4-4 shows a
distinct trend for the densification of films as a function of stress. Assuming relatively constant levels of hydrogen content and dangling bonds in the films, we hypothesize that the data shows less dense films at higher tensile stresses. A densification of the film is observed with decreasing stress levels, until the $C \times \rho$ value hits a constant value of about 0.855, at the region where stress transitions from tensile to compressive, and that value is maintained despite a variation in stress more than -1 GPa.

If FTIR measurements confirmed the premise of this trend, two conclusions could be drawn from this data. First, that the microstructure and specifically the density of the film can be modified with tensile stresses; however, the material does not experience densification in the compressive regime. Second, if future measurements of transport properties such as mobility exhibited differences between the different samples in compression, it can be better explained by the actual engineering of stress into the material, and not because of a change in microstructure of the film itself.
Figure 4-4: Measured stress as a function of $C \times \rho$, where $C$ encompasses constants from the Clausius-Mosotti relation and the material's polarizability. The grey lines are meant as a guide for the eye, showing first a linear decrease and then a constant value for stress over the range of the abscissa.
Chapter 5

Time-of-Flight for Mobility Measurements in an a-Si:H Thin Film

5.1 Basic theory of Time-of-Flight

The time-of-flight technique allows for the measuring of minority carrier drift mobility in a thin film. It is often used in lieu of more standard techniques such as Hall mobility; in the case of amorphous silicon, it is the only way to directly measure drift mobility, as most amorphous silicon when probed with Hall techniques yield a double sign reversal (double anomaly) [44], which invalidates the measurement. Although the interpretation of its data can be difficult, time-of-flight’s premise is simple: determine mobility by measuring the amount of time that it takes for a carrier to traverse the length of a sample.

Consider the definition of the drift velocity of a carrier under an electric field $\epsilon$. Namely,

$$\nu = \mu \epsilon \quad (5.1)$$

where $\mu$ is the carrier mobility and $\nu$ is the carrier’s velocity. If we consider a sample
size $d$, we can also express the carrier velocity as,

$$\nu = \frac{d}{t_d}$$  \hspace{1cm} (5.2)

where $t_d$ is the time that it took the carrier to drift across the distance $d$. If we combine equations (5.1) and (5.2), the carrier's mobility is shown to be,

$$\mu = \frac{d}{t_d \epsilon}$$  \hspace{1cm} (5.3)

Furthermore, if we note that for experimental simplicity and analysis the electric field can be applied over the same distance $d$ that the carrier moves through the bulk, this expression can be written as,

$$\mu = \frac{d^2}{t_d V_{dr}}$$  \hspace{1cm} (5.4)

where $V_{dr}$ is the driving voltage used to induce carrier drift through the sample.

A typical sample architecture for measuring hole mobility in a-Si:H is shown in 5-1.

![Typical a-Si:H sample architecture for hole mobility TOF](image)

**Figure 5-1:** Typical a-Si:H sample architecture for hole mobility TOF

An electric field is generated through the sample by applying a voltage $V_{dr}$ across
a top and backside contacts which sandwich an intrinsic a-Si sample. Subsequently a laser is used to optically excite the intrinsic a-Si near its top surface and generates electron hole pairs. The electric field separates the charges and sweeps electrons towards a thin n-doped a-Si layer, where they recombine. Conversely, holes are driven through the sample towards a thin p-doped a-Si layer, where they induce a voltage change \( V(t) \) at the backside contact. This voltage change can be used to determine the amount of time that the holes took to traverse the sample, and thus the material's hole mobility. \( C \) and \( R \) represent a lump capacitance and resistance for both the sample architecture and the measuring apparatus used to detect the voltage change \( V(t) \). Note also that it is enough to switch the positions of the p-doped and n-doped layers to measure electron mobility. Alternatively, one can substitute the n and p doped a-Si layers with an appropriately selected Ohmic and Schottky contact pair, to block the carriers to be measured from recombining at the top contact and only doing so though the backside contact.

Consider a circuit in which a voltage source is connected in parallel to a capacitance and a lump resistance. If we take the movement of the carrier through the bulk to be similar to a short, this simple circuit can be used to develop a model for the behavior of a carrier as it travels through a time-of-flight architecture. Because there is only one energy-storing element (namely the lump capacitance of the system), the model is first order [45]; furthermore the injection of carriers through optical excitation can be modeled as a step current being applied to this model. For the case of a hole, this instantaneous injection of charge on the cathode (backside contact) before holes reach it in the transit time \( t_d \) results in a current \( I(t) \) given by,

\[
I(t) = \frac{Q_p A}{t_d}, \quad 0 \leq t \leq t_d \tag{5.5}
\]

\[
I(t) = 0, \quad t > t_d \tag{5.6}
\]

where \( Q_p \) is the charge at the cathode induced from the injection of carriers, and \( A \) is the area of the cathode parallel to the sample. Converting to a voltage \( V(t) \), the
time-dependent behavior of a time-of-flight experiment approximated as a first order model is,

\[ V(t) = \frac{QpAR}{t_d} \left(1 - e^{-t/RC}\right) \]  

(5.7)

Note that the fractional quantity is a constant denoting an initial voltage, and thus the equation can also be written as \(V(t) = V_0 \left(1 - e^{-t/RC}\right)\). In order to determine the transit time \(t_d\), we consider the limits of when \(t_d\) is very small or very large compared to the system time constant, \(RC\). Namely, if \(t_d \ll RC\), the output voltage can be written as,

\[ V(t) \approx \frac{V_0 t}{RC} \quad 0 \leq t \leq t_d \]  

(5.8)

\[ V(t) = \frac{QpA}{C} \quad t > t_d \]  

(5.9)

For the case that \(t_d \gg RC\), the voltage can be written as,

\[ V(t) \approx V_0 \quad 0 \leq t \leq t_d \]  

(5.10)

\[ V(t) = 0 \quad t > t_d \]  

(5.11)

Thus from equations, we see that for both a high and low system time constant \(RC\), the transit time \(t_d\) of the carriers can be determined by recording the time evolution of the measured voltage, and noting the time in which the voltage either levels off, or drops to zero.

### 5.2 System design

A time-of-flight system typically requires three components: an oscilloscope to detect changes in the sample's current and/or voltage, a thin film sample with a contact architecture similar to the one derived above, and a laser to optically excite the
material being studied. The schematic in 5-2 shows a typical TOF setup.

![Figure 5-2: System schematic of typical TOF setup](image)

In order to appropriately choose each system component, an analysis follows based on material constraints, the physics of charge collection in a contacted structure, and the simplified first order model described previously.

### 5.2.1 RC-time constraints for a lumped-parameter TOF system model

The first constraint addresses the velocity at which an oscilloscope must be able to carry out the measurement given the sample architecture and the TOF system model. For a first order system subjected to a step input, the figures of merit for system response are given by,

\[
T_{10-90\text{Rise}} = 2.2RC 
\]

(5.12)

\[
T_{2\%\text{Stab}} = 4RC 
\]

(5.13)

where \(T_{10-90\text{Rise}}\) is the time it takes for the system signal to go from 10% of its final value to 90%, and \(T_{2\%\text{Stab}}\) is the time it takes for the system signal to reach and
remain within 2% of its final value.

For the specific case of a-Si:H, it is expected that average transit times $t_d$ will vary between 10-100 ns [46]. Referring to equations (5.12) and (5.13) as benchmarks, this indicates that a system would have to have a rise time on the order of 1 ns in order to accurately measure the lower end of this range. From equation (5.4), we can also construct mobility curves for materials with different mobility ranges, choosing a set voltage of 1V across the contacts as a typical for achieving electric fields on the order of $10^3$-$10^5$ V/cm [46]. Below 5-3 plots mobility and the required time resolution as a function of the transit distance $d$ in the sample.

![Figure 5-3: Required time resolution curves for TOF mobility measurement](image)

The figure plots typical curves for $1 - 0.001 \text{ cm}^2/\text{Vs}$ hole mobility for a-Si:H, as well as $10 - 100 \text{ cm}^2/\text{Vs}$ mobility of more exotic materials. For a typical device architecture of about 1 $\mu$m, the curves show that in this higher mobility regime, it is necessary to have an oscilloscope or other measuring apparatus capable of rise times.
in the 10-100 ps range.

5.2.2 Swept-charge physics and bias constraints from Hecht’s Law

In addition to ensuring that the measurement is taken at a sufficiently quick speed, one must ensure that enough charge is swept through and collected by the measurement apparatus to make the measurement accurate. By considering the physics of charges drifting in a trapping medium, the necessary constraints on the electric field and the distance between contacts can be determined. Consider first Hecht’s Law, relating the fraction of injected carriers collected at a contact sweeping carriers from a trapping medium,

\[ \frac{Q(t_d)}{Q_0} = \frac{\tau}{\tau_d} \left( 1 - e^{-t_d/\tau} \right) \]  

(5.14)

where \( t_d \) is the carrier transit time, and \( \tau \) is a characteristic recombination time of the medium. Assuming to first order that the potential in the medium is invariant during the carrier’s transit, the Einstein relation relates a carrier’s diffusivity to its mobility, namely,

\[ D = \frac{\mu kT}{q} \]  

(5.15)

where \( D \) and \( \mu \) are the carrier diffusivity and mobility, \( k \) and \( q \) are Boltzmann’s constant and the elementary charge, and \( T \) is the absolute temperature of the carrier in Kelvin. Likewise, the carrier diffusivity can also be used to express the diffusion length of the carrier in the material,

\[ L = \sqrt{D \tau} \]  

(5.16)

To determine the fraction of swept carriers strictly as a function of the driving voltage and the contact distance, consider a ratio \( x \) of the diffusion length to the transit distance \( d \),
\[ x = \frac{L}{d} \quad (5.17) \]

If we combine equations (5.14), (5.15), (5.16), (5.17), and rearrange equation (5.4) to solve for \( t_d \), we can express Hecht’s law in the form,

\[ \frac{Q(t_d)}{Q_0} = x^2 V_{dr} \frac{q}{kT} \left( 1 - e^{-\frac{kT}{q x V_{dr}}} \right) \quad (5.18) \]

Using equation (5.18), and assuming room temperature experimentation with a thermal voltage of \( kT/q = 25.85 \text{ mV} \), Fig. 5-4 plots the percentage of collected carriers as a function of the applied voltage over the distance \( d \). As a minimum threshold enabling accurate measurement, we seek the ratio of diffusion length to transit distance \( x \) that allows for 90% of the carriers to be collected at voltages on the order of 1V. The magnitude of the voltages must be in this range in order to maintain steady potentials on the order of tens of microseconds, which enables a switching on and off of the potential without inducing joule heating in the sample.

![Figure 5-4: Percentage of swept charge for TOF setup as a function of applied voltage](image_url)
For order of magnitude 1V, we find that 90% of carriers are swept through the contacts when the ratio of diffusion length to transit distance \( x = 0.35 \). With some a-Si:H devices having diffusion lengths of up to 800 nm [47], this implies that the time-of-flight setup requires a contact structure with a transit distance of no more than 2.3 microns.

### 5.2.3 Optical excitation constraints and ablation avoidance

Injection of carriers into the material requires a light source that must be carefully chosen. On the one hand, the wavelength of light chosen must be absorbed near the top surface of the sample, such that the generated carriers actually traverse the entire length of the sample and allow the calculation of the mobility through equation (5.4). This also ensures that either the n-doped thin layer or an appropriate Schottky contact can quickly sweep generated electrons, allowing only holes to move through the bulk of the sample.

On the other hand, the energy of the light must be carefully controlled such that it does not ablate the material, destroying it or in some cases actually recrystallizing that part of the sample. However, the source wavelength must also be energetic enough such that carriers are excited through the material’s band gap.

Below 5-5 shows the absorption depth to typical depth ratio for various thin film materials, as a function of the source wavelength. For an error in the distance traversed by the carriers comparable to the error in the time acquisition and voltage potential application components of the time-of-flight system, absorption depth to typical depth ratios on the order of 1% are required. For a-Si:H, this corresponds to source wavelengths smaller than 600 nm.

First order heat flow models and experiment [48] have shown a-Si:H to have an crystallization threshold fluence of about 300 mJ/cm\(^2\), and an ablation threshold fluence of 500 mJ/\(\mu\)J. The fluence of a laser \( F \) can be written as,

\[
F = \frac{hc}{\lambda A_s} \tag{5.19}
\]
where $h$ and $c$ are Planck's constant and the speed of light, $\lambda$ is the wavelength of the light source, and $A_s$ is the spot size of the source. Over a variety spot sizes used available in commercial laser systems, and wavelengths under 600 nm such that the appropriate absorption criterion are met, equation (5.19) yields fluences much less than 1 mJ/cm$^2$. Thusly, ablation criteria are not critical to a time-of-flight setup for a-Si:H, and the light source should be chosen exclusively to make sure that carriers are absorbed sufficiently close to the sample's top surface.
Chapter 6

Conclusions and Future Work

6.1 Conclusions

6.1.1 Stress modification through PECVD parameter variation

The variation of PECVD process parameters, was shown to be an effective way of controlling the stress in a-Si:H films. The material’s mechanical limits, both in buckling a delamination, where examined, and a pressure variation from 100 – 1000 mTorr was used to generate stresses from -983.4 MPa – 387.4 MPa. This broad range arising from pressure control demonstrates a simple way to engineer a desired stress into an a-Si:H film.

6.1.2 Morphology characterization through AFM and applications of fractal dimension

AFM measurements were used to characterize the surface of a-Si:H films. Despite exploring a large parameter space for depositing these films, little morphological difference was observed, with all films having similar roughnesses and domain distributions. It was hypothesized that the use of a fractal dimension measure could better distinguish between films that had been deposited in different conditions. The
overall similarity was also prevalent in the fractal dimension analysis, with all films producing very similar power density spectra. Fractal dimensions between $2.05 - 2.30$ were calculated, with no discernable trends across films deposited at different process pressures, power, and with different levels of stress.

It should be noted that PSD calculations of fractal dimension have shown significant differences between different deposition conditions for certain films [30]. However, almost invariably such films are usually in regimes much thicker than the submicron films that were deposited in this study. Thus the actual usefulness of fractal dimension as an all encompassing and unambiguous measure of films is still an open question.

6.1.3 Film densification and microstructure enhancement through the application of stress

The measurement of the index of refraction $n$ for the study's thin films found concrete trends between the stress in a material and its optical response; $n$ maintains a constant value of about 4.3 in the compressive stress regime, and then decreases linearly to about 3.7 when varying stress from 0 to 400 MPa. Although irrefutable conclusions cannot be made about the material when calculating the Clausius-Mosotti constant without determining the hydrogen and dangling bond content of the films, the trend appears to show a linear decrease in film density in the tensile stress regime up until compressive stresses. The material does not appear to densify in the compressive regime, despite a large stress variation of 0 to -1 GPa over those samples with engineered compressive stresses.

6.2 Future work

6.2.1 Time-of-Flight measurements of hole mobility in a-Si:H

With an adequate control over stress engineered into a-Si:H samples, the work begun here to measure mobility as a function of stress through time-of-flight measurements can proceed. Equipment acquisitions fulfilling the requirements described in Chapter
5 have been made in the Laboratory for Photovoltaic Research at MIT. The setup will be able to not only measure mobility of simple $p-i-n$ a-Si:H structures, but also of other thin films. Thus, it is the author's hope that engineering stresses in a-Si:H films will result in enhanced mobilities, and that in turn these films can be applied to commercial module applications.
Bibliography


