3D MEMS via (Post-)Buckling of Micromachined Structures 
and 
Integration of Bulk Nanoporous Elements in Microfluidic Devices 
by 
Fabio Fachin 
Submitted to the Department of Aeronautics and Astronautics 
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Abstract

The last two decades have seen a proliferation of fields and applications where microtechnologies have gradually replaced, and often outperformed, their macroscopic counterparts. From engineering to basic sciences, Micro-Electro-Mechanical-Systems (MEMS) are enabling a variety of functionalities that traditional technologies cannot provide, such as miniaturized biomedical platforms capable of detecting and targeting extremely rare particles in blood. Nonetheless, intrinsic limitations in state-of-the-art MEMS processes and materials are hampering further diffusion of microtechnologies, and this thesis work extends MEMS capabilities in two areas: (a) a new technique for three-dimensional (3D) structures for sensing and actuation; and (b) introduction of new bulk nanoporous elements in microfluidics to enhance the efficiency of existing microfluidic platforms and to enable access to sub-micron bioparticles. In the first area, although some efforts to achieve fully 3D microdevices are present in the literature, state-of-the-art MEMS devices are largely planar two-dimensional (2D) structures and are therefore intrinsically limited in their ability to sense and actuate. Here, a new approach to 3D MEMS is demonstrated where structures are designed to operate in the post-buckling regime, thus exploiting buckling phenomena to achieve functional elements that extend out of the wafer plane. An analytical approach to 3D MEMS design and characterization is presented, based on non-linear (post-)buckling of layered structures, including boundary flexibility (non-ideal clamping). One use of the model is the simultaneous extraction of residual stresses and boundary flexibility based solely on common microbridge test structures, with no need for multiple microbridge lengths, significantly reducing uncertainty (~20X) in the results compared to state-of-the-art characterization methods. A second use of the analytical model is for 3D MEMS design. Several 3D structural element concepts are experimentally demonstrated using CMOS, including an example of simultaneous three-axis thermal accelerometer design with enhanced 2D, and 3D sensing. These contributions extend the capabilities of state-of-the-art microfabrication procedures beyond planar layouts to 3D. Future work includes extension of the post-buckling design approach to elements other than microbridges (e.g., membranes) and to applications such as flow sensors and switches. In the second area of this thesis work, integration of
ultra-porous (99% porous) elements comprised of nanoporous forests of vertically-aligned carbon nanotubes (VACNTs) in MEMS is demonstrated, particularly their use in microfluidic applications for bioparticle manipulation. Introduction of porous materials in microfluidic devices significantly benefits MEMS by providing an alternative to current solid materials and designs (e.g., PDMS, silicon). The performance of some state-of-the-art microfluidic devices is hampered by detrimental flow characteristics that cause streamlines that drive particles away from the desired (solid) functional surfaces, hence hindering physical interaction between the target species and the functional elements. Porous microfluidic elements enhance particle-surface interactions by enabling fluid flow both around and through the functional elements, e.g., particles smaller than the VACNT pore size (~80nm) can be captured inside the porous elements. To date, inclusion of porous materials into microfluidic platforms has however largely been limited to low porosity and permeability polymer membranes, plugs and monoliths. Here, we demonstrate ultra-porous (99% porous) VACNT forests as a new microfluidic structural material. The in-plane geometry of VACNT elements can be accurately defined through photolithography of the CNT catalyst, while manipulation of VACNT growth conditions enables control of the elements’ out-of-plane height to create high aspect-ratio features up to mm-scale heights. Distinct from prior works where the effects of fluids on VACNT forests would result in either structural deformation or catastrophic forest collapse, VACNT elements have been integrated into microfluidic channels such that element geometry is preserved even under flow-through conditions. Simultaneous multiphysics (mechanical and chemical), multiscale (three orders of magnitude in size, from cells to viruses) bioparticle isolation on a single chip using VACNT designs is experimentally demonstrated. A direct comparison between nanoporous (VACNT) and solid (PDMS) designs shows increased (~7X) capture efficiency when transitioning to nanoporous elements. The fluid accessibility of VACNT elements is investigated, yielding permeability levels comparable to that of much larger macro-/micro-scopic porous elements. An analytical discussion of the effects of element porosity on permeability is also presented, revealing critical design considerations for porous materials in microfluidic applications. Additional efforts will be placed on further characterizing the microfluidic properties of nanoporous VACNT elements and the extension of these materials to fields beyond the biomedical sphere.

Thesis Supervisor: Brian L. Wardle
Title: Associate Professor of Aeronautics and Astronautics
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Acronyms and Symbols

2D ......................... two-dimensional
3D ......................... three-dimensional
CMOS ...................... complementary-metal-oxide-technology
CNT ....................... carbon nanotube
CTC ....................... circulating tumor cell
CVD ....................... chemical vapor deposition
DI  ......................... deionized
DRIE ....................... deep reactive ion etching
FE  ......................... finite element
IL  ......................... interference lithography
MEMS ..................... micro-electro-mechanical-systems
NO  ......................... nanostructured origami
PDMS ..................... polydimethylsiloxane
PJT ....................... polyimide joint technology
PTT ........................... pre-treatment time

SEM ........................... scanning electron microscope

VACNT ........................... vertically aligned carbon nanotube

$b$ ........................... width of element

$h$ ........................... thickness of element

$n$ ........................... total number of layers in a multilayered element

$w$ ........................... out-of-wafer-plane deflection

$A$ ........................... cross-sectional area

$N$ ........................... population size

$D$ ........................... diameter of feature

$E$ ........................... Young's modulus

$I$ ........................... second moment of area

$K$ ........................... nondimensional boundary flexibility index

$L$ ........................... length of element

$M$ ........................... bending moment

$P$ ........................... axial load, pressure

$Q$ ........................... volumetric flow rate

$R$ ........................... radius of curvature

$S$ ........................... pore size

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\( \kappa \quad \text{liquid permeability} \)

\( \kappa_T \quad \text{boundary flexibility} \)

\( \mu \quad \text{dynamic viscosity} \)

\( \nu \quad \text{Poisson's ratio} \)

\( \phi \quad \text{porosity} \)

\( \sigma_{\text{grad}} \quad \text{gradient stress inside a thin film material} \)

\( \sigma_{\text{mean}} \quad \text{mean stress inside a thin film material} \)

\( \sigma_{\text{residual}} \quad \text{total residual stress inside a thin film material} \)
Chapter 1

Introduction and Thesis Structure

Micro-electro-mechanical-systems (MEMS) are already playing dominant roles in a variety of sectors, from mechanical and aerospace engineering to basic sciences [27]. Without microtechnologies, many of the most impactful technological developments of the last two decades would have not been attained, including automotive safety systems (e.g., airbags) and personal computers. Operating at a scale much smaller than macroscopic devices, MEMS enable functionalities that would not otherwise be accessible, such as single cell detection for biomedical applications [28] or atomic force microscopy in materials science [29]. MEMS technology has driven many sectors and resulted in the rapid diffusion of platforms such as cellular phones whose market penetration increased from 34% in 2000 to about 93% in 2010 [30]. Nonetheless, further advancement and diffusion of microtechnologies is currently hindered by intrinsic limitations in state-of-the-art MEMS fabrication processes and materials, and this thesis work addresses two of these critical impediments: (a) the engineering need to create fully three-dimensional (3D) structures for 3D sensing and actuation; and (b) the need for highly fluid accessible, nanoporous materials both to overcome the fluid-dynamic limitations of existing solid microfluidic platforms and to access sub-micron biological species that cannot currently be targeted. Chapters 2 and 3 of this thesis are dedicated to the presentation of solutions to these two barriers (see also discussion below), while conclusions and additional perspectives on further development of the MEMS field are the focus of Chapter 4.
1.1 Three-Dimensional (3D) MEMS

Most current MEMS fabrication techniques are the direct descendants of the production processes that were introduced during the second half of the last century by the semiconductor industry, and whose primary goal is the creation of integrated circuits (ICs) on silicon chips [31]. These techniques are essentially two-dimensional processes where features are defined on the wafer plane with very limited possibility for creating functional elements that extend in the out-of-wafer-plane dimension. As a consequence, despite the introduction of some quasi-3D microfabrication processes during the last two decades (e.g., deep reactive ion etching - DRIE [31]), microfabricated devices are still largely planar, 2D structures that are intrinsically limited in their ability to sense and actuate in a three-dimensional (3D) fashion. As an example, multiple 2D accelerometer units are presently required to measure a fully three-dimensional acceleration field, which poses problems in terms of accuracy, reliability, as well as costs. In this thesis work we address this critical limitation in MEMS fabrication by proposing and demonstrating three-dimensional MEMS structures in the post-buckled regime. Buckling effects can in fact be exploited to cause controllable, large out-of-wafer-plane deformations of functional elements, thus representing a versatile approach to 3D MEMS that does not require any modification to state-of-the-art equipment and fabrication processes. An analytical approach to MEMS design and characterization is also discussed and applied to a 3D architecture for thermal accelerometer applications. The design and experimental demonstration of 3D MEMS via (post-)buckling of micromachined CMOS structures is the focus of Chapter 2.

1.2 Nanoporous Materials in Microfluidic Platforms

To date, MEMS fabrication processes have been unable to provide high-definition, micro-/nanoporous materials integrated into microfluidic devices. Solid materials such as silicon, glass and polymers are instead the dominant structural components in state-of-the-art microfluidic platforms, with applications ranging from particle sorting and filtration to health diagnostics [28,32]. As miniaturized detection methods are becoming increasingly sensitive, capable of
single cell [33, 34] and even single virus detection [35, 36], efficient capture of specific bioparticles is now the rate-limiting step of lab-on-a-chip assays for particle identification. Under this perspective, flow stagnation effects at the fluid-solid interface are particularly detrimental as they drive target particles away from the desired functional surfaces, thus hindering capture efficiency. Incorporation of porous materials in microfluidic technologies is therefore attractive, as this could result in fluid flow both around and through the functional features, thus enhancing particle-feature interactions as well as active surface compared to similar solid designs. To date, inclusion of porous materials into microfluidic platforms has however largely been limited to elements such as porous silicon [37], membranes [25, 38], and polymer/silicon monoliths [39-42] (see also Table 3.1), whose degree of geometrical definability is not sufficient to enable accurate flow control inside microchannels [43]. As a consequence, porous technologies are quite limited and consist of simple porous plugs that fill the microchannels for applications such as solid-phase extraction [44], or two-dimensional membrane elements sandwiched between microchannel layers for particle filtration [25]. Here we propose bulk, nanoporous forests of vertically aligned carbon nanotubes as a new ultra-porous material for use in microfluidic platforms. Distinct from prior research that utilized randomly aligned carbon nanotubes for applications such as optical tags or drug delivery [39], our work focuses on exploiting the morphology and properties of vertically aligned carbon nanotube (VACNT) forests (e.g., strength, patternability, high aspect ratio) to achieve increased (compared to both solid and porous state-of-the-art designs) bioparticle-solid surface interactions. The design, microfluidic integration, and experimental application of carbon nanotube (CNT)-enhanced biomedical MEMS devices are discussed in Chapter 3.
Chapter 2

3D MEMS via (Post-)Buckling of Micromachined Elements

Extension of MEMS devices to three-dimensional sensing and actuation requires the development of new techniques to allow design and fabrication of micro-functional elements that extend and operate outside the wafer plane. In this Chapter we present a new concept to 3D MEMS fabrication that exploits buckling phenomena to induce large, controllable out-of-wafer-plane deformations in functional CMOS elements. The discussion opens with a review of the current state-of-the-art in 3D MEMS fabrication techniques (Section 2.1), followed by an overview of the objectives and approaches for this research (Section 2.2). The Chapter progresses with the presentation of an analytical model for the (post-)buckling of microfabricated structures (Section 2.3) and its application to thin-film materials characterization (Section 2.4). Finally, the analytical design and fabrication of various 3D MEMS architectures is discussed in Sections 2.5-2.6, including an application example consisting of a 3D platform for acceleration sensing using thermal effects.
2.1 Background and Prior Work

The following is a review of the current literature in 3D MEMS and of the fabrication processes so far developed to achieve three-dimensional micromachined features. A brief overview of two traditional MEMS processes, *i.e.* bulk and surface micromachining, and complementary-metal-oxide-semiconductor (CMOS) technology, is also provided as these techniques constitute the fabrication tools utilized in this work.

2.1.1 State-of-the-art in 3D MEMS Manufacturing

Here we review some of the current approaches to 3D MEMS fabrication: Polyimide Joint Technology, Nanostructured Origami, Gray Scale Lithography, Deep Reactive Ion Etching, LIGA, Microstereolithography of SU-8, and Interference Lithography. Between these approaches, Nanostructured Origami, DRIE and Gray Scale Lithography are particularly relevant for the purposes of this thesis work as they are compatible with CMOS processing (see Section 2.1.2.2).

2.1.1.1 Polyimide Joint Technology

Polyimide joint technology (PJT), originally proposed by Ebefors *et al.* [1, 2], is a self assembling method for bending microfabricated structures based on thermal shrinkage/expansion of polyimide in V-grooves. The concept is schematically shown in Figure 2-1, where a silicon “leg” is actuated by electrical heating of the polyimide joint. One of the advantages of this technique is that it allows for both a static and a dynamic (actuator-like) mode: the leg’s out-of-plane static rotation can be controlled over a wide range by defining the curing temperature of polyimide, while the large thermal expansion of polyimide can be exploited to dynamically move the structure. PJT has been successfully applied to create, *e.g.*, micro flow sensors and micro robots (Figure 2-2). The technique has however a major limitation, *i.e.* it lacks positional locking capability. PJT does not in fact provide the opportunity to accurately “lock” the final out-of-plane position for any structural member, thus being impractical for applications that require positioning of the functional elements (*e.g.*, flow sensors, thermal sensors).
2.1.1.2 Nanostructured Origami

Nanostructured origami (NO) is a combination of techniques that takes inspiration from the Japanese art of paper folding and that enables three-dimensional microstructures through the deformation of patterned lower-dimensional elements (e.g., 2D beams and membranes) into 3D shapes. To date, three different Nanostructured Origami processes have been developed: NO via stressed hinges, NO via ion implantation, and NO via magnetic folding. As later discussed in Section 2.2, NO via stressed hinges and via ion implantation represent two key references for the buckling-based approach to 3D MEMS in this work, as they introduce the concept of residual stress exploitation to drive 2D functional elements in the out-of-wafer-plane direc-

Figure 2-1: The Polyimide Joint Technology process yields out-of-plane features through deformation of polyimide V-grooves [1].

Figure 2-2: Example of micro-robot fabricated using Polyimide Joint Technology [2].
Nanostructured Origami via Stressed Hinges: The NO via stressed hinges technique relies on the post-release, residual stress-induced curling (or bending) of thin films. This approach is schematically represented in Figure 2-3(a), and requires the presence of at least three layers: a sacrificial layer (e.g., silicon), a structural layer (e.g., SiN) and a stress layer (e.g., chromium). The approach consists of controlling the residual stress (more specifically, the gradient residual stress) inside the stress layer to cause an out-of-plane rotation of the structural element after the sacrificial layer is etched away. This technique allows for a wide range of fold angles, as well as for the ability to create more complex geometries by using a combination of multiple hinges (Figure 2-3(b)). However, the main drawback of this method is that residual stresses may be hard to control and post-deposition effects (such as thermal stresses due to ambient temperature changes) can cause significant structural deformation of the thin elements. As a consequence, it is difficult to create very accurate folds using this method. Arora et al. [45] show that devices designed to fold between 20° and 90° have approximately 90% yield, whereas folds between 120° and 180° have only 5% yield. Stiction issues are identified as the main cause of low yield of this technique. NO via stressed hinges is therefore impractical for applications that require high-definition, densely folded structures. Nonetheless, the technique demonstrates the possibility to induce out-of-plane deformation of structural microfabricated members through residual stress control, and can definitely be considered as a building block of the 3D MEMS work in this thesis.

Nanostructured Origami via Ion Implantation: Similarly to NO via stressed hinges, NO via Ion Implantation uses ion irradiation to cause large stress gradients in cantilevered elements and therefore significant structural bending at release (Figure 2-4). The fold angle and radius depend on the thickness of the cantilever, the ion dose and the sputter depth. In their work [4], Arora et al. irradiated silicon nitride cantilevers with Ga⁺ ions by using a dual beam FIB system. The results show that the fold angle increases nonlinearly with ion dose, as sputtering also re-
Nanostructured Origami via Magnetic Folding: The last approach to Nanostructured Origami uses a combination of nanomagnets and a rotating magnetic field to achieve folding forces and torques on microfabricated elements. The technique, initially presented by In et al. [46], is schematically depicted in Figure 2-5 and consists of two membranes that are connected via a compliant hinge whose faces are patterned with an array of nanomagnets (Figure 2-5(a)). Structural folding and alignment are then achieved through a combination of two different steps: first, the membranes are actuated from the flat to the folded state using a rotating external magnetic field that magnetizes the nanomagnets and creates a folding torque (coarse
alignment; Figure 2-5(b)); then, fine alignment is achieved through reciprocal attraction between nanomagnets on the opposing surfaces, a step that also corrects for possible errors both in hinge fabrication and in the first coarse alignment (Figure 2-5(c)). This approach is attractive in that the fabrication of the discrete elements is completely decoupled from the assembly process, and in that no additional locking mechanism is required once the final fine alignment is completed. The technique is however significantly limited in its ability to provide features with large out-of-plane dimensions, and is therefore confined to applications where high density and large surface area are desirable (e.g., supercapacitors).

2.1.1.3 Gray Scale Lithography

Developed in 1992 by M.R. Whitley et al. [47], gray scale lithography is a technique that allows creation of gradient height structures in MEMS. The approach consists of three key steps, as shown in Figure 2-6: (a) gray-scale mask design, (b) lithography and (c) dry anisotropic etching. Steps (a) and (b) yield a precisely designed 3D profile in a photoresist-masking layer by using a sub-resolution, two-dimensional binary optical mask and a photolithography stepper system together to locally modulate the intensity of ultra-violet (UV) light [6], while step (c) allows transfer of the 3D profile in the photoresist to the underlying (silicon) substrate by dry anisotropic etching (e.g., deep reactive ion etching - DRIE). A fundamental aspect of gray-scale lithography is the amount of different grey levels (or height levels) available to create the pat-
terns in the photoresist (and subsequently to substrate) [7]. Figure 2-7 shows an example of a three-level gray scale mask with its related photoresist structure. Two parameters characterize the mask, pitch and pixel size, which both contribute in determining the diffraction pattern and therefore the UV light intensity that the photoresist will be exposed to. From this perspective, gray scale limitations include resolution limits on minimum pixel size and maximum number of grey levels. Despite being an effective approach to achieve gradient heights in MEMS structures, grey scale lithography is still far from allowing the creation of fully three-dimensional micro-systems. Devices obtained via grey scale lithography are in fact only “quasi-3D”, where the out-of-plane portion of these systems is still defined by the traditional etching processes (e.g., DRIE) that are used to transfer the photoresist profile into the silicon.

![Gray-scale Patterned Optical Mask](image)

**Figure 2-6:** The three primary steps in gray-scale technology: (a) gray-scale mask design; (b) exposure and development of the 3D pattern in photoresist; (c) transfer of photoresist structure into the silicon substrate [6].

2.1.1.4 Deep Reactive Ion Etching (DRIE)

Deep reactive ion etching (DRIE) is a microfabrication process that enables creation of high aspect-ratio features through highly anisotropic etch sequences [31]. To date two different approaches to DRIE exist: Cryogenic [48] and Bosch Advanced Silicon Etch (ASE) [49]. The cryogenic approach, originally developed by Tachi et al. [50] in 1988, is a two-step process where a masked silicon wafer is first cooled down to -110°C (163 K) using liquid nitrogen, followed by SF₆/O₂ plasma etch. This very low temperature regime weakens the chemical reactions that result in isotropic etching, yet enables ion-bombardment of those non-masked surfaces.
directly exposed to the plasma, thus resulting in highly anisotropic etches. Compared to the pulsed Bosch process (see below), this technique yields higher sidewall smoothness. However, cryogenic DRIE is incompatible with standard masking materials as these crack at the extremely low temperatures at which this technique operates [48]. Distinct from the cryogenic approach, the Bosch ASE DRIE process alternates passivation (C4F8, 5-12sec) and etching (SF6, 5-15sec) steps to achieve aspect ratios of approximately 20 to 30:1, with etch rates between 1.5-4μm/min [31]. The Bosch process has been extensively analyzed during the two past decades, with several published works describing the optimal process conditions to achieve prescribed profiles (e.g., [51]), and it has been applied to a variety of applications including through-wafer electrical interconnects [52] and high-aspect-ratio micromolds [53]. Two state-of-the-art examples of high-aspect-ratio features created using the Bosch process are shown in Figure 2-8 [8]. Despite its ability to create high-aspect-ratio features, the DRIE process is limited to quasi-3D (i.e., extruded 2D) structures and it cannot be applied to the creation of structures that lay above the wafer plane.

2.1.1.5 LIGA

LIGA is a German acronym for Lithographie (X-Ray Lithography), Galvanoformung (Electrodeposition), and Abformtechnik (Molding) [54], and it indicates a process that enables creation of
high-aspect-ratio microstructures through the following steps (see also [9] and Figure 2-9): (1) a X-ray sensitive thick polymer photoresist (typically PMMA; thickness from μm to cm) is bonded to an electrically conductive substrate; (2) The resist is masked using a strong X-ray absorbing material and exposed to parallel beams of high-energy X-rays from a synchrotron radiation source; (3) The photoresist is developed, resulting in a three-dimensional (extruded 2D) structure; (4) The 3D mold is placed in an electroplating bath and a metal (e.g., nickel) is plated into the open areas of the polymeric mold; (5) Finally, the resist is chemically removed to produce a metallic mold insert which can either be the final product or a mold insert for subsequent precision plastic molding. The LIGA process has been applied to applications such as separation nozzles for uranium enrichment [54] and transmission lines and filters [55]. The cost of this technique is however elevated, thus favoring alternative approaches such as pseudo-LIGA which combines LIGA with DRIE fabrication approaches [31]. Similar to DRIE, LIGA is limited to the creation of quasi 3D (extruded 2D) structures of materials that can be electrodeposited.

2.1.1.6 3D MEMS Using Polymers

Our review of current approaches to 3D MEMS ends with an analysis of those works that use polymers as structural materials. Distinct from the approaches of the previous Sections, these
techniques haven’t emerged from the microelectronics realm, but rather from the rapid prototyping industry [31]. Polymers are in fact very advantageous when short fabrication times are required, as turnaround from design (e.g., CAD) to prototype typically does not exceed a few hours. Although a relatively large body of literature on polymer-based MEMS exists (e.g., replica molding - REM, micro-contact printing - μCP, and micro-transfer molding - μTM; [31]), here we focus on the two technologies that more than others have enabled successful creation of fully three-dimensional polymer microfeatures: microstereolithography of thick SU-8 resists and interference lithography.

**Microstereolithography of thick SU-8:** To date, SU-8 is probably the most utilized polymeric material in 3D MEMS fabrication. This acid-catalyzed negative photoresist is characterized by excellent sensitivity, high resolution, as well as good thermal and chemical stability [31]. SU-8 optical properties are extremely attractive for 3D microfabrication: SU-8 provides very-low optical absorption in the near UV region, which allows for very deep penetration of photons and hence structures with aspect ratios as high as 100:1 [31]. Next to very high aspect ratio structures, SU-8 can be used in combination with high-definition microlithography to enable complex three-dimensional patterns. Using this approach, Bertsch et al. have demonstrated SU-8 micro-turbines, imbricated strings, helicoid cogs as well as micro-gears (see Figure 2-11),

![Figure 2-9: The LIGA process [9].](image-url)
hence proving the design flexibility of this technique [10]. Nonetheless, the very polymeric nature of SU-8 poses some critically stringent limitations for applications where high strength and limited structural deformability are required (e.g., actuators, shock sensors): SU-8 Young’s modulus ranges between 3-4 GPa, and is about two orders magnitude lower than most MEMS structural materials (e.g., $E_{\text{Silicon}}=130$ GPa). High temperature applications are also incompatible with SU-8 technology. The practicality of this polymer-based approach to 3D MEMS is therefore dependent on the selected application and its structural requirements.

![Image](image-url)

Figure 2-10: Two examples of 3D structures created via microstereolithography of thick SU8 resists [10].

**Interference lithography:** Interference lithography (IL) involves the transfer of a periodic intensity pattern formed by the interference of multiple beams of light into a photoresist [11]. The process is schematically shown in Figure 2-11(a) and consists of three main steps. First, a positive photoresist is exposed to a periodic light intensity distribution, followed by development, to create an interference lithography template (ILT). The ILT is then infiltrated with a selected pre-polymer (e.g., PDMS) and cured. Finally, the ILT/polymer composite undergoes UV flood exposure and development to create a 3D elastomeric/air network. An example of 3D PDMS network created via IL is presented in Figure 2-11(b). IL is attractive in that it enables rapid fabrication of large-area, periodic 3D templates on a sub-micrometer scale, with accurate control of both structural symmetry and volume fraction. The overall film thickness is however strictly limited by the absorption properties of the photoresist utilized to create the ILT. To date, the
maximum height of IL-based devices is confined to micron levels.

![Process schematic](image1)

![Example device](image2)

(a) Process schematic  
(b) Example device

Figure 2-11: Interference lithography enables 3D periodic patterns in PDMS substrates [11].

### 2.1.2 Traditional Microfabrication Techniques

#### 2.1.2.1 Bulk and Surface Micromachining

Bulk micromachining and surface micromachining constitute the principal microfabrication tools used by the current MEMS industry [31]. In bulk micromachining, features are etched into the bulk of crystalline (e.g., silicon - Si) and non-crystalline (e.g., quartz) substrates. To date, a variety of bulk micromachining etching approaches have been developed, both dry (e.g., plasma etching and reactive ion etching - RIE) and wet (e.g., KOH, TMAH and EDP), according to the phase (gas or liquid) of the selected etchant. Bulk micromachining has been widely used to create elements such as beams, membranes and other large features for applications from pressure sensors to accelerometers [27]. On the opposite side, surface micromachining creates features by building them up layer-by-layer on the surface of a substrate. Surface micromachining exploits a series of sacrificial and structural layers: a sacrificial layer is oftentimes deposited and patterned first, followed by deposition of the structural layer; the sacrificial layer is then etched away to release the structural layer, thus creating components such as free standing beams and cantilevers. Similar to bulk micromachining, surface micromachining has also been widely used for applications such as accelerometers for air-bag systems. One of the ad-
vantages of surface micromachining is its compatibility with IC processes (CMOS or Bi-CMOS) to achieve fully integrated devices. From a 3D fabrication perspective, both bulk and surface micromachining are limited in their ability to provide highly out-of-plane functional elements. Both techniques were in fact developed and designed to create planar 2D elements. Nonetheless, in this work we demonstrate the possibility to achieve 3D structures by combining bulk micromachining approaches with CMOS microfabrication. The method exploits residual stress control to induce buckling of CMOS structures at release, as later discussed in Section 2.2.

2.1.2.2 Complementary-Metal-Oxide-Semiconductor (CMOS)

Complementary-metal-oxide-semiconductor (CMOS) is a microfabrication process that is commonly used in the IC industry. CMOS consists of four major steps [31]: deposition, patterning, doping and etching. The technique starts from a silicon substrate on which a thin film (e.g., SiO₂, Au) is deposited by chemical vapor deposition (CVD) or physical vapor deposition (PVD). A light-sensitive photoresist layer is then deposited on top of the thin layer and patterned using photolithography, followed by optional doping (typically through ion implantation). Finally, an etching sequence is performed to transfer the pattern from the photoresist to the underlying layer. This deposition-patterning-doping-etching process is repeated as many times as the total number of layers that are required by the application, ultimately resulting in thin, two-dimensional (2D) devices. From a design perspective, one of the main drawbacks of CMOS fabrication is that it provides very limited flexibility in terms of device cross-section and overall fabrication sequence. CMOS foundries are in fact very reluctant to consider any modification in their processes, as this often results in yield reduction. Only minimal design options are therefore available when using CMOS, such as wafer selection and additional pre- or post-CMOS steps (e.g., pre-CMOS annealing). Thermal budgets also pose significant restrictions to MEMS designers. Post-CMOS processing temperatures should in fact not exceed 450°C, which inherently excludes any high temperature deposition and annealing steps from all post-CMOS sequences. As an example, post-CMOS thermal budgets are incompatible with carbon nanotube (CNT) fabrication as well, which requires temperatures on the order of 700°C to 1000°C.
Despite these limitations, in this thesis work we demonstrate extending CMOS processing to 3D MEMS fabrication as well. Our approach combines CMOS, residual stress control and bulk etch processes to create structural elements that are designed to operate in a post-buckled regime, as we describe in the next Section.

2.2 Objectives and Approach: 3D MEMS via Controlled Buckling of Microfabricated CMOS Beam Structures

In this Section we introduce a new strategy to 3D MEMS that is based on micromachined elements operating in the post-buckling regime. First, a review of the effects of residual stresses on the post-release deformation of micromachined structures is presented (Section 2.2.1), followed by a description of how such effects are used in our work to create three-dimensional MEMS elements (Section 2.2.2).

2.2.1 Residual Stress-Induced Deformation of Micromachined Elements

The final geometry of any MEMS structure is directly dependent on its residual stress state. Residual stresses (also referred to as intrinsic stresses) arise from production and indicate a condition in which a thin film is subjected to mechanical stress in its as-deposited state [31,56]. Residual stresses are determined by many factors, including thermal mismatch between the film and the substrate and lattice imperfections [57]. Description of the residual stress state in a film is not trivial, as stress is often not uniformly distributed inside the structure. A generally accepted representation for the residual stress field ($\sigma_{\text{residual}}$) in an as-deposited isotropic thin film material is [58]:

$$\sigma_{\text{residual}} = \sum_{i=0}^{\infty} \sigma_i \left( \frac{z}{h} \right)^i$$

(2.1)

where $\sigma_{\text{residual}}$ is the total residual stress in the film, $\sigma_i$ is the $i^{th}$-order stress component, and
\[ z \in [-h/2, h/2] \] is the coordinate across the film thickness \((h)\), with the origin lying on the film mid-plane. Although Equation (2.1) defines the total residual stress as a summation of an infinite number of stress components, in MEMS practice only the first two stress terms are generally considered: \(\sigma_0\), the mean residual stress (constant through thickness); and \(\sigma_1\), the gradient residual stress (linear and anti-symmetric through thickness). Also for the purposes of this work, (2.1) is reduced to:

\[
\sigma_{\text{residual}} = \sigma_0 + \sigma_1 \frac{z}{h} = \sigma_{\text{mean}} + \sigma_{\text{grad}} \frac{z}{h}
\]

where we define \(\sigma_0 = \sigma_{\text{mean}}\) and \(\sigma_1 = \sigma_{\text{grad}}\). Within the MEMS community, tensile stresses are typically defined as positive mean stresses \((\sigma_0 > 0)\), whereas positive gradient stresses \((\sigma_1 > 0)\) define those stress states where the film becomes gradually more tensile as one gets closer to the film's top surface \(i.e., z = h/2\). An example of as-deposited thin film material subjected to the stress state of (2.2) (compressive mean stress, positive gradient) is shown in Figure 2-12(a), where a schematic representation of the through-thickness residual stress profile is included as well.

Residual stresses become particularly important at release. Once the substrate (or sacrificial layer in general) is removed, thus leaving the film unconstrained, the system evolves to relieve \(i.e.,\ cancel or minimize\) residual stresses through mechanical deformation of the thin structure. For instance, a film characterized by compressive mean residual stress \(i.e., \sigma_{\text{mean}} < 0\) will undergo elongation at release (Figure 2-12(b)), whereas films with positive gradient stresses \(i.e., \sigma_{\text{grad}} > 0\) will curl (or bend) upwards. The “direct” effects of mean and gradient stress on free standing structures are therefore significantly different: while the former causes in-plane deformations, gradients cause out-of-plane deformation (bending) of the structural features. Gradient-induced deformation of micromachined structures represents the working principle behind most current approaches to 3D MEMS \(e.g.,\ Polyimide Joint Technology, Nanostructured Origami\) as discussed in Section 2.1.1.

Nonetheless, here we show that mean residual stresses can achieve very large out-of-plane deformations (larger than by gradient effects) “indirectly” through exploitation of \textit{buckling} phe-
nomena. Within the materials and structures community, the term buckling indicates a structural instability that elements such as columns, beams, and membranes undergo when subjected to compressive loads that exceed a critical level, typically referred to as critical buckling load, thus resulting in very large structural deformations usually associated with “failure” of the element [12]. An example load-deformation curve for a bar that is subjected to compressive axial loading is presented in Figure 2-13, where creating 3D structures through buckling of micro-machined members becomes apparent. As the compressive load \( P \) increases (lower, straight solid line), the bar shortens but maintains a straight, planar configuration. This scenario holds until the critical buckling load \( \bar{P} \) is reached. At this point, the deformation path is characterized by a bifurcation, and the structure can evolve either in a straight configuration (upper, dashed line) or in a buckled configuration (right, solid line). In practice, the former scenario never occurs as it requires the absence of any material, geometrical, and load imperfections or asymmetries. Instead, once the critical load is reached, the structure undergoes buckling and its configuration suddenly transitions from planar to out-of-plane (see also Figure 2-14). Noticeably, any increase in applied load beyond the critical load causes significant non-linear deformation in the structure, as well as significant out-of-plane bending. The presence of this highly non-linear post-buckled load-deformation region in the response of structures subjected to compressive loads is extremely relevant for the scope of this thesis, as it allows large out-of-plane deformations of constrained MEMS structures by exploiting compressive mean residual stresses and buckling phenomena. This is in contrast to the other 3D stress-based techniques (e.g., Nanostructured Origami) that rely on gradient stresses. Thin film materials could be deposited on a substrate and their residual stress controlled to yield a relatively high compressive stress state in the film. The structure could then be released to create a fully constrained structural element (e.g. a microbridge) that would buckle under the effects of its compressive mean stress, thus yielding a functional element located well above the wafer plane (Figure 2-14). Design of micromachined elements in the post-buckled regime represents the approach to 3D MEMS that is adopted in this work. Furthermore, the post-buckled elements are stiff structures relative to those that can be achieved by the other 3D techniques in Section 2.1.
2.2.2 Design of 3D MEMS Operating in the Post-Buckling Regime

Whereas most designs and applications see buckling as a detrimental effect leading to device failure, the objective of this work is to demonstrate 3D MEMS devices that operate in the post-buckling regime. Our approach follows the discussion of Section 2.2.1, where we introduced the idea of functional 3D MEMS elements through accurate residual stress manipulation and process control (e.g., etching, release). The goal here is to demonstrate this capability, looking forward to new devices with fully 3D functionalities (e.g., 3D thermal sensing, 3D flow sensing) through analytical modeling, characterization, and design of buckled CMOS beam structures,
Compressive load

Critical (buckling) load

Unstable, straight configuration

Bifurcation

Stable, buckled configuration

Stable, straight configuration

End deflections, $\Delta$

Figure 2-13: Schematic of the load-deformation curve for a buckled bar subjected to compressive axial loads. (Adapted from [12])

Figure 2-14: Large compressive mean stresses can cause buckling and large out-of-plane deformations in micromachined “bridge structures”. Not to scale.

thus also extending the CMOS microfabrication technique to 3D MEMS processing as well. A schematic of a possible 3D architecture via buckled microbridges is shown in Figure 2-15, where the application of such 3D designs to some of the above mentioned functionalities is introduced as well.
To fulfill these objectives, the following is investigated in this thesis:

- **Development of an analytical model for the non-linear (post-)buckling of microfabricated beam structures.** The (post-)buckling of micromachined structures depends on many factors, including device geometry, residual stresses, as well as fabrication process specifics. Design of 3D MEMS in the post-buckling regime requires modeling of the effect of all such elements on the final device, and in this work we develop a new analytical tool for analyzing the post-buckling of micromachined beam structures. The model, presented in Section 2.3, takes into account non-linear geometrical effects, residual stresses (both gradient and mean) as well as boundary flexibility, thus providing an analytic tool that can be used for both design and characterization of MEMS elements.

- **Thin-film characterization using analytical tool.** Current thin-film characterization techniques are based on structural models that do not take into account the effects of highly non-linear deformations nor boundary non-ideality, thus providing inaccurate estimates of the complete stress state of thin-film materials. Here we propose a new approach to multilayered thin film characterization that uses analytical results to significantly reduce uncertainty on the extracted stresses. The method is described in Section 2.4, and it enables simultaneous extraction of both residual stresses (mean and gradient) and boundary flexibility based solely on experimental measurements of microbridge test structures. The technique eliminates the need for both multiple microbridge lengths and cantilevers deflections, thus significantly simplifying the characterization process and thereby lowering its overall cost.

- **Extension of CMOS process to 3D MEMS fabrication.** We recall from Section 2.1.2.2 that CMOS processes were originally developed for fabrication of IC components, *i.e.* of planar 2D elements. Extension of CMOS to 3D fabrication is however attractive, as it would take advantage of the very high quality and yield of CMOS processes for applications well beyond IC. In this work, we extend the capabilities of CMOS processing beyond 2D MEMS fabrication using post-release buckling control to achieve 3D microfabricated elements.
CMOS provides MEMS designers relatively limited flexibility in terms of cross section design and process control, thus intrinsically limiting control over the residual stresses as well. As a consequence, pure residual stress manipulation (i.e., via process parameter control such as temperature of deposition) is not a viable option for controlling the post-release deformation of CMOS structures. Here, we overcome this additional CMOS limitation by developing four device architectures that enable control over the post-release deformation of CMOS elements. These four architectures are applicable to other microfabrication techniques as well, as we discuss in Section 2.5.

- **Experimental demonstration of 3D MEMS designed to operate in the post-buckling regime.** Demonstration of 3D functionalities via buckled designs represents the ultimate goal of this work. The last part of this Chapter (Section 2.6) is therefore dedicated to the presentation of both a 3D MEMS analytical design procedure that we developed and CMOS 3D MEMS example structures, including a 3D platform for acceleration sensing using thermal effects.

### 2.3 Analytical Model for the Non-Linear Buckling of Layered MEMS Beam Structures

MEMS design consists of a highly multidisciplinary process, where functional requirements must meet fabrication and economic considerations. To facilitate MEMS engineers in the design process, a large number of computer-based tools have been developed during the past few decades, from layout editors to multiphysics finite element (FE) software. Using these tools MEMS designers have been able to significantly reduce the number of iterations, and therefore the cost, associated with the development of new MEMS technologies, thus fostering the recent diffusion of microsystems across multiple fields, from electronics to biomedicine.
Figure 2-15: “Up-and-down” buckled microbridges for 3D MEMS: Buckling effects can be exploited to achieve 3D MEMS for a number of applications from flow sensors to 3D thermal sensing. Not to scale.

[32,56]. Nonetheless, to date few analytical works exist that address the structural performance of Microsystems (see next Section). The lack of analytical design tools is especially relevant when material and structural design are considered: given that the final shape - and therefore the performance and functionality - of MEMS devices is highly dependent on factors such as residual stresses from production and packaging effects (see also Section 2.2.1 and [31]), MEMS designers would greatly benefit from analytical tools capable of accurately extracting intrinsic/package-induced stresses, as well as of predicting the effect of such stresses on the devices. Here, we introduce a new analytical model for the non-linear post-buckling of layered beam structures, including the effect of residual stresses (both mean and gradient) and boundary flexibility. The analytical tool is a key component of our approach to 3D MEMS using post-buckling, and it can be applied to both material characterization and device design. Furthermore, the model is applicable to macro-scale structures as well.
2.3.1 Analytical Model Derivation

We consider the multi-layered beam\(^1\) of Fig. 2-16(a) (length \(L\), width \(b\), and thickness \(H\)), modeled as a homogenized structure characterized by effective weighted-properties\(^2\) in bending \((\bar{EI})\) and extension \((\bar{EA})\) [59], effective thickness \(\bar{h}\), and constrained at both ends by torsional

\[^1\]The analysis holds also for isotropic plate layers as discussed in Appendix A, and in this thesis we make distinction between beam and plate when working with effective properties. As a matter of fact, many of the MEMS test structures analyzed here are plates.

\[^2\]See Appendix A for a description of the procedure utilized for computing the effective weighted-properties of the layered films in this work. The method uses straightforward and well-known classical laminated theory [59]. A summary of the CMOS material properties is included in Appendix A as well.
springs (Figure 2-16(b)). This allows all future calculations, including gradients, to be considered as if the beam were homogeneous. The torsional spring constant \( (\kappa_T) \) represents the structure's boundary flexibility, dependent on the fabrication process details (e.g., underetch). The in-plane boundary condition is assumed to be perfectly fixed (no in-plane sliding), and the released beam structure has the following residual stress state form [58] as in Equation 2.2:

\[
\sigma_{\text{residual}} = \sigma_{\text{mean}} + \sigma_{\text{grad}} \frac{z}{h}
\]

where \( \sigma_{\text{mean}} \) and \( \sigma_{\text{grad}} \) are the mean and gradient stress components, respectively. Assuming that the out-of-plane (z-axis) deflections - \( |w(x)| \) - are much smaller than \( L \), elastic Euler-Bernoulli beam-column theory leads to the following non-linear, governing equations (see also Appendix C and [60–62]):

\[
\overline{EI} w^{IV}(x) + \int_{0}^{L} \frac{E A_{\text{mean}}}{2L} w^I(x)w^I(x)dx \Bigg|_{0}^{L} w^{II}(x) = 0
\]

\[
M(x) = \overline{EI} w^{II}(x) + \frac{T}{h} \sigma_{\text{grad}}
\]

where \( w^m = \frac{dm}{dx} \) (with \( m \) being a Roman numeral), \( M(x) \) is the bending moment inside the structure, \( A \) and \( T \) are the effective total cross-sectional area and second moment of inertia of the homogenous beam, respectively (see Appendix A), and \( x \) is the axial coordinate (see Figure 2-16(a)). The boundary conditions for this system are:

\[
w(0) = 0; \quad M(0) = \kappa_T w'(0)
\]

\[
w(L) = 0; \quad M(L) = -\kappa_T w'(L)
\]

where the dependence of the solution on boundary flexibility \( (\kappa_T) \) becomes apparent: "very small" \( \kappa_T \) values result in a simply-supported boundary condition \( (M(0) = M(L) \approx 0) \), whereas "very large" \( \kappa_T \) values result in a clamped boundary condition \( (M(0) = M(L) > 0) \), or the well-known geometric boundary condition of \( w'(0) = w'(L) = 0 \). Equations (2.6)-(2.7) do not how-
ever allow one to quantify “how small” or “how large” \( \kappa_T \) needs to be in order for a specific beam to behave as simply-supported or as clamped. To overcome this issue, we employ the results of N. M. Newmark in [13] for the linear buckling of a beam with torsional springs to derive an alternative formulation of (2.6)-(2.7). As shown below, this alternative formulation allows one to quantify the minimum boundary flexibility level at which a microbridge structure becomes effectively clamped, thus providing a reference value that can be used to define the effective boundary condition of microfabricated structures. In [13], Newmark analyzes the effect of end-fixity on the buckling of columns, finding the following relationship between critical buckling load \( P_{\text{crit}} \) and boundary flexibility \( \kappa_T \):

\[
P_{\text{crit}}(\kappa_T) = \frac{\pi^2EI}{L^2} \left( \frac{0.4 + \varphi}{0.2 + \varphi} \right)^2 = PEuler \left( \frac{0.4 + \varphi}{0.2 + \varphi} \right)^2, \quad \varphi = \frac{EI}{\kappa_T L} \tag{2.8}
\]

which can be rewritten in non-dimensional form as:

\[
\frac{P_{\text{crit}}(\kappa_T)}{PEuler} = \left( \frac{0.4 + \varphi}{0.2 + \varphi} \right)^2 \tag{2.9}
\]

where \( \frac{P_{\text{crit}}}{PEuler} \) is the non-dimensional critical buckling load and \( PEuler \) is the critical load for the simply-supported case. Equation (2.9) is plotted in Figure 2-17 for a polysilicon/dielectric bi-layer film (\( L=400\mu m, b=40\mu m, \bar{h}=2.91\mu m, \bar{E}=169\)GPa). The non-dimensional critical buckling load ranges from 1 for simply supported beams (\( \kappa_T \rightarrow 0 \), or \( \varphi \rightarrow \infty \)) to 4 for clamped structures (\( \kappa_T \rightarrow \infty \), or \( \varphi \rightarrow 0 \)), as is well known. The results of Figure 2-17 show the existence of two boundary flexibility values, \( \kappa_{T,ss} \) and \( \kappa_{T,clamped} \), below and above which the column can be effectively considered simply-supported (\( \kappa_T < \kappa_{T,ss} \); left, orange shadowed region in Figure 2-17) or clamped (\( \kappa_T > \kappa_{T,clamped} \); right, purple shadowed region in Figure 2-17) with respect to buckling load, as no significant variation in critical buckling load is observed within these two \( \kappa_T \) ranges. This finding is extremely relevant, as it points to a region where current structural models that assume boundary ideality, with \( \kappa_{T,ss} = 0 \) or \( \kappa_{T,clamped} = \infty \), fail. To properly account for the effect of boundary flexibility on our CMOS multilayered structures, in this work we define
\( \kappa_{T,ss} \) and \( \kappa_{T,clamped} \) as those boundary flexibility values below/above which less than 0.1% variation in critical buckling load is observable as compared to the ideal simply-supported/clamped cases. The \( \kappa_{T,ss} \) and \( \kappa_{T,clamped} \) boundary flexibility values for the polysilicon microbridge of Figure 2-17 were respectively quantified as \( 1.5 \times 10^{-9} \) Nm and \( 1.2 \times 10^{-4} \) Nm, thus pointing to a very large region (spanning about 5 orders of magnitude) where traditional approaches are not applicable. Later it will further be shown that the micromachined CMOS beams studied here are characterized by a non-ideal boundary condition.

It is useful to express boundary non-ideality by normalizing \( \kappa_T \) by \( \kappa_{T,clamped} \) to yield a flexibility index (\( K \)), defined as:

\[
K = \frac{\kappa_T}{\kappa_{T,clamped}} = \begin{cases} 
0, & \kappa_T < \kappa_{T,ss} \\
\kappa_T / \kappa_{T,clamped}, & \kappa_{T,ss} \leq \kappa_T \leq \kappa_{T,clamped} \\
1, & \kappa_T > \kappa_{T,clamped}
\end{cases} \Rightarrow \text{Simply-supported}
\]

\[
\Rightarrow \text{Clamped}
\]

Equation (2.10) allows one not only to differentiate between those values of \( \kappa_T \) that result in simply-supported (\( K = 0 \)) or clamped (\( K = 1 \)) boundaries, but also to quantify the non-ideality.

Figure 2-17: Dependence of the non-dimensional critical buckling load on boundary flexibility for a polysilicon microbridge (\( L=400\mu m \), \( b=40\mu m \), \( t=2.91\mu m \), \( E=169\text{GPa} \)).
of boundaries (e.g., $K = 0.6$ indicates a boundary 60% between simply-supported and perfectly clamped). Using (2.10) in (2.6)-(2.7), the following alternative statement of the boundary condition equations is obtained:

$$w(0) = 0; \quad M(0) = K\kappa_{T,\text{clamped}} w'(0)$$  \hspace{1cm} (2.11)

$$w(L) = 0; \quad M(L) = -K\kappa_{T,\text{clamped}} w'(L)$$  \hspace{1cm} (2.12)

where the dependence of the system's behavior on boundary ideality ($K$) is now clear. Assuming a sinusoidal post-buckled shape for the structure [12]:

$$w(x) = C_1 \sin \lambda x + C_2 \cos \lambda x + \frac{x}{L} + C_4$$  \hspace{1cm} (2.13)

with $C_1$, $C_2$, $C_3$, and $C_4$ being constants, and substituting in (2.11)-(2.12), the following system of equations can be derived:

$$
\begin{bmatrix}
D_{11} & D_{12} & 0 & 0 \\
D_{21} & D_{22} & 0 & 0 \\
sin(\lambda L) & \cos(\lambda L) - 1 & 1 & 0 \\
0 & 1 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
C_1 \\
C_2 \\
C_3 \\
C_4
\end{bmatrix}
= 
\begin{bmatrix}
\frac{(\bar{A} \bar{h})}{6} \\
\frac{(\bar{A} \bar{h})}{6} \\
\sigma_{\text{grad}}
\end{bmatrix}
$$  \hspace{1cm} (2.14)

where:

$$D_{11} = K\kappa_{T,\text{clamped}} \left[ \lambda - \frac{\sin(\lambda L)}{L} \right]$$

$$D_{12} = \frac{EI\lambda^2}{L} - K\kappa_{T,\text{clamped}} \left[ \frac{\cos(\lambda L) - 1}{L} \right]$$

$$D_{21} = \frac{EI\lambda^2}{L} \sin(\lambda L) + K\kappa_{T,\text{clamped}} \left[ \frac{\sin(\lambda L)}{L} - \lambda \cos(\lambda L) \right]$$

$$D_{22} = \frac{EI\lambda^2}{L} \cos(\lambda L) + K\kappa_{T,\text{clamped}} \left[ \lambda \sin(\lambda L) + \left( \frac{\cos(\lambda L) - 1}{L} \right) \right]$$
Given the intrinsic stresses ($\sigma_{\text{mean}}$, $\sigma_{\text{grad}}$) and the boundary flexibility ($K$), (2.14) depends only on the post-buckled deformation wavelength ($\lambda$). This constrained problem (the solution must satisfy Equation 2.4) can therefore be solved for any combination of intrinsic stresses and boundary flexibility using a numerical method (e.g., Newton-Raphson), providing a full description for the post-buckling of micromachined beams in the form:

$$w(x) = f \{\sigma_{\text{mean}}, \sigma_{\text{grad}}, K\}$$

Equation (2.15) is plotted in Figures 2-18 to 2-20 for a polysilicon/dielectric bilayer film ($L = 400\mu\text{m}$, $b = 40\mu\text{m}$, $h = 2.91\mu\text{m}$, $E = 169\text{GPa}$), showing the effect of mean and gradient stress and boundary flexibility on the structure's post-release deformation. The effect of $\sigma_{\text{mean}}$ on the midpoint out-of-plane deformation amplitude, $w(L/2) = w_c$, is presented in Figure 2-18, where larger (compressive) mean stress values yield larger deflections. It is important to notice that three of the four loading conditions in Figure 2-18 exceed the critical buckling load for the structure (~34MPa), thus yielding large out-of-plane deflections. On the contrary, the solid blue line ($\sigma_{\text{mean}}=-20\text{MPa}$) represents a configuration in which the structure is not buckled and is characterized by negligible out-of-plane deflections (very small, $<0.01\mu\text{m}$, gradient-induced deflections are present). In Figure 2-19 we then show the dual effect of gradient stresses: in addition to modulating the deformation amplitude (with larger gradients resulting in larger deformations), gradient stresses also determine (together with boundary flexibility $K$; see below) the direction in which the beam buckles. Finally, the influence of boundary flexibility is presented in Figure 2-20. Noticeably, the microbridge behaves very differently at different $K$ values. For those cases where the boundary can be approximated as simply-supported ($0 < K < 0.1$) the beam shows downward (negative $z$-axis) deflections, whereas larger flexibility values ($K \geq 0.1$) are associated with positive deflections. Being that the boundary's spring effect is very small at low $K$ values, simply-supported beams deflect according to the shape dictated by their gradient stress: beams with positive gradient stresses deform into a "smiling beam" configuration (negative or downwards deflections), whereas negative gradients lead to a "frowning beam" configuration. Hence the downward deflections and the "smiling beam" configuration of the $K=0$ beam of Figure 2-20 ($\sigma_{\text{grad}}=+40\text{MPa}$). Conversely, large $K$ values result in large boundary spring reac-
tion forces that cause the beams to buckle in a direction opposite to that of simply-supported beams, as seen in all the beams with $K > 0.1$ in Figure 2-20. It is also important to notice the effect of boundary flexibility on the post-buckled shape of microbridges, and particularly on the slope at their extremities: whereas the simply-supported ($K = 0$) beam shows a large finite slope at its root, all the other cases are characterized by negligible slopes. The distinct effects of mean and gradient stresses and boundary flexibility on the beams' deformation (i.e., amplitude modulation and direction control) can be exploited to tailor the post-release configuration of micromachined elements and to create 3D structures.

![Graph showing effect of mean residual stress on post-buckling deformation of polysilicon/dielectric multilayered microbridges](image)

Figure 2-18: Effect of (compressive) mean residual stress on the post-buckling deformation of polysilicon/dielectric multilayered microbridges ($L=400\,\mu m \times b=40\,\mu m \times h=2.91\,\mu m$, $E=169\,GPa$).

### 2.3.2 Model Validation: Buckling of a 7075-T6 Simply-Supported Aluminum Beam

The analytical model was validated through comparison with other analytical results available in the current buckling literature [12, 13, 56, 58, 63]. As a validation example, in Figure 2-21 we
Figure 2-19: Effect of gradient residual stress on the post-buckling deformation of polysilicon-/dielectric multilayered microbridges (L=400μm x b=40μm x h=2.91μm, E=169GPa).

Figure 2-20: Effect of boundary flexibility on the post-buckling deformation of polysilicon-/dielectric multilayered microbridges (L=400μm x b=40μm x h=2.91μm, E=169GPa).
present the response of a simply-supported 7075-T6 aluminum beam \((L=4\text{ in}, b=1\text{ in}, H=0.1\text{ in}, E=10.4\times10^6\text{ lb/in}^2, \alpha=13.1\times10^{-6}/\circ\text{F})\) subjected to both mean and gradient residual stress. This plot is in agreement with the results R.M. Jones presents in Chapter 2.9.6 of "Buckling of Bars, Plates and Shells" [12], and it illustrates several relevant aspects associated with the buckling of beams. First of all, one can notice that the graph is bounded on the top by a horizontal line, which corresponds to the critical buckling load \((P_{\text{critical}})\); for simply-supported beams, \(P_{\text{critical}} = P_{\text{Euler}} = \frac{\pi^2EI}{L^2}\). \(P_{\text{critical}}\) represents the maximum axial compressive load that a simply supported beam with no gradient residual stress (hence no initial deflection) can withstand before buckling out-of-plane. In this gradients-free scenario, once buckling occurs, the reaction load \(P\) stays constant, and additional increase in compressive mean stress is relieved through out-of-plane deformation of the structure. This behavior is however modified when gradient stresses are present in the structure, as they cause the column to deflect even when no compressive load is applied. As a consequence of the gradient-induced initial deflection, the application of any compressive load now results in out-of-plane deformation (bending) of the structure. This important effect of gradient stresses on the buckling of beam structures is further discussed in Section 2.3.3, where we introduce the concept of deformation maps as applied to their use in 3D MEMS design.

2.3.3 Uses of the Analytical Model: an Analytical Approach to 3D MEMS Design and Characterization

The analytical tool can be applied to both 3D MEMS design and to thin-film characterization. The derived analytical relation, Equation (2.15), expresses the out-of-plane deformation of a microbridge as a function of its residual stresses and boundary condition, and can therefore be applied both to directly quantify the effect of \(\sigma_{\text{mean}}, \sigma_{\text{grad}}, \) and \(K\) on the structure's deforma-

---

3Note that in [12] the mean and gradient stresses are applied in the form of "thermal" loads. Residual stress can be modeled via thermal loads in the 1-dimensional case through the thermal expansion coefficient \(\alpha\) as: \(\sigma_{\text{mean}} = \bar{E}\alpha\Delta T_{\text{avg}}\) and \(\sigma_{\text{mean}} = \bar{E}\alpha\Delta T_h\), where \(\Delta T_{\text{avg}}\) and \(\Delta T_h\) are the average and through-thickness bar temperature changes as described in [12].

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Figure 2-21: Effect of mean and gradient stress on a 7075-T6 simply-supported ($K = 0$) aluminum beam ($L=4\text{in}$, $b=1\text{in}$, $H=0.1\text{in}$, $E=10.4\times10^6\text{lb/in}^2$, $\alpha=13.1\times10^{-6}/\circ\text{F}$; plot created for comparison with [12], Chapter 2.9.6, Figure 2-76).

...tion, or to infer the residual stress state and boundary flexibility of a specific structural element from experimental measurements of microbridge test structures. The former approach, that we refer to as "design mode", is based on the direct application of (2.15). Given the complete stress state ($\sigma_{\text{mean}}, \sigma_{\text{grad}}$, $K$) for a specific material combination/fabrication process, Equation (2.15) can be used to design and predict the post-release configuration of a micromachined bridge structure, including transverse loading to predict deflection mode shape, (out-of-plane) deformation details, as well as internal stresses (see also Appendix C and specifically Equation (C.10)). Conversely, a second use for the analytical model enables intrinsic stresses and boundary condition characterization of a specific material combination based on experimental microbridge test structure deflection measurements ($w_{\text{experimental}}$). This approach is referred to as "stress extraction mode". From a mathematical standpoint, the stress extraction approach can be expressed as:
\[
\{\sigma_{\text{mean}}, \sigma_{\text{grad}}, K\} = f^{-1}(w_{\text{experimental}})
\]  

(2.16)

where (2.16) is the inverse of (2.15), thus showing the complementarity between the design and stress extraction modes. Experimental results of the application of the analytical tool to both material characterization and device design in this work are presented in Sections 2.4 and 2.6.

**Deformation maps, and their application to MEMS design and characterization**

Equations (2.15) and (2.16) can be combined into an analytically derived graphical tool that we refer to as a buckled beam deformation map. Deformation maps contain the relationship between the (out-of-plane) deflection of a microbridge and its residual stresses and its boundary condition (see Figure 2-22), thus providing a compact description of the effect of the complete stress state on the post-release evolution of a microstructure. This is distinct from other representations such as those of Figures 2-18 to 2-20, as these provide information on the effect of one parameter at a time. Depending on the application, deformation maps can be multi-dimensional (analyzing the effect of multiple parameters - e.g., mean and gradient stresses - on the structure's performance) or monodimensional (relating out-of-plane deflections to one parameter only - e.g., mean residual stress). As an example, in Figure 2-22(a) we present a two-dimensional deformation map showing the effect of mean residual stress \(\sigma_{\text{mean}}\) and effective boundary condition \(K\) on the deformation of a polysilicon/dielectric bilayer film \(L = 400\mu m, b = 40\mu m, \bar{h} = 2.91\mu m, \bar{E} = 169\) GPa, \(\sigma_{\text{grad}} = +40\) MPa). Here the effect of boundary flexibility on the beam's structural response is apparent: microbridges with flexible boundaries buckle at lower loads (lower \(\sigma_{\text{mean}}\)) and deform more (larger deflection for the same mean stress) than more effectively clamped structures. Remarkable is also the decrease of gradient stress \(\sigma_{\text{grad}}\) effect on the center deflection as \(K\) reaches unity (i.e., beam is perfectly clamped), which can be noticed from the reduction in "0-load" displacement (i.e., the center deflection, \(w_c\), associated with \(\sigma_{\text{mean}} = 0\)) as \(K\) increases.

Deformation maps also help visualize the "design" and "stress extraction" modes mentioned above. When used in design mode, deformation maps allow one to predict the post-release
configuration of a microbridge based on information on the structure's intrinsic stress state and boundary condition, as per (2.15). An example of deformation map used in design mode is presented in Figure 2-22(b) (black, solid arrows), where the post-release center deflection is predicted as 2.4 μm. Conversely, when used in stress extraction mode, deformation maps allow layered thin-film stress characterization based on experimental measurements of the post-release deformation of microbridge test structures. An example of deformation map used in stress extraction mode is presented in Figure 2-22(b) (purple, dashed arrows), where the (compressive) mean residual stress is quantified as 70 MPa. Note that as used in these explanatory examples (Figure 2-22(b)), $K$ and $\sigma_{grad}$ are presumed known. The technique presented herein (see Section 2.4) can extract $\sigma_{mean}$, $\sigma_{grad}$, and $K$ simultaneously, or can be combined with other techniques such as cantilever curvature to assess $\sigma_{grad}$. $K$ is a notably difficult quantity to obtain experimentally, but it may conceptually be obtained via detailed FE models or cantilever loading experiments.

### 2.4 CMOS Thin-Film Material Characterization Using Developed Analytical Tools

Characterization of thin-film layered materials is critical to the development of many MEMS devices. Residual stresses from production determine both the final shape and the performance of microdevices, and should therefore be accurately assessed. To date, thin-film characterization involves the use of multiple types of test structures, each aimed at extracting one specific component of the complete stress state [58]. For instance, mean compressive stress is typically determined using critical length approaches based on arrays of clamped-clamped beams of different lengths [31], whereas gradient stresses are estimated from curvature measurements of released microcantilevers [64]. Although commonly used by the MEMS community, these approaches to stress characterization are costly (their accuracy is directly proportional to the number of different types of test structures utilized) and unable to take into account the effect of boundary flexibility on the structures’ deformation (the boundaries are instead assumed
(a) Two-dimensional deformation map showing the effect of $\sigma_{\text{mean}}$ and $K$ on the microbridge deformation. * the displacement for the curve represents the absolute value of the actual displacements (see discussion in Section 2.3.1 and Figure 2-20 regarding direction of buckling with $K \neq 0$).

(b) Deformation maps can be used both for structural design (design mode) and for material characterization (characterization mode).

Figure 2-22: Two examples of deformation maps (two-dimensional (a), and one-dimensional (b)) and their uses. Results for a polysilicon/dielectric multilayered microbridge ($L=400\mu m \times b=40\mu m \times h=2.91\mu m$, $\overline{E}=169$GPa) with $\sigma_{\text{grad}}=+40$MPa$/$$\mu m$. 

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ideal, e.g. infinitely stiff ($K = 1$) in the case of clamped-clamped beams). The latter issue is especially relevant as it both limits the methods’ accuracy in extracting stresses, and it results in the inability to fully characterize the stress state of thin-films using one type of test structure only. The (out-of-plane) deformation of micromachined structures is in fact directly dependent on boundary flexibility, with stiffer boundaries resulting, for example, in lower deflections and higher buckling loads. Neglecting boundary flexibility, current characterization methods are therefore “misinterpreting” experimental evidence [58, 65], and consequently inaccurately estimating the stress state in the films. Furthermore, by assuming that the structures’ boundaries are infinitely stiff, these techniques are incorrectly eliminating the effect of gradient stresses on the mechanics of clamped structures, making their post-release deformation dependent on mean stress effects only. As a consequence, more than one type of test structure is currently required to fully characterize the stress state in a thin-film material (e.g., microbridges for mean stress extraction, and cantilevered beams for gradient stress extraction).

Given the limitations discussed above, we propose a new approach to stress characterization that uses the analytical results of Section 2.3 to fully characterize the complete\(^4\) stress state (i.e., mean and gradient stresses, and effective boundary condition) in layered thin-film materials based solely on experimental data on the post-release deformation of microbridge test structures, with no need for multiple lengths\(^5\). The method consists of applying (2.16) to a large population ($n \geq 20$, [66]) of microbridge test structures with identical material composition, followed by least squares minimization. To ensure that all variables ($\sigma_{\text{mean}}, \sigma_{\text{grad}}, K$) are uniquely characterized, the experimental data vector - $\mathbf{u}_{\text{experimental}}$ - in (2.16) should contain at least three independent $u$ measurements (i.e., three independent datapoints) per test structure. In this work, experimental deflection measurements at locations $x = \{L/6, L/3, L/2\}$ along the microbridge test structures are used (see Figure 2-23(a)); this choice maximizes the distance between measurement locations and is effective for demonstration purposes as it provides a

\(^4\)Note that here and in the extant work (e.g., [31, 56]), the “complete” stress state is defined as the superposition of average mean stress with average or effective gradient (linear variation through film thickness) stress.

\(^5\)In line with other works, the stress characterization approach here presented assumes accurate knowledge of material properties (films’ elastic moduli) and structural geometry (thickness, width) for the structures. If these parameters are not available or have not been accurately measured, additional material characterization campaigns need to be performed, as discussed in Section 2.4.3.
lower accuracy bound for the method per test beam (the method's uncertainty on extracted stresses can in fact be lowered by using more than three independent deflection measurements per test beam). In Sections 2.4.1-2.4.2 we present the results relative to the application of our method to the characterization of multi-layered thin-film CMOS materials, comparing the results to state-of-art techniques.

Figure 2-23: Profilometric images of (a) a 400μm long buckled CMOS microbridge and (b) a 300μm released CMOS cantilever. Both structures are composed of the same polysilicon/dielectric multilayered material (b=40μm x H=3.3μm).
2.4.1 Complete Characterization of Layered CMOS Thin-Films Using Solely Microbridge Test Structures

In Table 2.1 we summarize the characterization results for four different material combinations (see Table A.1) using (2.16) in combination with a single microbridge test structure length (L=400µm). For each material combination, a set of thirty 400µm-long microbridges was fabricated using a commercial CMOS foundry and released outside the foundry in a commercial facility. The structures' post-release deformation was measured using non-contact white light interferometry (Zygo™; vertical, Z-direction resolution=0.1nm [67,68]; see also Table B.1). The results of Table 2.1 show (compressive) mean stresses ranging between 12 and 108 MPa, thus demonstrating the method's capability to characterize structures subjected to both large and small compressive stresses. This is in contrast with critical length methods that encounter difficulties in quantifying small compressive stresses due to their inability to distinguish between mean stress and gradient stress effects [69]. The method yields ±10MPa uncertainty (± indicates 1σ level) on mean stresses, approximately one order of magnitude better than extant methods using the same type and number of test structures. The reduction in uncertainty is largely attributable to proper accounting for boundary flexibility here, with the results for the CMOS structures analyzed here pointing to non-perfectly clamped boundaries with K=0.9, i.e., 10% less stiff in bending than a perfectly-clamped boundary. Note that the method's uncertainty is dependent on three factors: any numerical errors in the solution of (2.14), variability in the fabrication and etch processes, and measurement/input errors. For the results herein, a convergence analysis was performed that showed less than ±0.1 MPa variation in the results as the source of numerical error (roundoff) tolerance was decreased (in this work, the error tolerance was controlled through the "explicit tau error tolerance" in the numerical software Matlab®). The results of Table 2.1 are therefore representative of the intrinsic variability in the CMOS processes and the wet-etching technique used to create the CMOS structures in this work, and standard measurement and input error sources. In Table B.1 we present a survey of the experimental test structure measurements for the materials in this thesis.
Table 2.1: Characterization of thin-film, layered CMOS films using solely one type of microbridge test structure (i.e., cantilevers were not used) of length $L=400\mu m$ ($\pm$ indicates $1\sigma$ level). A population of $N=30$ was used for each beam compositions.

<table>
<thead>
<tr>
<th>Beam Composition*</th>
<th>$\bar{E}$ [GPa]</th>
<th>$h$ [µm]</th>
<th>$\sigma_{\text{mean}}$ [MPa]</th>
<th>$\sigma_{\text{grad}}$ [MPa]</th>
<th>$K$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysilicon/Dielectric bilayer</td>
<td>169</td>
<td>2.91</td>
<td>-107.8±10.8</td>
<td>40.1±3.6</td>
<td>0.90±0.03</td>
</tr>
<tr>
<td>Dielectric bilayer/ILD/Oxide</td>
<td>176</td>
<td>2.90</td>
<td>-91.5±8.7</td>
<td>42.1±3.7</td>
<td>0.92±0.03</td>
</tr>
<tr>
<td>Al/Poly/Dielectric bilayer</td>
<td>180</td>
<td>2.92</td>
<td>-37.1±8.5</td>
<td>27.8±2.5</td>
<td>0.91±0.03</td>
</tr>
<tr>
<td>Al/Dielectric bilayer</td>
<td>165</td>
<td>2.90</td>
<td>-12.7±6.8</td>
<td>-2.72±2.3</td>
<td>0.89±0.04</td>
</tr>
</tbody>
</table>

*See table B.1 for details.

As previously mentioned, a single microbridge test structure length is sufficient to characterize the complete stress state ($\sigma_{\text{mean}}, \sigma_{\text{grad}}, K$) of layered thin-film materials using our method. The uncertainty associated with a single microbridge length is in fact comparable to that achievable when multiple test structures lengths are used, as shown in Table 2.2. Here we compare the results obtained using (2.16) in combination with either a single ($L=400\mu$m) or multiple microbridge ($L=200, 400, 600\mu$m) test structure lengths when characterizing the same polysilicon/dielectric bilayer film. To perform the analysis where multiple test structure lengths were used, two additional sets of 200µm- and 600µm-long microbridge beams were fabricated and measured using non-contact profilometry (see Table B.1). The results show less than 3% difference between the stress estimates provided by the two analyses (with the same population size: $N=30$), thus indicating that a single microbridge can suffice for characterizing the complete stress state of layered thin-film materials. This is distinct from prior critical length approaches that necessarily use multiple microbridge lengths to characterize the mean stress component in thin-films [31, 63], thus making the approach herein an effective tool to minimize the wafer area that needs to be allocated for test structures.

Finally, in Table 2.3 we compare the results of the method (using a single microbridge length) with that of extant characterization techniques (critical length approaches for mean compressive stress [63], cantilever curvature for gradient stress extraction [64]). The new approach provides one order of magnitude improved (i.e., reduced) uncertainty in mean stresses than prior methods ($\pm 10.5$ MPa versus $\pm 43.5$ MPa), a result that holds even under the assumption of per-
fect clamping for the structures \((i.e., K = 1)\). The analytical method's overall uncertainty is further reduced (from \(\pm 10.5\text{MPa}\) to \(\pm 8.91\text{MPa}\) for mean stresses, and from \(\pm 3.6\text{MPa}\) to \(\pm 3.1\text{MPa}\) for gradient stresses) when moving from a three parameter \((\sigma_{\text{mean}}, \sigma_{\text{grad}}, K)\) to a two parameter \((\sigma_{\text{mean}}, \sigma_{\text{grad}})\) extraction, a result due to the reduced uncertainty on \(K\) (from \(\pm 0.03\) to \(\pm 0\)).

It is however important to notice that setting \(K = 1\) also causes "misinterpretation" of the experimental measurements by the analytical method, and therefore an overestimation of the extracted mean stresses (~10% overestimation for the structures analyzed here). Misinterpretation of experimental evidence represents a key limitation of state-of-the-art techniques (e.g., critical length approaches), as they assume perfect clamping for the structures. On the other hand, the results of Table 2.3 show that gradient uncertainty is slightly greater for the analytical method as for prior techniques that directly measure gradients via curvature measurements of cantilevered beams [64]. This result is due to the decay of gradient effects at large boundary stiffness levels \((\sim 0.6<K<1)\), which causes the deformation curves associated with different gradient values to be almost coincident (see also the discussion in Section 2.3.3 and Figure 2-22). As a consequence, the analytical method encounters difficulties in differentiating between deformations associated with similar gradient values \((i.e., \sim 3-5\text{MPa})\), hence resulting in higher gradient uncertainty. To improve this for the analytical method at large \(K\) values, information on the post-release deformation \((i.e., \text{curvature})\) of cantilevers can be used to reduce uncertainty in gradient stresses, hence moving from a three parameter \((\sigma_{\text{mean}}, \sigma_{\text{grad}}, K)\) to a two parameter \((\sigma_{\text{mean}}, K)\) extraction as discussed in Section 2.4.2.

Table 2.2: Comparison between characterization results for a polysilicon/dielectric bilayer film \((b=40\text{µm} \times h=2.91\text{µm}, \bar{E}=169\text{GPa})\) using either a single \((L=400\text{µm})\) or multiple \((L=200, 400, 600\text{µm})\) microbridge test structure lengths, without any cantilever measurement. The same population size \((N=30)\) was used for both analyses \((\pm\) indicates 1σ level).

<table>
<thead>
<tr>
<th>Characterization method</th>
<th>(\sigma_{\text{mean}}) [MPa]</th>
<th>(\sigma_{\text{grad}}) [MPa]</th>
<th>(K) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single microbridge length ((L=400\text{µm}))</td>
<td>-107.8±10.8</td>
<td>40.1±3.6</td>
<td>0.90±0.03</td>
</tr>
<tr>
<td>Multiple microbridge lengths ((L=200, 400, 600\text{µm}))</td>
<td>-106.9±10.5</td>
<td>39±3.4</td>
<td>0.91±0.04</td>
</tr>
<tr>
<td>Difference (%)</td>
<td>-0.7</td>
<td>+2.8</td>
<td>-1.1</td>
</tr>
</tbody>
</table>
2.4.2 Complete Characterization of Layered CMOS Thin-Films using Microbridge and Cantilevered Beam Test Structures

To reduce the $\sigma_{\text{grad}}$ uncertainty of the analytical method at large $K$ values ($-0.6 < K < 1$), information on the post-release deformation of cantilevered test structures can be used in combination with microbridges to reduce uncertainty on gradient stresses. This alternative approach draws from the work by Chu and Mehregany [64] and others where gradient stress is calculated from curvature measurements of released cantilevers. Gradient stress and cantilevered beam curvature are known from classical mechanics to be related through the following formula (see also [56]):

$$\sigma_{\text{grad}} = \frac{\bar{E} \bar{h}}{R}$$

(2.17)

where $R$ is the cantilever post-release radius of curvature, $\bar{E}$ is the film effective Young's modulus and $\bar{h}$ is the beam effective thickness. Equation (2.17) does not depend on boundary ideality $K$. Using this result, the gradient uncertainty of the analytical method can then be improved (i.e., reduced) using the following two-step approach: First, experimental measurements on the post-release deformation of cantilevered test structures is combined with (2.17) to extract the gradient stress in the films. The extracted gradient stress values are then implemented in a modified, two-parameters version of (2.16) to extract $\sigma_{\text{mean}}$ and $K$ as:

$$\{\sigma_{\text{mean}}, K\} = f^{-1}\{\omega_{\text{experimental}}, \sigma_{\text{grad}}\}$$

(2.18)

In Table 2.3 we compare the performance of the analytical method in characterizing the same polysilicon/dielectric multilayered material, either with or without using cantilever test structures. For these analyses, an additional set of 300$\mu$m-long cantilevers was fabricated and the post-release deformation measured using non-contact profilometry (Zygo, see Figure 2-23(b) and Table B.1). The results show $\sim$25% decrease in gradient uncertainty plus an additional five-fold decrease in mean stress uncertainty when cantilever test structures are used, thus making the uncertainty on the extracted stress by the approach herein more than an order of magni-
tude lower than that of prior techniques using the same number and type of test structures. A three-fold improvement in boundary flexibility uncertainty is observable as well, with the results pointing to a non-ideal boundary condition with $K = 0.89$. Note that in this comparison the number of test structures is comparable, but the number of datapoints and method of acquisition is not, e.g., the microbridge tests use 3 deflection measurements per sample, while critical buckling requires only an observation of whether the test structure is/is not buckled. Last, note that boundary flexibility $K$ is not obtainable with any well-known prior technique, and is a highly useful parameter (highly process and etch dependent) to quantify. Future work should investigate these points further.

Table 2.3: Comparison between extraction results obtained using the analytical method with and without cantilever test structures, and prior characterization approaches. The results are for a polysilicon/dielectric bilayer film ($L=200, 400, 600\mu m, b=40\mu m, h=2.91\mu m, N=30$; ± indicates $1\sigma$ level).

<table>
<thead>
<tr>
<th>Characterization method</th>
<th>$\sigma_{\text{mean}}$ [MPa]</th>
<th>$\sigma_{\text{grad}}$ [MPa]</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single microbridge length, Eq. (2.16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Three parameters extraction</td>
<td>-107.0±10.5</td>
<td>40.1±3.6</td>
<td>0.90±0.03</td>
</tr>
<tr>
<td>Two parameters extraction ($K=1$)</td>
<td>-116.1±8.9</td>
<td>38.3±3.1</td>
<td>1</td>
</tr>
<tr>
<td>Single microbridge length plus cantilevers, Eqs. (2.17)-(2.18)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Two parameters extraction ($\sigma_{\text{grad}}$ from cantilever curvature)</td>
<td>-105.1±2.1</td>
<td>37.0±2.9</td>
<td>0.89±0.01</td>
</tr>
<tr>
<td>One parameter extraction ($\sigma_{\text{grad}}$ from cantilever curvature; $K=1$)</td>
<td>-111.5±1.8</td>
<td>37.0±2.9</td>
<td>1</td>
</tr>
<tr>
<td>Critical buckling length, [63]</td>
<td>-71.5±43.5</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Cantilever curvature, [64]</td>
<td>-</td>
<td>37.0±2.9</td>
<td>1</td>
</tr>
</tbody>
</table>

2.4.3 Discussion of the Method’s Limitations and Extendability to Package-Induced Stress Characterization

The analytical approach presented has several positive attributes including more cost-effective design and characterize their structures. The uncertainty on extracted stresses and boundary flexibility of the characterization technique is however dependent on two main factors that
should be given further consideration:

- **Uncertainty in material properties.** Similar to prior approaches to thin-film characterization, the stress estimates provided by the analytical method depend on the material property values used in the analyses (*i.e.*, films' moduli; see Appendix A). Performing the same analysis with different moduli values will result in different extracted stresses. As a consequence, MEMS designers should place particular emphasis on using accurate material properties for their characterization campaigns. To account for statistical uncertainty in materials properties, the analytical method could be used in combination with a Monte Carlo approach [66]. The effective bending ($\overline{EI}$) and axial ($\overline{EA}$) moduli (see Appendix A) for the layered thin-film materials could also be experimentally quantified through bending and tensile tests [59]. The material properties for the structures in this work were provided by the foundry.

- **Deflection measurement errors.** The method depends on errors in the post-release deformation measurements for the test structures. Non-contact, high-resolution profilometry techniques (*e.g.*, Zygo, Wyko) or SEM imaging provide lower measurement errors and are therefore be preferred. The vertical (z-axis) resolution of the Zygo optical interferometer used in this work is 0.1nm [67].

The method can be extended to tensile stress extraction, as well as to package-induced stress characterization, as discussed below.

- **Characterization of single material layer stresses.** The technique presented in this work models the composite structures as homogenous, using a weighted description for the material properties of the beams. This is highly useful and practical for layered materials, common in nearly every MEMS structures. The analytical technique can therefore provide stress information on the homogenized model structure, but it cannot compute the individual stress contribution of each material layer composing the original element (*i.e.*, the single film residual stress
values $\sigma_{residual,i}$ in Figure 2-16(a)). If information on the residual stress in each material layer is necessary (e.g., layer-by-layer stress information is typically required in materials science), the analytical technique can be applied after each fabrication step so that the properties of each material layer can be assessed one after another. Alternatively, state-of-the-art characterization methods such as substrate curvature measurement could be pursued as well [31].

- **Characterization of tensile mean residual stresses.** Being based on measurements of the out-of-plane deformation of microbridge test structures, the analytical method is particularly applicable to the extraction of compressive mean residual stresses. Tensile stresses do not cause buckling and large out-of-plane deformation of microbridge test structures, and therefore cannot be quantified using the procedure discussed above. Nonetheless, tensile mean stress extraction is still achievable through a modified version of the analytical technique, where out-of-plane deformation of the test structures is induced by applying known/measured compressive mechanical stress to the whole chip. Comparing the pre- and post-stressed microbridge configurations, the residual tensile mean stress inside the structures can then be extracted. Preliminary work on this topic allowed characterization of tensile CMOS films (polysilicon/ILD/metal) with uncertainty between ±10 and ±20 MPa.

- **Characterization of package-induced stress.** Following a procedure similar to that described above for extracting tensile mean stresses, the analytical method can be extended to packaging stress characterization as well. The effect of packaging on a test chip is directly comparable to that of an applied mechanical stress, as described above. By comparing the as-fabricated and the packaged configurations of a microbridge, the analytical method can be utilized to quantify the stress induced by packaging effects as well.
2.5 3D MEMS Architectures via Post-Buckling within CMOS Constraints

We recall from Section 2.3.1 that the post-release deformation of micromachined bridges depends on both device geometry, residual stresses, and boundary flexibility. More specifically, we have shown that mean and gradient residual stresses determine both the amplitude and the direction of the beams' out-of-plane deformation, and that large compressive mean stresses can cause significant out-of-plane deflections through buckling phenomena. Residual stress control has therefore been identified as a possible strategy to 3D MEMS in the post-buckled regime. However, the possibility to control residual stresses is highly dependent on the selected fabrication process and is not always possible. While fabrication techniques such as surface micromachining are flexible in that they allow residual stress manipulation through, for example, intra-deposition steps (e.g., annealing) and cross section design (e.g., by tailoring the balance between tensile and compressive layers), other techniques such as CMOS allow very limited (if any) residual stress control. Creation of 3D structures using CMOS is therefore challenging, as the out-of-plane deformation of microfabricated elements cannot be controlled through residual stress design in this case. To overcome this fundamental limitation, here we propose four different architectures to control the post-release deformation of CMOS structures independent of their intrinsic stresses. The architectures are respectively labeled as patches, step ups, runners and tethers, and they make use of fabrication details, of “support” structural elements, and of residual stress knowledge to control and/or induce out-of-plane deformation of microfabricated elements. In the following Sections, each architecture is experimentally demonstrated through post-release buckling control of multilayered CMOS microbridges (dielectric/ILD/oxide, \( \sigma_{\text{mean}} = -91.5 \text{MPa}, \sigma_{\text{grad}} = 42.1 \text{MPa}, \) and \( K = 0.92; \) see also Tables A.1 and B.1). The unbiased, post-release configuration for the controlled CMOS microbridges is presented in Figure 2-24, where the structure is buckled upwards (i.e., positive z-axis or above the wafer plane) due to its large compressive mean stress and large (positive) gradients.
A first architecture to 3D MEMS exploits “patches” of thin-film materials that are strategically placed either on the top or the bottom surface (and most typically near the root) of the structure to be controlled (see Figure 2-25(a)). The patches are made of materials with known residual stress, and this stress can be tailored to apply an external moment that forces the controlled elements to deform in a direction opposite to what its intrinsic stress state would otherwise dictate. Films with both large mean and gradient residual stresses are preferable for use in patches, as large mean stresses yield significant control torques while large gradients manipulate the local curvature of the controlled element. A schematic of the patch architecture is presented in Figure 2-25(a), where compressive patches are used to cause downward (negative z-axis) deflection of a microbridge with positive gradient stresses. Similarly, patches with large tensile mean stress (or highly-compressive but placed on the bottom surface of the controlled structure) could be used to cause upward deflection of structural elements characterized by negative gradients. An experimental example of patches applied to the control of a dielectric bilayer/ILD/oxide microbridge is shown in Figure 2-25(c), where a 2μm-thick oxide patch (σ\text{mean} \approx -71\text{MPa}) is used to induce downward deflection of the structure (Δw_c = |w_{c,unbiased} - w_{c,biased}| = 16.2\text{µm}). From a designer standpoint, the patch architecture is flexible as it allows simple control the applied moment, e.g., by selecting a different material for the patches or by tailoring their geometry (thickness, length), but it is also limited in that the final structure is not identical to the original
(a) *Patches* (compressive and negative gradient residual stress) cause downward moments and manipulate the local curvature to bias the structure's post-release deformation.

(b) *Step up's* (compressive) bias the post-release deformation by causing both a downward moment and a non-zero slope at the beam's root.

---

Figure 2-25: Schematic of and experimental result for the application of the *patch* and *step up* architectures to the post-release deformation control of dielectric bilayer/ILD/oxide microbridges ($\sigma_{\text{mean}}=-91.5\text{MPa}$, $\sigma_{\text{grad}}=42.1\text{MPa}$, $K=0.92$).

---

One (i.e., a microbridge with no patches on top). For applications where the presence of patches is unacceptable, an additional post-release etch step could be envisioned that would solely etch the patches, or a higher etch-selectivity material could be used for the patches such that they could be removed during the release step by extending the duration of the etching sequence. An alternative formulation of the patch architecture is the *step-up* architecture (Figure 2-25(b)).
The step-up architecture is similar to patches in that knowledge of the residual stress in thin film layers is used, but it also differs as no overlap between the controlled structural element and the control film is present in this case. Conversely, the control layer is now located at (and aligned with) the very extremity of the controlled structure, thus biasing the structure’s deformation by inducing a non-zero slope at the root. Compressive/tensile films can therefore be used as step up materials to induce downward/upward deflection of structures with positive/negative gradients. An application example of the step up architecture is presented in Figure 2-25(c), where the technique is applied to the same dielectric bilayer/ILD/oxide microbridge \((\Delta w_c = |w_{c, unbiased} - w_{c, biased}| = 15.7\, \mu m)\). Compared to patches, the step up architecture is advantageous in that it does not affect the geometry of the controlled structure, albeit it is limited in terms of control force tailorability as the beneficial effect of stress gradients in manipulating the curvature of the controlled structure is mitigated to a large degree in this architecture.

### 2.5.2 Runners

A third architecture for 3D MEMS makes use of “support” structural elements that are (initially) connected to the controlled structure and that force it to deform in the direction dictated by the residual stress in the support elements. A schematic example of such architecture is shown in Figure 2-26(a), and it consists of connecting (e.g., through some connecting bridges) the controlled beam to an additional microbridge that runs parallels to it - hence the name runner. The runner is characterized both by a large compressive mean stress (ideally large enough to cause buckling), and by a gradient stress opposite in sign to that of the controlled structure. By designing the etching sequence such that the runner is released prior to the controlled structure \(i.e.,\) the runner is free to deform while the controlled structure is still fully constrained), the post-release deformation of the controlled beam can be biased independent of its gradient stresses. In Figure 2-26(b) we present the results relative to the application of the runner architecture \((3.3\, \mu m\text{-thick oxide/ILD/metal multilayer; } \sigma_{\text{mean}}=-43.5\text{MPa, } \sigma_{\text{grad}}=-80.6\text{MPa})\) to the control of a dielectric bilayer/ILD/oxide microbridge, where the runner forces the microbridge
to deflect downwards despite the positive gradient stress inside the structure. Additional considerations regarding the application of runners to 3D MEMS design include: a) Once the controlled structure has been fully released, the connecting bridge elements can be either left in place or removed. If bridge removal is required, these elements could, e.g., be designed and fabricated using higher etch-selectivity materials such that they could be removed during the release step by extending the duration of the etching sequence; b) The runner architecture can be exploited to cause buckling in microbridges whose mean stress would otherwise not suffice to induce buckling. The critical buckling load for a shallow arch is in fact lower than that for a perfectly flat column having the same geometrical/material properties [12]. The out-of-plane deflections that the runner induces on the controlled microbridge (thus effectively making it a shallow arch) may therefore suffice to lower the critical buckling load below the mean residual stress level of the structure, hence resulting in buckling of the microbridge; c) Additional investigations to determine the optimal configuration (e.g., number, length, width, material composition) for the elements connecting the runners and the controlled structure are required. In this work, either 2 or 3 connecting bridges were utilized based on the results of finite element (FE) analyses which showed that the runners’ post-release deformation was maximized as the number of connecting elements decreased (the option of using solely one connecting bridge was however discarded, as this configuration was shown to be very sensitive to imperfections in etching processing and bridge placement).

2.5.3 Tethers

The fourth proposed architecture to 3D MEMS draws inspiration from current 3D microfabrication techniques (e.g., Nanostructured Origami; see Section 2.1) and combines buckling phenomena and gradient effects to achieve structural elements that are positioned high above the wafer plane. In detail, the approach exploits tethers, i.e. slender cantilevered members, that protrude from the sides of a buckled microbridge (see Figure 2-27). Critical to the approach are the tethers’ placement along the beam length and material composition. In order to maximize device height, the tethers’ attachment point should coincide with the point of maximum
Figure 2-26: Schematic and two examples of the application of the runner architecture to the post-release deformation control of dielectric bilayer/ILD/oxide microbridges. The runner is made of a 3.3μm-thick oxide/ILD/metal multilayer ($\sigma_{\text{mean}}=-43.5\text{MPa}$, $\sigma_{\text{grad}}=-80.6\text{MPa}$, $\kappa=0.92$).

Slope along the buckled microbridge. The tethers should then be made of a (layered) material with large gradient stress, such that additional height can be gained by exploiting the tethers’ gradient-induced bending (obviously, the tethers’ bending direction should be compatible with that in which the microbridge buckles). Experimental demonstration of this approach to 3D MEMS is presented in Section 2.6, where the architecture is applied to the design of a 3D platform for acceleration sensing using thermal effects.
2.6 Analytical Design of 3D MEMS via (Post-)Buckling: a 3D Sensing Case Study

Demonstration of 3D functionalities via buckled designs represents the ultimate goal of this MEMS work. The aim of this Section is that of combining the tools developed in the previous Sections (i.e., the analytical model for the non-linear buckling of microfabricated layered structures - Section 2.3; the analytical thin-film characterization technique - Section 2.4; and the proposed architectures to 3D MEMS - Section 2.5) to devise a 3D sensor that is designed to operate in the post-buckling regime. More specifically, here we describe the design and CMOS fabrication of a platform for 3D acceleration sensing using thermal effects. This application was selected in light of our collaboration with MEMSIC Inc., an enterprise that specializes in the commercialization of CMOS MEMS technologies, including thermal accelerometers [70]. The working principles and design specifications of the proposed application are described in Section 2.6.1, while the analytical design procedure and the experimental results are presented in Sections 2.6.3.
2.6.1 Acceleration Sensing Using Thermal Effects

To date, several architectures to acceleration sensing using MEMS platforms have been developed and commercialized. Each of these platforms is based on a different physical working principle, from pressure sensing using thin film membranes [56] to capacitive sensing using proof-mass translation [31, 71]. In this work we focus on a category of MEMS accelerometers that exploits thermal effects to sense acceleration, i.e. thermal accelerometers. Thermal accelerometers resolve acceleration fields based on the analysis of the thermal profile of a selected working fluid (e.g., $N_2$, $SF_6$). A schematic representation of a single-axis thermal accelerometer is presented in Figure 2-28: the device is composed of a heater, two thermopiles (centered around the heater) and a working fluid, all contained in a sealed cavity. The role of the heater is that of warming its surroundings, thus creating a thermal profile in the working fluid that under nominal conditions (i.e., when no acceleration is applied) resembles the symmetrical profile of Figure 2-28(a). On the other hand, the thermopiles act as temperature sensors, and in the zero-acceleration scenario that we just described they would both measure the same temperature (i.e., $\Delta T = T_A - T_B = 0$). The temperature profile's symmetry is however broken when the device undergoes acceleration, as convection occurs in the working fluid hence resulting in a skewed temperature profile such as that of Figure 2-28(b). As a result, the temperature readings by the two thermopiles do not coincide in this case. This finite temperature difference ($|\Delta T| = |T_A - T_B| > 0$) between the two thermopiles can then be used to resolve the acceleration field [14].

The above device configuration enables acceleration sensing solely along one axis, but it can be easily extended to dual-axes acceleration sensing by combining multiple sets of thermopiles. An example of two-axes thermal accelerometer is presented in Figure 2-29, where we show the top view of one of MEMSIC Inc.'s commercial CMOS thermal accelerometers. Briefly, the device consists of a main frame composed of four diagonal beams that intersect at the center, where a hollow square heater element is located; several additional beams structures are then connected to the main frame, creating a web of thermopiles that are used to sense the temperature.

\[\text{Note that the cavity's geometrical definition is dependent on design considerations, the selected fabrication process, and packaging details.}\]
profile in the cavity. Despite its structural complexity, this device can be idealized as the combination of one heater and two sets of thermopiles, as we schematically indicate in the Figure. The two sets of thermopiles sense temperature gradients along the x- and y-axes, such that the 2D acceleration field can then be resolved.

Figure 2-28: Thermal accelerometers resolve acceleration fields by measuring the temperature profile of a selected working fluid [14].

2.6.2 Limitations of State-of-the-art MEMS Thermal Accelerometers

In Figure 2-30 we present the numerical results for the lateral (in-plane acceleration) and vertical (out-of-plane acceleration) thermal sensitivity of a MEMSIC Inc. accelerometer that was
introduced in the previous Section. Thermal sensitivity plots are useful design tools in that they identify those regions of the cavity that are the most sensitive (in terms of temperature gradients) to accelerations, hence indicating the locations where thermopiles should be placed, if possible. The non-optimality of the current planar thermal accelerometer designs becomes apparent in Figure 2-30(a), where we show the lateral thermal sensitivity for the device (acceleration along the negative x-axis). While the regions with highest thermal sensitivity (bright red and bright blue shades) are located well above the heater/wafer plane, the thermopiles are instead positioned on the wafer plane, and hence in a region with sub-optimal sensitivity. The thermopile placement is even less optimal when considering accelerations along the out-of-plane (z-axis) direction. This is shown in Figure 2-30(b), where we present the vertical thermal sensitivity plot for the device. Clearly, the current planar thermopile architecture is not suitable for out-of-plane acceleration detection, both because the thermopiles are located in a moderately low thermal sensitivity region and because the two thermopiles would provide the same
temperature reading. Redesign of this technology to enable thermopile architectures beyond planar designs is therefore attractive, both to enhance sensitivity to in-plane accelerations and to enable simultaneous three-axial acceleration sensing using a single device.

Figure 2-30: Lateral and vertical thermal sensitivity plots for a model two-axis CMOS thermal accelerometer. (Thermal sensitivity plots courtesy of Dr. Stefan Nikles, MEMSIC Inc.)
2.6.3 3D MEMS Platform for Simultaneous Three-Axial Acceleration Sensing Using Thermal Effects

We recall from Section 2.6.1 that extension of thermal accelerometer technology to 3D sensing requires the ability to fabricate functional elements (specifically, thermopiles) that extend above the wafer plane. Here we propose a new architecture for thermal accelerometers that combines buckling phenomena and residual-stress control to enable 3D sensing on a single device. The proposed architecture is presented in Figure 2-31(a), and consists of the following structural/functional components:

- Out-of-plane tethers
- Buckled microbridges
- Heater
- X-Y Thermopile
- Z Thermopile

(a) Device schematic

![Device schematic](image)

(b) Lateral and vertical thermal sensitivity plots

![Thermal sensitivity plots](image)

Figure 2-31: 3D MEMS structures in the post-buckled regime can enable simultaneous three-axes acceleration sensing using thermal effects. (Thermal sensitivity plots courtesy of Dr. Stefan Nikles, MEMSIC Inc.)

- A non-buckled (in-plane) microbridge, at whose center is located a heater;
Two buckled (out-of-plane) microbridges, one on each side of and running parallel to the microbridge containing the heater element, and at whose centers are located the X-Y thermopiles;

Two sets of highly-curved tethers, one on each buckled microbridge, at whose extremities are located the Z thermopiles.

This design enables acceleration sensing in a way that is analogous to that of the commercial device in the previous Section (i.e., acceleration is resolved through the analysis of the thermal profile of a selected working fluid), yet it differs from that architecture in that: (a) the X-Y thermopiles are located above the wafer plane, in a higher lateral thermal sensitivity region; and (b) the tether elements allow placement of an additional set of thermopiles above the heater, in a high vertical thermal sensitivity region, hence enabling Z-axis acceleration sensing as well. An example of thermopile placement for both the X-Y and the Z thermopiles for our 3D platform is shown in Figure 2-31(b), where we present the lateral and vertical thermal sensitivity plots for the device. The proposed architecture may allow placement of all thermopiles in high sensitivity regions, thus representing an attractive design alternative. To demonstrate the feasibility of this new design, the following sections focus on the design and experimental demonstration of the “buckled microbridge + tether” 3D platform of Figure 2-31(a).

2.6.3.1 Analytical Design Procedure

In this Section we discuss the design of the “buckled microbridge + tethers” 3D assembly of Figure 2-31(a). The device layout is presented in Figure 2-32, where the geometrical parameters have been indicated as well: \( L_m \) and \( w_m \) - the length and width of the main microbridge; \( L_{te} \) and \( w_{te} \) - the tethers’ length and width; \( L_{cb} \) and \( w_{cb} \) - the length and width of the connecting bridges; and \( d \) - the distance between the root of the main microbridge and the tethers’ attachment point. The films’ thickness \( (h) \) as well as the available materials were set by the CMOS fabrication process and the bulk etch sequence (isotropic plasma etch) to 3.3\( \mu \)m and to the materials of Table 2.1, respectively. In this work, a dielectric/ILD/oxide multilayer film was
selected for both the main microbridge and for the tethers, as this material is characterized by both large mean and large gradient residual stresses (for ease of discussion, the material properties and residual stress state for this multilayered film are reported again in Table 2.4 below).

![Diagram of a buckled microbridge and tethers architecture](image)

**Figure 2-32:** Schematic representation of a “buckled microbridge + tethers” architecture that exploits buckled microbridges and out-of-plane tethers to create highly three-dimensional MEMS features.

**Table 2.4:** Material properties and residual stress state for the dielectric/ILD/oxide multilayered CMOS films constituting the “buckled microbridge + tethers” assembly.

<table>
<thead>
<tr>
<th>$E$</th>
<th>$h$</th>
<th>$\sigma_{\text{mean}}$</th>
<th>$\sigma_{\text{grad}}$</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[GPa]</td>
<td>[µm]</td>
<td>[MPa]</td>
<td>[MPa]</td>
<td>[-]</td>
</tr>
<tr>
<td>176</td>
<td>2.9</td>
<td>-91.5±8.7</td>
<td>42.1±3.7</td>
<td>0.92±0.03</td>
</tr>
</tbody>
</table>

First, the microbridge length and width were respectively set to 400µm and 40µm, as test structure results always showed the occurrence of buckling for this configuration (see also Table B.1). The length of the connecting bridges was then set to 30µm, as this is the minimum etch opening size allowed by the CMOS process. The connecting bridges width was also set to 30µm, thus yielding a square layout for these elements. The last three parameters ($L_{te}$, $w_{te}$, and $d$) were then determined using the following analytical procedure (see also Figures 2-33 to 2-35): (a) residual stress knowledge was combined with deformation maps (design mode, see Section 2.3.3) to predict the final out-of-plane configuration for the main microbridge; (b) the analytical tool was used to identify the point of maximum slope along the buckled microbridge length.
(hence setting \(d\)); and (c) residual stress knowledge was combined with analytical results on the post-release microbridge deformation to determine the tether geometry (i.e., \(L_{te}, w_{te}\)) that would position the thermopiles (i.e., the tethers' tips) to appropriate height above the heater. Given the intrinsic stresses of Table 2.4 and the geometrical parameters above, application of the deformation map method predicts a buckled configuration for the main microbridge, with a center deflection of approximately 3.9\(\mu\)m (Figure 2-33). The post-release microbridge shape and slope are presented in Figures 2-34 and 2-35, respectively. For the design considered here, the points of maximum slope along the microbridge are located approximately 103\(\mu\)m from either root of the beam. Accordingly, the tethers' attachment point \(d\) was set to 103\(\mu\)m. Information on the tethers' curvature \((R=12.26\,\text{mm})\) is then used to determine the required tethers' length, yielding \(L_{te} \approx 120\,\mu\)m. Finally, the tethers' width \(w_{te}\) was set to 20\(\mu\)m, based on experimental results on cantilevered test structures that showed best repeatability when \(L_{te}/w_{te} < 10\).

The final device parameters are summarized in Table 2.5.

### Table 2.5: Geometrical parameters for the “buckled microbridge + tethers” 3D platform of Figure 2-32.

<table>
<thead>
<tr>
<th>Main microbridge</th>
<th>Connecting bridges</th>
<th>Tethers</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L_m) [(\mu)m]</td>
<td>(w_m) [(\mu)m]</td>
<td>(L_{cb}) [(\mu)m]</td>
</tr>
<tr>
<td>400</td>
<td>40</td>
<td>30</td>
</tr>
</tbody>
</table>

### 2.6.3.2 Experimental

In Figure 2-36 we show the experimental results for the “buckled microbridge + tethers” 3D platform, whose design was presented in the previous Section. The device was fabricated using commercial CMOS foundry processes, with the structures released outside the foundry in a commercial facility through an isotropic plasma etch step. Dicing was performed commercially as well, followed by profilometry (Zygo) of the as-fabricated structures. Figure 2-36(a) contains an oblique plot of the final released structure. Here, the three-dimensionality of our design
becomes apparent: the main microbridge is clearly out-of-plane, a result of the large compressive residual stresses in the material, while the tethers extend even further out-of-plane due to gradient-induced bending effects. In detail, the final location for the microbridge center (i.e.,
Figure 2-35: Optimization of thermopile location through tether layout using the analytical tool.

X-Y thermopiles) and for the tethers' tips (i.e., Z thermopiles) are +3.84μm and +7.59μm above the wafer plane, respectively, in very good agreement with that predicted by the analytical tool (see Figure 2-35). The excellent alignment between the tether's tips and the microbridge center is further highlighted in Figure 2-36(b), where we present a surface profile plot of the device. This architecture demonstrates 3D MEMS functional elements that are designed to operate in the post-buckled regime. Next steps include the design and fabrication of a thermal accelerometer device based on this design, to demonstrate both increased lateral sensitivity and simultaneous three-axial sensing using a single platform. Additional considerations for this device include the tethers' flexibility and their interaction with the working fluid under applied acceleration fields, which could result in significant non-linear response and dynamic sensitivities. Furthermore, fabrication processes should be selected that minimize variability in boundary flexibility across structures/wafers: in Section 2.3.1 we have shown that even small variations in boundary flexibility (K) can yield significant changes in the structural response of buckled structures (see Figure 2-17), and that these changes are more significant at moderate flexibility levels (0.1 < K < 0.8).
Figure 2-36: Experimental results of the post-release configuration of a “buckled microbridge + tethers” assembly.

2.7 Perspectives and Future Work

Three-dimensional MEMS structures are attractive as they could enable new functionalities for a variety of applications, from sensing to actuation. In this work, we have introduced and demonstrated a new approach to 3D MEMS that uses residual stress-induced buckling phenomena to create out-of-wafer-plane functional elements. The approach makes use of an analytical model for the non-linear buckling of multilayered microfabricated beam structures.
that we developed, and that can be applied to both device design and thin-film residual stress characterization. The analytical characterization technique was applied to several multilayered thin-film CMOS materials, and provides uncertainty superior (i.e., reduced uncertainty) compared to that state-of-the-art characterization methods. The technique also has the potential of reducing the overall complexity and cost of characterization campaigns, as it eliminates the need for both multiple microbridge test structure lengths and for cantilevered test beams. Creation of three-dimensional MEMS structures was experimentally demonstrated through a number of architectures, including four different designs (patch, step up, runner, tether) that enable control of 3D structures independent of the intrinsic stresses in the films. The devices were fabricated combining state-of-the-art CMOS and bulk etching processes, thus extending the capabilities of CMOS fabrication beyond planar layouts. An application example of the use of 3D platforms to enable three-axial thermal accelerometer devices was discussed as well. Limitations of the proposed approach include possible non-linear device performance (e.g., sensitivity) due to increased structural compliance (compliant tethers and device elements), as well as a likely limited range of use in terms of boundary flexibility near fully clamped ($K > 0.8$).

Future work in the field of 3D MEMS operating in the post-buckled regime includes the extension of this work to geometries beyond beams. The analytical model here developed could be extended, e.g., to membranes and shells, thus moving to higher dimensional elements. Buckling of membranes and plates has been extensively analyzed during the second half of the last century, and many works are present in the current literature that focus on this topic (e.g., [12, 59]). Devices that exploit membrane elements operating in the post-buckling regime are however extremely rare in the MEMS community (examples include, e.g., [72, 73]), as buckling is typically seen as failure. Demonstration of the feasibility of devices that exploit buckling as a design tool could therefore enable a variety of new functionalities that are currently unavailable to the MEMS community. Additional work includes the development of a more rigorous procedure for tensile and package-induced stress characterization using the analytical tool. This extension was outside the scope of this work, and was only covered briefly in Section 2.4.3. Finally, next steps include the optimization of the 3D device architecture presented in Section 2.6, e.g.,
using the analytical tool to analyze the stresses inside the structure and to design against failure. A demonstration device for three-axis acceleration sensing based on this design should be pursued as well, and future work should combine the analytical design tool with multiphysics FE techniques to characterize the interaction between the working fluid and the compliant structural elements and hence to predict any non-linear performance (e.g., sensitivity) of the device.
Chapter 3

Integration of Bulk Nanoporous Elements in Microfluidic Devices

Introduction of high-definition, nanoporous materials in biomedical MEMS devices was pursued in this work. Nanoporous elements could provide access to smaller sub-micron particles that cannot currently be targeted (e.g., HIV virus), and they could significantly improve the overall performance of microfluidic platforms by overcoming the structural limitations of solid designs (e.g., detrimental flow patterns at the fluid-solid interfaces). In this Chapter, we explore the use of ultra-porous (99% porous) forests of vertically aligned carbon nanotubes (VACNTs) as new microfluidic structural elements. The discussion opens with a review of the state-of-the-art in microfluidic technologies for bioparticle isolation/manipulation (Section 3.1), followed by an overview of the objectives and approach for this work (Section 3.2). The microfluidic integration of VACNT forests is then presented in Section 3.3, accompanied by experimental results on flow characteristics through VACNT nanoporous elements (Section 3.4). Finally, a comparison between the performance of solid (PDMS) and nanoporous (VACNT) technologies for a specific application, and experimental results on the application of the VACNT technology to multiscale bioparticle isolation and manipulation, are presented in Sections 3.5-3.6, respectively.
3.1 Background and Prior Work

Most clinical diagnostic and biological studies require the isolation of specific biomolecules from complex samples such as blood, saliva and cell culture supernatant. Many bioparticles of interest are however both very small in size and extremely rare, thus making their identification and isolation difficult. Despite these challenges, MEMS platforms have been proven extremely successful for uses in bioparticle isolation and manipulation, and are largely outperforming their macroscopic counterparts. The following is a review of the current literature in microfluidic technologies for bioparticle isolation and manipulation. Microfluidic platforms that use solid materials (e.g., silicon, polymers) for their functional features are the current standard in bioMEMS technology: an overview of the principles behind these technologies and a discussion of their limitations are presented in Section 3.1.1 and 3.1.2, respectively. Alternative approaches that exploit porous materials in microfluidic platforms are then introduced in Section 3.1.3.

3.1.1 State-of-the-art in Microfluidic Technologies that use Solid Materials as Structural Features

Solid materials such as silicon, polymers, and glass are the dominant structural elements in state-of-the-art microfluidic devices. These materials have been widely explored during the past three decades, and are the core of a variety of miniaturized biomedical platforms for applications ranging from particle concentration to global health diagnostics. Broadly speaking, microfluidic technologies that utilize solid materials for their structural elements are divided in two distinct branches: the first includes those techniques that differentiate particles based solely on physical properties (e.g., size-based filtration), while the second branch comprises bioMEMS architectures that exploit surface chemistry and biomolecular recognition to target particles of interest. Both approaches are presented below, where we report on those device architectures that are most closely related to the objectives of this work.

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1The reader is referred to [28,32] for a more extensive overview of the state-of-the-art in microfluidic technologies for uses beyond bioparticle isolation.
3.1.1.1 BioMEMS Platforms for Bioparticle Isolation and Manipulation based on Particles’ Physical Properties

The first branch of solid microfluidic platforms entails those technologies that enable biological targeting and manipulation based solely on the particles’ physical properties (e.g., size, optical polarizability). To this category belong, e.g., size-based filtration [74], optical trapping [75], dielectrophoresis [76] and deterministic hydrodynamics [19]. Compared to other microfluidic technologies that target particles using chemical affinity, these approaches are typically simpler and often easier to develop, yet they offer significantly lower specificity.

**Sized-based filtration:** More commonly known as “filtration”, sized-based filtration is a technology in which particles are isolated based on their geometrical size (e.g., hydrodynamic cross section), typically through the use of membranes that either span a single microchannel [17] or connect multiple fluidic ducts [77] (see also Figure 3-1). Although membranes are in effect porous microfluidic elements, they are considered a solid technology as their functional elements are typically created from a bulk body of solid material using, e.g., anisotropic etching techniques. To date, a large variety of membrane architectures have been developed, each characterized by different pore geometry and size (see, e.g., Figure 3-2 and [17]), thus making this technology applicable to the isolation of particles over multiple orders of magnitude, from cells to bacteria [74]. Size-based filtration represents one of the simplest approaches to bioparticle manipulation, but it is significantly limited in terms of isolation specificity as it does not allow to selective isolation of one particle type (conversely, any particle larger than the pore size will be filtrated).

**Optical trapping:** First published in 1986 under the name of “single-beam gradient force trap” [75], optical trapping is a technique that uses highly-focused laser beams to apply attractive and/or repulsive forces to particles - both biological and otherwise - based on their optical refractive index. The optical trap method has been used in a variety of applications, including

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2This is distinct from other approaches where porous materials such as polymer monoliths are used to create the membrane elements (see Section 3.1.3).
Figure 3-1: Membranes can (a) span a single microchannel or (b) connect multiple fluidic ducts.

Figure 3-2: Overview of pore geometries for microfluidic membranes [17].

Particle guidance and transport [78] as well as particle sorting [79]. One of the latest developments in optical trapping are the so called “optical tweezers”, i.e. an approach to bioparticle manipulation in which the system under study (e.g., a bacterium) is held at both ends by two separate control elements (e.g., micro-spheres) that are themselves controlled through two distinct optical traps [78]. This technique enables, e.g., selective and controlled deformation of single biological particles and is therefore particularly attractive for applications such as In vitro mechanical characterization of biological species. Such an application of the optical tweezers technique was recently demonstrated by Dao et al. [18], who applied the method to the mechanical testing of human red-blood cells (Figure 3-3).
Dielectrophoresis: Dielectrophoresis exploits non-uniform electric fields to manipulate bioparticles based on their dielectrical properties. This method was first developed in 1978 by Pohl [80] and others, who demonstrated the technique by applying it to the manipulation of living cells. To date, dielectrophoresis has been applied in a variety of sectors, from fluid fractionation and characterization of biological analytes to purification of larger meso-scale biological components [76].

Deterministic hydrodynamics: An alternative approach to sample fractionation uses deterministically-designed hydrodynamic flows in microchannels to separate bioparticles without the need for sample pre-processing [19,20]. This method is schematically represented in Figure 3-4(a), and it exploits the asymmetrical bifurcation of laminar flow around obstacles to deterministically sort particles based on their size. This technique is also known as “bumping”, and it has been applied to the fractionation of micron-sized particles such as cells and bacteria [20]. An experimental example of the bumping method is shown in Figure 3-4(b), a state-of-the-art silicon-based device for separating particles between 0.4μm and 1μm in size using this technique.
Figure 3-4: Deterministic hydrodynamics ("bumping") exploits asymmetric bifurcation of laminar flow around obstacles to deterministically sort particles based on their size: (a) schematic of working principle [19] and (b) device example [20].

3.1.1.2 BioMEMS Platforms for Bioparticle Isolation and Manipulation based on Surface Chemistry and Biomolecular Recognition

A large portion of state-of-the-art microfluidic devices makes use of surface chemistry and biomolecular recognition to selectively identify and separate biological particles in complex samples. These approaches utilize surface modified, or functionalized, elements that selectively bind to target particles using mechanisms such as antigen-antibody interactions [32], thus providing higher specificity than those methods which separate particles based solely on physical properties (e.g. size; see previous Section). To date, several approaches that use chemical functionalization have been developed, including solution-phase techniques such as immuno-magnetic beads [21] and on-chip flow cytometry [22], as well as solid-phase techniques such as affinity chromatography [23,81]. Although there is no fundamental difference between solid and solution phase techniques in terms of isolation principles, the latter group is usually characterized by higher specificity.
**Functionalized magnetic beads (liquid-phase):** A first liquid-phase approach to bioparticle manipulation is one in which functionalized, magnetic nano- and micro-beads are used to selectively identify and manipulate biological particles in solution. An example architecture of this approach is schematically presented in Figure 3-5 which enables particle isolation using the following approach: First, permanent magnets or electromagnets are used to immobilize the magnetic beads (Figures 3-5(a)-(b)), followed by injection of biological samples in the channel (Figure 3-5(c)); particle isolation is then achieved through specific binding of target antigens to the functionalized beads (Figure 3-5(d)) which are finally released through termination of the magnetic field (Figure 3-5(e)), thus resetting the device. Magnetic beads have found applications in a variety of fields, including particle separation, immuno-assays, resonance imaging, and drug delivery [21].

![Figure 3-5: Application of functionalized magnetic beads to bioparticle isolation [21].](image)

**Flow cytometry (liquid-phase):** Flow cytometry is a technique that enables the analysis of complex samples using the following three steps [28]: (a) a sample of interest is suspended in a solution of known composition; (b) the resulting mixture is excited using a single wavelength laser beam; (c) the mixture's electron emission is analyzed using a digital apparatus and compared to the (known) emission of the control solution to reveal the composition/properties of the original sample. Flow cytometry provides information on both physical and chemical prop-
erties, and can be extended to particle counting as well. A particularly interesting variant of flow cytometry is *fluorescence-activated cell sorting* [22], as this technique provides manipulation capabilities as well. Fluorescence-activated cell sorting is a method for sorting a heterogeneous mixture of biological cells into two or more wells, one cell at a time. The technique uses hydrodynamic focusing and vibrating apparatus to create liquid droplets containing one cell each; the droplets are then analyzed using standard flow cytometry, and diverted into one of the wells depending on the cytometry results. Fluorescence-activated cell sorting is an effective approach for bioparticle identification, sorting and characterization; Nonetheless, its stringent requirements in terms of complex, bulky (and costly) electro-mechanical apparatus (see, e.g., [22] and Figure 3-6) are preventing its extension to applications such as global health diagnostics.

![Schematic of the experimental setup for a typical fluorescence-activated cell sorter](image)

**Figure 3-6:** Schematic of the experimental setup for a typical fluorescence-activated cell sorter [22].

**Affinity chromatography (solid-phase):** Among solid-phase techniques, affinity chromatography has been given particular attention by biomedical researchers [81]. Affinity chromatography uses highly specific biological interactions (e.g., antigen-antibody) between functionalized microfluidic features (e.g., silicon pillars, see below) and particles in a flow to selectively isolate biospecies in complex samples such as whole blood, with no need for preprocessing. Devices based on affinity chromatography can perform complex assays on very small volume samples, without the need for any sophisticated apparatus (a syringe pump and an optical microscope
often suffice). These characteristics are making affinity chromatography a prime choice in the global health community, as this technology could provide a means to cheap diagnostic health care systems for currently underserved regions. An example of the application of affinity chromatography to health diagnostics is the work of Cheng et al. [23], where the authors demonstrate a PDMS-based microfluidic device for label-free CD4+ T cell counting of HIV infected subjects (see Figure 3-7). The method requires only a fingerprick (300μL) of patient blood, a syringe pump to inject the sample in the device and an optical microscope, and it is therefore very attractive for resource-limited settings. Next to this device, a second example

Figure 3-7: An affinity chromatography-based device for CD4+ T cell counting of HIV infected patients [23].

of the application of affinity chromatography to health diagnostics is the MEMS platform that Nagrath et al. [24] developed for isolation of rare circulating tumour cells (CTCs) in the blood of cancer patients (the working principle, the device geometry, and an application example for this technology are presented in Figure 3-8). Similar to the CD4 cell counting device described above, the CTC-chip requires only a fingerprick of patient blood to perform the assay. In this device design, the sample is injected through an array of functionalized silicon posts, resulting in specific circulating tumor cell (CTC) isolation through physical interaction between the bioparticles and the functional surfaces. The CTC-chip has been applied to the diagnosis of several types of cancer (e.g., lung, prostate, breast), and it was demonstrated to successfully identify CTCs with 99% accuracy. All in all, the CD4 and CTC platforms are effective and rather inexpensive devices that are based on microfluidic affinity chromatography and that are promising candidates for managing HIV/cancer patients in resource limited settings. A significant chal-
Challenge with these technologies is however to achieve sufficient physical interaction between the bioparticles and the functional surfaces to promote binding. Both the CD4 and CTC architectures are based on solid (PDMS or silicon) functional elements, and their isolation efficiency is therefore limited by detrimental flow stagnation effects at the fluid-solid interface (see also 3.1.2). Incorporation of porous elements in affinity chromatography technologies to overcome the limitations of solid designs is a primary objective for this thesis work.

Figure 3-8: Circulating Tumour Cells (CTCs) isolation in whole blood: (a) Working principle, (b) device layout, and (c) an application example of an affinity chromatography MEMS device for isolation of CTCs in cancer patients [24].

3.1.2 Limitations of State-of-the-art Microfluidic Platforms

MEMS technologies are revolutionizing the way biomedical practices and research are conducted, and are progressively being applied to a larger variety of sectors from diagnostics to non-invasive robotic surgery. Nonetheless, the potential and further diffusion of miniaturized biomedical platforms is currently hampered by some critical impediments: detrimental flow characteristics due to no-slip conditions at the edge of solid elements, difficulty in accessing sub-micron particles, and limited design flexibility.

Detrimental flow characteristics at the fluid-solid interfaces: Many state-of-the-art microfluidic technologies require physical interaction between the target particles and the functional elements. An example of such technologies is affinity chromatography, where binding between the functional moieties and target species is exploited to achieve isolation. The presence of a

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flow stagnation region around any solid feature in a flow is therefore detrimental to these platforms, as these stagnation regions result in streamlines that take particles away from the functional element surface, and hinder desired particle-surface interaction [43]. A demonstration of the negative effects of flow stagnation is shown in Figure 3-9(a), where we present experimental results on the flow of 10μm beads around a cylindrical solid PDMS micropost (D=500μm; flow rate= 10μL/min). Noticeably, the particles' streamlines never terminate on the post's surface, a result that holds even for those particles that approach closely aligned with the post centerline³ (see insets of Figure 3-9(a)). In this work, we investigate this impediment by transitioning from solid to nanoporous (VACNT) microfluidic elements. Transitioning from solid to porous elements could in fact reduce detrimental flow characteristics and provide increased functional area through particle flow inside the functional features (see Figure 3-9(b)).

**Difficulty in accessing sub-micron particles:** Biological samples are complex fluids containing particles of very different sizes and shapes. As an example, in Figure 3-10 we present a chart containing an overview of some of the particles that can be found in human blood, differentiating in terms of both size and quantity. Clearly, each particle type is characterized by very distinct properties: while cells average ~10μm in size and are present in rather limited quantities, particles such as exosomes and proteins exist in large numbers but are very small in size (1-10nm). Having dimensions on the order of micrometers, biomedical MEMS platforms are very efficient at manipulating species such as bacteria and cells, whose dimensions are comparable to that of the functional features in the devices. Isolation of smaller sub-micron particles is however not trivial using current bioMEMS technologies, as these particles escape the size limitations of photolithography. Integration of nano-scale elements in microfluidic platforms is therefore exciting, as it could enable access to a largely unexplored sub-micron particle region and enable new applications such as Hepatitis-C (HCV) diagnostics or new HIV diagnostics solutions for global health platforms. In this work, we explore the integration of nanoporous CNT elements in microfluidic devices and demonstrate their applicability to the isolation of a variety

³Note that a particle approaching in perfect alignment with the post centerline would likely come in contact with the feature, because a stagnation point is present at the front edge of the feature. This is unique streamline is however not shown here.
(a) Flow of 10μm beads around a single (isolated) cylindrical (D=500μm) solid PDMS micropost. Flow stagnation around the solid feature limits particle interaction with the functional feature.

(b) Transitioning from solid to porous elements could modify streamlines and provide increased functional area through particle flow inside the functional features.

Figure 3-9: Comparison between particle flows around solid and porous elements (cylindrical post). (a) Snapshot of movie on experimental flow of 10μm beads around a cylindrical (D=500μm) solid PDMS micropost. (b) Schematic visualization of particle streamlines around solid and porous cylindrical microposts.

of bioparticles, from cells (~10μm) to viruses (~10nm).

**Limited design flexibility:** Ideally, one microfluidic platform would suffice to perform a variety of assays, from cell counting for HIV applications, to particle sorting and global health diagnostics. However, such a platform does not yet exist. Current microfluidic technologies are instead highly specialized technologies that are typically designed for solely one application.
Figure 3-10: Bioparticle quantity and size in blood. Carbon nanotube-based biodevices (NEMS) could allow access to particles that current microsystems (MEMS) cannot manipulate.

As an example, affinity chromatography platforms can only identify one species, as per what is dictated by the functionalization process. If more than one type of particle is to be identified, biologists need to either modify the functionalization process for the device or resort to a different type of microfluidic platform, thus increasing the duration and costs associated with the biomedical investigation. In this work, we address this critical impediment by devising new nanoporous, carbon nanotube-based platforms that enable simultaneous multiscale, multiphysics isolation of bioparticles on a single chip.

### 3.1.3 State-of-the-art in Porous Materials in BioMEMS

In an effort to provide an alternative to solid microfluidic designs and their intrinsic limitations, bioMEMS platforms that exploit porous materials for their functional elements have been recently investigated. Incorporation of porous materials in microfluidic devices is attractive for a
variety or reasons, including improved streamlines and larger functional surface compared to similar solid designs [82]. To date, inclusion of porous elements in microfluidic platforms has however been limited to membranes sandwiched between microchannel layers or monoliths that fill the inside of channels; as a result, porous technologies have not yet become a real alternative to solid designs as they cannot provide functionalities and, especially, flexibility comparable to that of state-of-the-art microfluidic platforms. Below, we provide a general overview of three porous technologies that were given the most attention by the bioMEMS community during the past two decades.

**Porous membranes:** Porous membrane elements were introduced in Section 3.1.1.1, and are commonly used in applications that require particle filtration capabilities [74, 77, 83]. Membranes enable size-based filtration, where particles are mechanically isolated on a mesh of pores (see Figures 3-1 and 3-2) based on their physical size. Size-based isolation is non-specific as it does not allow differentiation of different particle types; rather, the method can solely discriminate particles that are larger than a critical threshold, as per what defined by the membrane’s pore geometry [17, 38]. The average pore size for state-of-the-art membranes is around 1μm and porosity does not typically exceed 40-50%. As an example, in Figure 3-11 we present state-of-the-art results on the isolation of platelets in blood using polycarbonate membranes [25]. A critical drawback of membranes is their extremely limited flexibility in terms of feature geometrical design, as they are two-dimensional (2D) elements that can only be defined on a plane.

**Stationary porous monoliths:** A second approach to bioparticle isolation using porosity exploits stationary monoliths for applications such as electrochromatography (polymer monoliths; [26]) and catalyst support in flow reactors (silica monoliths; [42]). A typical configuration for this type of devices is the so-called “capillary column”, of which an example is presented in Figure 3-12 [26]. Here, the “brain-like” grainy structure typical of monoliths is clearly shown; these elements are typically characterized by porosities ranging between 40% and 70% and pores/grains approximately 1-5μm in size. Compared to membranes, porous monoliths of-
fer additional flexibility in that they enable both size-based filtration and specific bioparticle isolation [26]. Monoliths also enable quasi-3D feature patterning, although their geometry can only be defined via the non-porous channel walls.

Figure 3-12: State-of-the-art capillary column architectures exploit (a) porous polymer monoliths that fill (b) (solid) channels, here fused silica [26].

**Porous silicon:** Originally discovered by A. Uhlir in 1956 [84], porous silicon was first given significant attention by the scientific community in 1990 when L.T. Canham demonstrated that this material could yield, under particular laser excitation conditions, two-dimensional quantum effects with emissions far above the band gap of bulk crystalline Si [85]. From a mate-
rial perspective, porous silicon is an alternative morphological form of single-crystal silicon, and it is obtained by anodic attack in concentrated hydrofluoric acid solutions [86]. This process results in nanopores approximately ~6-10nm in size and porosity ranging between 50-70% [37]. To date, porous silicon has found application in a variety of fields, including silicon-on-insulator technologies [86], mass spectrometry [87], as well as in biological platforms for enzyme immobilization [88] and optical biosensing of protein binding [89]. Nonetheless, similar to the porous technologies previously described, this material does not provide the flexibility (both in terms of feature patternability and in terms of particle targeting) required to constitute a feasible alternative to solid designs.

3.2 Objectives and Approach: Integration of Bulk Nanoporous Elements in Microfluidic Devices

The aim of this work is to create new capabilities in biomedical microdevices through the integration of ultra-porous (99% porous) forests of vertically aligned nanotubes (VACNTs) in microfluidic platforms. Our research aims at overcoming the limitations of state-of-the-art bioMEMS devices (see Section 3.1.2) by providing an alternative to current solid designs, and by enabling access to a largely unexplored spectrum of sub-micron particles (e.g., virus, exosomes) that macro- and micro-scale technologies are largely unable to access and manipulate (see Figure 3-10).

Dispersed, randomly-oriented CNTs have already been adopted in a number of biomedical applications, from biological imaging techniques (e.g., optical tags) to electrical label-free biospecies detection [90]. The findings by Kam et al. [91] and Pantarotto et al. [92] that suggest that functionalized CNTs can enter cells without toxicity have particularly fostered research into the use of CNTs in biomedicine, leading to applications such as CNT-mediated delivery of small drugs and bio-macromolecules [93] as well as in vivo tumor targeting using carbon nanotubes [94]. However, current approaches to CNT-based biomedical devices do not take advantage of the physical properties of carbon nanotube forests (e.g., tailorability, aspect ratio,
porosity), thus being unable to provide functionalities beyond what is allowed by individual CNT intrinsic properties and surface chemistry. Here we explore the potential of patterned, functionalized, nanoporous forests of VACNTs as a new structural material for biomedical applications [95]. The following experimental approach is adopted:

- **Integration of patterned VACNT forests into microfluidic devices.** A significant challenge for this research is to achieve microfluidic integration of the VACNT forests while preserving the features' structural properties. Prior attempts to integrate VACNT-elements with fluids have resulted in either VACNT element deformation [96] or catastrophic forest collapse [97]. Preservation of the forests' structural properties (e.g., feature/element geometry) is paramount for applications that require accurate control of the fluid dynamics in the channel, and it is therefore a critical requirement within the aims of this thesis work. Here, we develop an approach that exploits soft lithography of polymer materials (i.e., PDMS) to enable successful microfluidic integration of the VACNT features grown using standard chemical vapor deposition (CVD), preserving the VACNT element's geometric properties even under flow-through conditions.

- **Investigation of the fluid transport properties of ultra-porous VACNT forests.** The performance of any functional element in a microfluidic device is dependent on several factors, including its geometrical layout and material properties. In this work, we investigate the fluidic properties of patterned VACNT elements and compare them with that of state-of-the-art solid and porous bioMEMS technologies. An analytical discussion on the effect of porosity on the permeability of porous structures is included as well, showing important considerations that need to be understood when designing porous microfluidic platforms.

- **Comparison between the isolation efficiency of solid and nanoporous platforms with identical geometrical layout.** The effects of transitioning from solid to nanoporous designs are investigated, showing a modification of fluid streamlines and increased capture efficiency when porous VACNT elements are utilized. The ability of VACNT designs to en-
able particle flow through the functional features is also addressed, demonstrating that significant increases in active surface area can be achieved through nanoporous designs.

- **Design and fabrication of VACNT-enhanced biomedical platforms for simultaneous multiphysics, multiscale bioparticle isolation and manipulation.** As previously mentioned, a primary aim of this work is to enhance the performance of current microfluidic platforms by transitioning from solid to porous designs. Part of this Chapter is therefore dedicated to the experimental demonstration of specific bioparticle isolation and manipulation using nanoporous bioMEMS elements. Isolation of particles over 4 orders of magnitude in size (from viruses to cells) is demonstrated, as well as the possibility to perform simultaneous multiphysics (mechanical and chemical), multiscale bioparticle isolation using a single device.

This work is a collaboration with Prof. Mehmet Toner and Grace D. Chen of the BioMEMS Resource Center of the Massachusetts General Hospital, Charlestown, USA. The functionalization and isolation tests presented in this work were performed by Ms. Chen.

### 3.3 Microfluidic Integration of Nanoporous VACNT Forests

Distinct from prior works where the effects of fluids on CNT forests would result in either structural deformation or catastrophic forest collapse (see, e.g., [96, 97]), here we demonstrate effective integration of CNT elements in microfluidic channels, with the forests' structural properties being preserved even under flow-through conditions. Furthermore, the approach provides feature definability comparable to that of state-of-the-art solid techniques: the in-plane geometry of VACNT elements can be accurately (~1μm) defined through photolithography independent of channel boundaries, while manipulation of CNT growth conditions enables control of the forest out-of-plane configuration (height) to create very high aspect-ratio elements up to mm-scale in height.
3.3.1 Methods

A schematic depiction of the overall approach is presented in Figure 3-13. First, the nanoporous elements are patterned and grown following the approach by Garcia et al. [98] (see also [99]). Standard photolithography is used to pattern plain <100> 152mm (6") diameter silicon wafers, followed by electron beam deposition of a 10nm Al₂O₃ layer and a 1nm Fe layer. Catalyst areas are then defined by photoresist lift-off: soaking the wafer in acetone for 8 minutes with mild sonication. CNT growth is performed in a 102mm (4") diameter quartz tube chemical vapor deposition (CVD) furnace at atmospheric pressure using reactant gases of C₂H₄, H₂ and He (400/400/1900 sccm). Catalyst annealing is carried out in a reducing He/H₂ environment at 680° C, leading to the formation of iron (Fe) catalyst nanoparticles ~10 nm in diameter. C₂H₄ is then introduced into the furnace to initiate CNT growth, occurring at a rate of approximately 100μm/min until the flow of C₂H₄ is discontinued. The technique results in forests of multi-walled vertically-aligned carbon nanotubes (3-4 concentric walls; Figures 3-14 and 3-13(a)), with an average tube diameter of 8 nm and an average inter-CNT spacing of ~80nm, thus yielding a 1% volume fraction of CNTs [100]. The vertical-alignment of the nanotubes in the forest is noticeable in the insets of Figure 3-15(a) (scanning electron microscope (SEM)). This fabrication method enables the creation of very high aspect ratio structures more efficiently than some state-of-the-art MEMS processes. For example, whereas deep reactive ion etching (DRIE) can create elements up to hundreds of microns deep at a rate of approximately 2-4μm/min [31], our technique yields VACNT elements up to several millimeters in height at a rate of ~100μm/min. Incorporation of the patterned CNT structures into devices is achieved using standard soft lithography techniques (see Figure 3-13(b)). Polydimethylsiloxane (PDMS) channels (2cm long, 3mm wide, 100μm tall) are fabricated from SU-8 photoresist negative molds, and bonded to the silicon wafers containing the VACNT elements after oxygen plasma surface treatment. In Figure 3-15 we present both a schematic and a device example of a patterned VACNT element (rectangular array of 20μm diameter cylindrical pillar elements) integrated in a microfluidic device. Functionalization of the VACNT elements is performed based on the non-covalent method demonstrated by Chen et al. in [101]. This method makes use of Tween-20, an am-
Figure 3-13: Integration of ultra-porous VACNT elements in microfluidic channels: schematics of fabrication, functionalization and bio-identification. Not to scale.
Figure 3-14: Transmission electron microscopy (TEM) showing the multi-walled structure (3-4 concentric walls) for the vertically aligned carbon nanotubes (VACNTs) in this work.

A phophilic molecule that yields a monolayer coverage of the VACNTs, which allows the as-grown nominally hydrophobic CNT surfaces to become hydrophilic, and also suppresses non-specific binding (NSB) of proteins [101]. First, 1,1 carbonyldiimidazole (CDI) is reacted with Tween 20 for 2 hours at 40°C, resulting in CDI-activated Tween. Pressure-driven injection of a solution of CDI-activated Tween (1 wt% in water) into the microchannel (Figure 3-13(c)) is used to functionalize the micropatterned CNT elements, followed by flushing using deionized (DI) water. A second (optional) functionalization step is then performed to enable selective biological recognition of target species [43]. A solution containing avidin in buffer is injected into the channels, resulting in a covalent link between the avidin and the Tween-activated nanotubes. For the experiment on capturing model viral particles, the avidin-coated CNTs were used to directly bind with biotin-coated nanoparticles. For experiments on *Escherichia coli* bacteria capture, a biotinylated anti-*Escherichia coli* antibody was injected after the avidin step. Remarkably, although all the functionalization methods in this work are based on wet chemistry, no post-growth forest treatment is required to ensure that the forest elements’ geometric properties are maintained: even after wetting and flow-through, the CNT elements preserve their geometry (see also Section 3.3.2 below).

Finally, particle isolation is achieved through pressure-driven injection of biosamples in the microchannel and through the nanoporous elements (Figure 3-13(d)). The ultra-porous VACNT elements are unique in that they enable simultaneous multiphysics, multiscale isolation of mul-
A nanoengineered biodevice for bioparticle isolation. Insets show SEMs of patterned VACNT forests.

Figure 3-15: Example of nanoengineered biomedical device for multiscale bioparticle isolation using VACNT elements.

Particles that are larger than the average intra-CNT spacing (~80nm) do not enter the forest and can be isolated on the elements' external surfaces both using chemical affinity (red, diamond particles) and via mechanical filtration (blue, spherical particles). At the same time, particles smaller than the average intra-CNT spacing can flow through the nanoporous features and can be isolated on the elements' internal and external functionalized surfaces (green, diamond particles).
3.3.2 Experimental

In the current literature, several works report on the detrimental effects of fluids on carbon nanotube forest geometries. As an example, Futaba et al. [97] address the catastrophic structural collapse of CNT forests subjected to liquid droplets (Figure 3-16(a)), while De Volder et al. [96] have recently demonstrated the possibility to exploit liquid capillarity-driven deformation to form CNT forests into diverse 3D configurations (Figure 3-16(b)). Preservation of the CNT forests' structural properties (e.g., element geometry) is however critical for microfluidic applications (biomedical and others) that require accurate control of the fluid dynamics in the channels, including this thesis work. To demonstrate the ability to integrate ultra-porous VACNT elements in microfluidic channels, we studied the effect of each fabrication step on a cylindrical (500μm in diameter, 100μm tall) VACNT micropost device that was fabricated following the procedure described in the previous Section. The results are presented in Figure 3-17, where we compare the micropost's geometry in the as-grown, post-integration (wet) and operational (i.e., flow through) configurations. For these experiments, fluorescent (red) antibodies and fluorescent (green) 20μm beads were used to enhance image contrast and to visualize the particle flow around the element. Noticeably, the element's geometry is preserved up to 99% of the original shape even under flow-through conditions. To our knowledge, this is the first integration of bulk porous CNT elements in microfluidics, thus establishing a new ultra-porous nano-scale microfluidic technology.

3.4 Fluid Accessibility of VACNT Forests

This Section is dedicated to the investigation of the fluidic properties of VACNT forests. First, experimental results on the structures’ fluid permeability are presented and compared to the fluid accessibility of other state-of-the-art porous microfluidic technologies. The discussion continues with an analytical analysis of the effect of structural porosity on the fluidic permeability of porous materials, revealing important performance aspects that need to be taken into
account when designing porous microfluidic platforms. The possibility to tailor the permeability of VACNT forests through manipulation of CNT growth material and process parameters is also demonstrated.

3.4.1 Fluid Permeability of VACNT Elements

At the low Reynolds regimes ($Re < 10$) typical of microfluidic devices [102, 103], the flow inside a porous material may be described by Darcy’s Equation [104]:

\[
Q = -\frac{k A}{\mu} \Delta P
\]

where $Q$ [m$^3$s$^{-1}$] is the volumetric flow rate, $\Delta P$ [Pa] is the pressure drop along the channel, $A$ [m$^2$] and $L$ [m] are the cross-sectional area and length of the porous channel, $\mu$ [kg m$^{-1}$s$^{-1}$] is the dynamic viscosity of the fluid, and $k$ [m$^2$] is the fluid permeability of the porous media. Fluid permeability is a measure of the ability of a porous material (e.g., a membrane) to transmit fluids [105]. Highly permeable materials are attractive for microfluidic applications as they min-
Figure 3-17: Experimental results on microfluidic integration of an ultra-porous VACNT micropost using the proposed approach. The element's structural properties are preserved even under operational (flow-through) conditions as evidenced by the element diameter (right).

Imimize back-pressure ($\Delta P$) for a specific flow rate, thus also requiring less powerful (and typically smaller) injection systems. In Table 3.1 we present the experimental results on the permeability of our VACNT elements, comparing them to the fluidic properties of other state-of-the-art porous materials (see Section 3.1.3). The permeability experiments were performed as follows: first, a rectangular (2mm wide, 200$\mu$m deep, 100$\mu$m tall) VACNT element was integrated into a PDMS channel (see Section 3.3.1) and wetted using 0.5% Tween in DI water; a solution of 0.1% Tween in DI water ($\mu$=0.001Kg m$^{-1}$s$^{-1}$) was then injected for 2 minutes at a fixed inlet pressure of 2psi, and all the outlet flow collected into an Eppendorf tube; finally, the volume of the collected outflow was measured and used to compute the flowrate, which was then input in (3.1) to extract the permeability value ($\kappa$) [106]. Using this procedure, the fluidic permeability of the (baseline) VACNT structures was quantified as $5.4 \times 10^{-14} \pm 8.3 \times 10^{-15}$ m$^2$. Interestingly,
this permeability value is comparable to or higher than that of other larger (*i.e.*, characterized by larger features/pores) as well as similar porous technologies. This result is somewhat counterintuitive, as one would expect materials with larger pores to be most accessible to fluids. The large difference in permeability between VACNT elements and porous silicon is also not obvious, as these elements have similar pore dimensions. The high permeability of our VACNT forests can however be explained by classical analyses of the effect of porosity on permeability, as described below.

Table 3.1: Overview of porous technologies for microfluidic devices.

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
<th>Feature size*</th>
<th>Pore size*</th>
<th>Porosity*</th>
<th>Permeability*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer membranes</td>
<td>Neeves and Diamond [25]</td>
<td>4µm</td>
<td>1µm</td>
<td>40</td>
<td>3.60E-15</td>
</tr>
<tr>
<td>Polymer monoliths</td>
<td>Urban and Jandera [40]</td>
<td>4.3µm</td>
<td>4µm</td>
<td>57</td>
<td>8.90E-14</td>
</tr>
<tr>
<td></td>
<td>Du <em>et al.</em> [41]</td>
<td>3.5µm</td>
<td>1-6µm</td>
<td>71</td>
<td>6.00E-14</td>
</tr>
<tr>
<td>Silica monoliths</td>
<td>Fletcher <em>et al.</em> [42]</td>
<td>1.25µm</td>
<td>4.16µm</td>
<td>70</td>
<td>7.65E-14</td>
</tr>
<tr>
<td>Porous silicon</td>
<td>Lysenko <em>et al.</em> [37]</td>
<td>16nm</td>
<td>7nm</td>
<td>60</td>
<td>6.40E-18</td>
</tr>
<tr>
<td>VACNT (baseline)</td>
<td>Fachin <em>et al.</em> (this work)</td>
<td>8nm</td>
<td>80nm</td>
<td>99</td>
<td>5.40E-14</td>
</tr>
</tbody>
</table>

* value computed by averaging the data contained in each source.

3.4.2 Analytical Discussion of the Effect of Structural Porosity on the Fluidic Permeability of Porous Materials

Macro- and meso-scale porous materials such as granites, millstones and fine powders were given particular attention during the second half of the last century [102, 105, 107, 108], as they were starting to be considered for applications such as water distillation and temperature control in highly exothermic reactions. Between others, Sabri Ergun (1952) studied the flow through porous materials by modeling their internal structures, including regular beds of aligned pillars (equivalent diameter $D$; height $\gg D$) that lay perpendicular to the flow direction and that are spaced apart by a distance $S$ (see inset of Figure 3-18(a)). In his work [109], Ergun derived the following semi-empirical expression that relates feature size ($D$ [m]), structural porosity ($\phi$ [-]),
and fluid permeability (\( \kappa \ [m^2] \)):

\[
\kappa_{Ergun} = \frac{1}{c} \frac{\phi^3}{(1-\phi)^2} D^2
\]  

(3.2)

where \( c \ [-] \) is a constant dependent on both the pillars' geometry (e.g., squares vs. cylinders) and the feature's size scale (e.g., macroscopic vs. microscopic). In Ergun's meso-scale experiments (average pillar diameter between 0.5-0.8mm), the constant \( c \) was quantified as 150. Note that for the case of cylindrical pillars the porosity (\( \phi \)) can be expressed as [102]:

\[
\phi = 1 - \frac{\pi D^2}{4 (S+D)^2}
\]

(3.3)

where \( S \) is the distance between each pillar in the structure. Equation (3.2) allows one to distinguish between the effects of size and structural porosity on the permeability of porous materials. On one hand, given a certain porosity level \( \phi \), fluid permeability is proportional to the second power of the feature size (i.e., \( \kappa \sim D^2 \)). Designs with larger features (e.g., unconsolidated rocks) are therefore generally more fluid accessible than smaller elements (e.g., sands), a result that matches intuition. On the other hand, less intuitive is the effect of structural porosity, which is plotted in Figure 3-18(a) for a porous material with \( D=1 \) m. Noticeably, the functional dependence of permeability on porosity changes significantly at different porosity levels: while permeability is linearly proportional to structural porosity at moderate porosity levels (0.3 \( \sim < \phi \sim < 0.8 \)), its dependence on porosity is highly non-linear at both very small (0 \( < \phi < 0.3 \)) and very large (0.8 \( < \phi < 1 \)) porosities. The effect of porosity on permeability at different porosity regimes can be summarized as:

\[
\kappa = \begin{cases} 
\phi^3, & 0 < \phi < 0.3 \\
\phi, & 0.3 \leq \phi \leq 0.8 \\
\frac{1}{(1-\phi)^2}, & 0.8 < \phi < 1
\end{cases}
\]

(3.4)

The presence of two highly non-linear regions in the porosity-permeability relation of porous materials is extremely relevant from a designer's perspective, as it suggests ways to significantly
decrease/increase the permeability of porous devices by designing in the very small/very large porosity regions. This possibility becomes apparent in Figure 3-18(a), where drastic (>10^3 m^2) decreases/increases in permeability can be noticed at both ends of the porosity spectrum. The possibility to enhance device permeability through porosity control is particularly attractive for miniaturized platforms where feature size is limited compared to larger technologies. The results above can be used to rationalize the findings of Section 3.4.1, where we showed that nano-scale VACNT elements yield permeability comparable to, or even higher than, that of larger micro-scale porous materials (see Table 3.1). Our VACNT forests are ultra-porous (99% porosity), and therefore fall within the large non-linear permeability-porosity region (i.e., 0.8 < φ < 1) of Equation (3.4) and Figure 3-18(a). As a consequence, VACNT elements yield permeability comparable to that of much larger macro-/micro-scale porous materials yet at a significantly smaller (i.e., nano) scale, thus favoring further miniaturization of MEMS devices. To further clarify the effect of porosity on the permeability of porous structures, in Figure 3-18(b) we plot Ergun's formula (Equation (3.2)) for each microfluidic technology of Table 3.1. Despite that the nature of these porous technologies deviates from Ergun's original structural model (i.e., regular beds of aligned pillars), good agreement between theoretical and experimental results is observed. Most importantly, Figure 3-18(b) allows one to visualize the effect of large porosity (99% porosity) on the permeability of VACNT structures. Our nanoporous VACNT technology takes advantage of the large non-linear permeability increase at high porosity levels, while all other porous platforms fall within the linear permeability-porosity region. As a result, the nanoporous VACNT elements yield permeability significantly higher than that of similar nano-scale technologies, thus being as accessible to fluids as larger micro-/macro-scale materials.

---

4 Note that the Ergun's curves presented here were plotted assuming c = 150 in (3.2), as per Ergun's original work. However, c is an empirical constant and as such would likely differ between one porous technology and another. Future work should include further material characterization efforts to determine the constant c for each porous technology.
(a) The effect of porosity on permeability: Ergun (1952) derived a semi-empirical expression (Equation (3.2)) that relates feature size \( (D) \), structural porosity \( (\phi) \), and fluid permeability \( (\kappa) \) in porous materials [109].

\[
\kappa = D^2 \phi^3 \left[ \frac{1 + \phi}{1 - \phi} \right] \frac{1}{D = 1 \text{ m}}
\]

The ultra-high porosity (99%) of our nanoporous VACNT features yields permeability comparable to that of larger micro-scale platforms.

(b) Ergun's curves for several state-of-the-art porous microfluidic technologies.

Figure 3-18: Analytical and experimental results on the effect of feature size and porosity on the permeability of porous microfluidic materials.
3.4.3 Tailoring the Permeability of VACNT Forests Through the Control of Material and Growth Process Parameters

In Section 3.4.2 we have shown that the permeability of porous materials is directly dependent on their porosity, and that very high porosity levels (>80%) are associated with large non-linear increases in permeability as per Ergun's formula (Equation (3.2)). Here we further investigate tailoring of the permeability of VACNT forests through manipulation of both material (e.g., catalyst thickness) and CNT growth process parameters (e.g., temperature ramp-up time, growth temperature). In particular, (3.3) defined the porosity of porous materials as a function of both feature size \(D\) and the average distance \(S\) between each feature in the material (see inset of Figure 3-18(a)). Material and CNT growth process parameters could therefore be controlled to manipulate both \(D\) and \(S\), thus also modifying the structure's porosity and permeability. In this work, we undertook two different approaches to forest manipulation, both of which aimed at increasing intra-CNT spacing (i.e., the average distance between single nanotubes in the forest). The first approach is based on fine tuning the growth process conditions to increase the size and spacing between catalyst islands prior to CNT growth initiation. This method was presented by Nessim et al. [110] and others (e.g., [111, 112]), and it consists of varying the \(H_2\) pre-treatment time (PTT) to modify the Fe catalyst nanoparticle size. In this thesis work, the \(H_2\) pre-treatment time was increased by 8 minutes compared to baseline growth, yielding the VACNT forest morphology shown in the center column of Figure 3-19. Compared to baseline forests, the +8PTT structures yield larger intra-CNT spacing (~93nm vs. 80nm for baseline structures) and a 70% increase in fluid permeability \(\kappa = 9.3 \times 10^{-14} m^2\) vs. \(\kappa = 5.4 \times 10^{-14} m^2\), thus demonstrating the possibility to tailor forest permeability using this method. Next to this, a second approach to permeability control was undertaken that uses control of catalyst thickness to yield forests with larger intra-CNT spacing. Between others, this approach to forest morphology control was presented by Wei et al. [113], who demonstrated a strong correlation between catalyst film thickness and the average CNT diameter and spacing. In this thesis work, the catalyst thickness was doubled (from 1nm to 2nm) resulting in forests shown in the right column of Figure 3-19. These structures are characterized by an average of 98nm intra-CNT spacing, and yield a
103% increase in forest permeability \((\kappa = 1.1 \times 10^{-13} \text{m}^2)\) compared to baseline devices. These results are a demonstration of manipulation of forest permeability through control of material and growth process parameters. However, further optimization of the proposed approaches is required to improve the CNT vertical-alignment - and therefore minimize the tortuosity [102] - for the modified forest designs.

<table>
<thead>
<tr>
<th></th>
<th>Baseline</th>
<th>+8min Pre-treatment time</th>
<th>+1nm Fe catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td><img src="image1.png" alt="SEM Baseline" /></td>
<td><img src="image2.png" alt="SEM Pre-treatment time" /></td>
<td><img src="image3.png" alt="SEM Fe catalyst" /></td>
</tr>
<tr>
<td>Liquid permeability, (\kappa) [m²]</td>
<td>(5.4 \times 10^{-14} (\pm 8.3 \times 10^{-15}))</td>
<td>(9.3 \times 10^{-14} (\pm 1.9 \times 10^{-15}))</td>
<td>(1.1 \times 10^{-13} (\pm 1.8 \times 10^{-14}))</td>
</tr>
</tbody>
</table>

Figure 3-19: The permeability of VACNT forests can be manipulated by controlling both growth process (pre-treatment time - PTT) and material parameters (catalyst thickness).

### 3.5 Enhanced Isolation Efficiency by Nanoporous Microfluidic Platforms

State-of-the-art microfluidic platforms for specific bioparticle isolation are limited by streamlines that take particles away from the functional element surface and hinder desired particle-surface interactions. In this Section we demonstrate desirable flow field modification and enhanced isolation efficiency by nanoporous microfluidic elements and designs.

#### 3.5.1 Flow Control of Micro- and Nano-Particles Using Nanoporous Designs

In Figure 3-20 we present experimental results on the flow of 10μm beads and 10-20nm quantum dots around solid (PDMS) and nanoporous (VACNT) microposts. Both the solid and the porous elements are 100μm tall and 200μm in diameter. 0.5% Tween-20 in DI water was used
to treat the VACNT device after fabrication to make the surfaces hydrophilic, and to block non-specific binding. The samples were injected into the channels using a syringe pump set to 10 μL/min flow rate, and time-lapse image recording was performed using a fluorescent microscope.

Clearly, particle flow is significantly modified when transitioning from solid to porous designs. In the former case, 10μm-sized particles approaching with a trajectory closely aligned with the PDMS element's centerline do not reach the surface of the solid microposts\(^5\) (Figure 3-20(a)), where particle streamlines move particles away from the feature itself [43]. Conversely, in the nanoporous case, particles approaching from the same position do reach the surface of the nanoporous element (green, bottom curve in Figure 3-20(b)) and could be isolated on the element's external surface using, e.g., chemical affinity (see below). This large difference in particle flow between the solid and nanoporous designs is the result of the ability of the VACNT elements to allow flow both around and through the nanoporous features, thus pulling particle streamlines significantly tighter to (and indeed through) the functional elements compared to solid designs.

In addition to enabling fluid flow through the functional elements, nanoporous materials also provide access to smaller, sub-μm species (e.g., viruses, exosomes). Particles smaller than the average intra-CNT spacing (~80nm) can penetrate the VACNT elements, and could be isolated inside the microfluidic elements, e.g., using chemical affinity (see below). Experimental evidence of particle flow through VACNT elements is shown in Figure 3-20(b) (yellow, upper line), where we present the trajectory of a fluorescent quantum dot (10-20nm size) flowing through a nanoporous cylindrical element from a movie of the flow (see also [43]). Particles flow inside the nanoporous elements also results in a significant increase in functional surface area for the device. Both the external and the internal surfaces of the VACNT elements could in fact be exploited to isolate bioparticles, both via mechanical particle filtration and using biochemical particle recognition (see Sections 3.2 and 3.6). For the cylindrical feature layout considered here (100μm tall, 200μm in diameter), transitioning from a solid to a porous design yields a ~250X

\(^5\)The reader is referred to [43] for a more detailed discussion on the interception efficiency/probability of solid and VACNT cylindrical features.

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(a) Flow of 10μm beads around a solid PDMS micropost with streamline indicated.

(b) Flow of 10μm beads (green, bottom line) and 10-20nm quantum dots (yellow, top line) around and inside a nanoporous VACNT micropost (white circle) and around (streak at top in 7s and 8s frames).

(c) Snapshots showing the flow of a fluorescent quantum dot (10-20nm in size) through a nanoporous VACNT micropost

Figure 3-20: Flow of 10μm beads and 10-20nm quantum dots around (a) a solid (PDMS) micropost and (b-c) around and through a nanoporous (VACNT) micropost of the same diameter.

increase in functional surface area⁶.

⁶This value was computed assuming perfect vertical alignment of the CNTs in the forest, as well as 8nm average CNT diameter and 1% volume fraction.
(a) Isolation of 2μm (red) and 40nm (green) biotin-coated beads using avidin-functionalized, cylindrical (D=40μm, H=100μm) PDMS and VACNT microposts.

(b) Particle capture results for the specific isolation of 2μm beads using solid (PDMS) and nanoporous (VACNT) microfluidic elements.

Figure 3-21: Comparison between bioparticle isolation using functionalized solid (PDMS) and nanoporous (VACNT) microfluidic devices with identical geometrical and device layout and test conditions.
3.5.2 Isolation Efficiency of Solid and Nanoporous Microfluidic Platforms with Identical Geometrical Layout

In this Section we investigate bioparticle isolation efficiency of nanoporous VACNT designs, and compare it with that of traditional microfluidic approaches that use solid materials (PDMS) for the functional elements. In detail, here we present experimental results on the isolation of 2\(\mu\)m (red) as well as 40nm (green) biotin-coated fluorescent beads using cylindrical (100\(\mu\)m tall, 1000\(\mu\)m in diameter) microfluidic elements (Figure 3-21). The nanoporous VACNT elements were fabricated using the procedure described in Section 3.2, while standard soft lithography [114] was used to create the solid PDMS elements. For these experiments, the nanoporous elements were functionalized using 1 hour incubation with CDI-activated Tween-20, followed by 1 hour incubation with 20ug/ml NeutrAvidin in PBS. The PDMS elements were instead pretreated with 4\%(v/v) solution of 3-mercaptopropyltrimethoxysilane in ethanol for 30 min at room temperature, followed by incubation with 0.01 \(\mu\)mol/mL GMBS in ethanol for 15 min at room temperature and by 1 hour incubation with 20\(\mu\)g/ml NeutrAvidin in PBS. These functionalization procedures yield specific binding between the biotin-coated beads and the avidin-coated functional elements. The isolation results are presented in Figure 3-21(a), where we show a microscopy image of the devices after sample injection and flushing using DI water\(^7\). Noticeably, a significantly greater amount of particles are isolated by the nanoporous design. Whereas in the solid case particles can only be isolated on the external surface of the PDMS element, the nanoporous design allows particles smaller than the average intra-CNT spacing (~80nm) to flow through VACNT element, thus greatly increasing the amount of active surface for the device (~50X for the geometrical layout in these experiments). As a result, the nanoporous design outperforms the solid device in terms of isolation of smaller (green) 40nm beads. Next to this, the results show that nanoporous designs are more efficient at isolating larger particles as well. This is shown by the larger number of (red) 2\(\mu\)m beads that are binding to the external surface.

---

\(^7\)In [43] we demonstrated that differences in surface functionalization between the nanoporous VACNT and solid PDMS devices are not responsible for disparity in isolation efficiency between the two designs. Differences in particle isolation efficiency between the nanoporous and solid devices in this work can therefore be attributed to porosity.
of the VACNT element in Figure 3-21(a), as well as by the results of Figure 3-21(b) where we plot the number of 2μm particles captured by the solid and porous designs over time. More precisely, a ~7X enhancement in capture efficiency by nanoporous designs is found for the devices in this work. Particle-surface interactions (and specific binding) are therefore significantly enhanced by transitioning from solid to VACNT designs.

3.6 Multiphysics, Multiscale Bioparticle Isolation via Nanoporous Elements

Ideally, one microfluidic platform would suffice to perform a variety of assays, from cell counting for HIV applications to particle sorting for global health diagnostics. However, we recall from Section 3.1.2 that such platform does not yet exist. Current microfluidic technologies are instead highly specialized platforms, typically designed for solely one application, thus requiring the use of multiple devices when more than one bioparticle or pathologic condition needs to be investigated. In this Section we present experimental evidence of the ability of our nanoporous VACNT technology to enable simultaneous multiscale, multiphysics bioparticle isolation on a single chip. Isolation of biological species over 3 orders in magnitude in size is demonstrated using several device layouts, including one that enables simultaneous manipulation of three different particle types using both mechanical filtration and chemical biomolecular recognition. Application of the VACNT technology to sample concentration and depletion is also demonstrated.

The possibility to perform simultaneous multiscale isolation using VACNT microfluidic platforms was first introduced in Section 3.5, where we showed capture of bacteria- and virus-like particles using a single cylindrical nanoporous element (Figure 3-21). In this Section, we further investigate the unique structural and fluidic properties of VACNT elements to demonstrate isolation of several biological species simultaneously, exploiting both mechanical manipulation and filtration and chemical biomolecular recognition.
In Figure 3-22 we present experimental results on specific capture of biological particles over 3 orders of magnitude in size using three distinct VACNT platforms. 10μm CD4+ T-cells are isolated on a single cylindrical micropost (500μm in diameter; Figure 3-22(a)), while 1μm *Escherichia coli* bacteria are captured using an array of VACNT micropillars (30μm in diameter, 15μm spacing; Figure 3-22(b)). For these experiments, the VACNT elements were wet-
functionalized with either anti-CD4 or anti-\textit{E. coli} antibodies (~10nm in size), thus resulting in specific bioparticle isolation\textsuperscript{8} on the elements' external surfaces (note that both CD4 cells and \textit{E. coli} bacteria are larger in size than the average intra-CNT spacing - ~80nm - and therefore cannot infiltrate the nanoporous elements). Finally, in Figure 3-22(c) we present a platform that combines surface chemistry and mechanical filtration to simultaneously isolate 1\(\mu\)m bacteria-like beads and 40nm virus-like avidin-coated particles on a single chip. The device consists of a rectangular VACNT element (500\(\mu\)m wide, 200\(\mu\)m long) that is integrated in a microfluidic channel and that was biotin-functionalized using the procedure described in Section 3.5.2. The VACNT element mechanically filters the 1\(\mu\)m sized (green) particles (which are larger than the 80nm spacing between individual nanotubes in the forest), and at the same time chemically captures the 40nm virus-like (red) beads (which can flow through the nanoporous structure and can therefore be isolated on the element’s internal surfaces). Enabling particle isolation both on the external and on the internal surfaces of the functional elements, our VACNT technology yields a significant increase in active surface (~200–400X for the devices analyzed here) compared to solid designs. VACNT-enhanced bioMEMS are therefore a versatile approach to bioparticle isolation, enabling access to a large spectrum of sub-\(\mu\)m particles that current microfluidic technologies do not address.

To further demonstrate the flexibility of our VACNT technology, in Figure 3-23 we present an additional device configuration that enables simultaneous isolation of three different particle types ranging 3 orders of magnitude in size: blue 15\(\mu\)m polystyrene beads, red 2\(\mu\)m biotin-coated particles, and green 40nm biotin-coated beads. The device consists of an array of cylindrical micropillars (30\(\mu\)m diameter, 100\(\mu\)m tall) that are spaced 5\(\mu\)m apart from each other and that were wet functionalized using avidin (see Section 3.5.2). The VACNT platform combines micro- and nano-porosity to achieve simultaneous mechanical filtration and chemical bioparticle capture: the intra-pillar distance (5\(\mu\)m) defines the microscale pores, while the intra-CNT spacing (~80nm) defines the nanoscale porosity. Particles larger than the micro-scale pores

\textsuperscript{8}The reader is referred to Section 3.5.2 and [43] for a comparison between the isolation efficiency our VACNT technologies and that of similar state-of-the-art solid platform. For the results in this work, a 6-7X enhancement in capture efficiency can be seen when transitioning from solid to nanoporous designs.
cannot penetrate the array of functional elements and are mechanically filtrated at the front edge of the device, as is the case for the blue 15μm polystyrene beads. On the other hand, particles that are smaller than the micro-pores yet larger than the average intra-CNT spacing can enter the functional array of elements (but not the nanoporous micropillars) and are captured on the micropillars' surfaces using chemical affinity (red 2μm beads). Finally, particles whose size is below the nano-pore threshold can flow through the VACNT micropillars and are isolated inside the functional elements using chemical biorecognition (green 40nm beads). This example demonstrates the ability of VACNT-enhanced microfluidic devices to enable simultaneous multiphysics, multiscale bioparticle isolation on a single chip, a functionality that could be exploited and benefit a number of fields beyond the biomedical sphere (e.g., fuel cells, water desalination).

The patternability and integrity of VACNT elements can also be exploited to manipulate bioparticle in flows. Here, we demonstrate this functionality by designing a device that enables selective concentration and depletion of particles in heterogenous samples based on their size. The device is shown in Figure 3-24 and it consists of a “Y-shaped" nanoporous element that funnels into a narrow 50μm channel at whose end is located a primary (or concentrator) outlet. A secondary (waste) outlet is then located further down the device, completely separated from the primary outlet by a diamond-shaped PDMS element placed around the concentrator. No functionalization was performed in this case other than Tween-20 treatment to make the elements hydrophilic. The samples are injected using a syringe pump and bioparticle manipulation is achieved based on particle size. On one side, 10μm (green) bacteria-like particles cannot flow through the Y-shaped element’s walls (these particles are larger than the intra-CNT spacing), and are forced into the central channel by shear forces before eventually terminating in the concentrator outlet. On the opposite side, 40nm (red) virus-like particles are smaller in size than the spacing between single nanotubes in the forest and can therefore flow through the Y-element and into the secondary outlet. The VACNT platform here presented is a simple yet effective approach to particle depletion and concentration that does not require any chemical functionalization. This design could find applications, e.g., in diagnostic platforms or it...
Figure 3-23: Simultaneous multiphysics, multiscale bioparticle isolation using an array of functionalized VACNT micropillars.

could be used as first stage in multi-purpose streamlined devices where particle pre-sorting is required.

3.7 Perspectives and Future work

BioMEMS designs with ultra-porous nanoporous elements could resolve the issue of detrimental stagnation effects typical of state-of-the-art microfluidic platforms that use solid materials (e.g., silicon, PDMS) for their functional elements, thus potentially increasing isolation efficiency and overall device performance. Nanoporous devices could also enable access to sub-micron particles (e.g., exosomes) that escape the size limitations of current micro-scale biomedical devices, hence extending the applicability of bioMEMS devices to new areas such
HIV diagnostics. In this work, we have introduced and demonstrated nanoporous forests of vertically-aligned carbon nanotubes (VACNTs) as a new structural/functional material for microfluidic applications. Distinct from previous works that exploited functionalized dispersed CNTs for applications such as CNT-mediated drug delivery, our approach exploits the structural properties of VACNT forests (e.g., patternability, ultra-high porosity) to enable multiphysics, multiscale isolation of several biospecies on a single chip. The method enables successful integration of VACNT elements in microfluidic channels, with the forests' structural properties maintained even under flow-through conditions. Isolation of particles over 3 orders of magnitude in size (from cells to viruses) was experimentally demonstrated, with our nanoporous devices yielding ~7X enhancement in isolation efficiency compared to identical solid designs. Simultaneous isolation of three distinct particle types using a single device was also demonstrated, combining mechanical filtration and chemical biomolecular recognition to enable bioparticle capture both on the external and on the internal surfaces of the nanoporous VACNT elements.
Looking forward, additional research efforts should be placed on further investigating the fluidic properties of nanoporous VACNT forests beyond what was discussed in this work. As an example, properties such as tortuosity and fluidic drag [102] should be investigated and taken into account in some potential future designs. Further characterization of the effects of both material (e.g., catalyst thickness) and growth process (e.g., pre-treatment time) parameters on forest morphology should also be pursued to enable broader control over both intra-CNT spacing and tube diameter. The methods presented in this work allow control solely over the average properties of VACNT elements, and they do not enable large modifications in forest morphology (e.g., modification of intra-CNT spacing using our approach is limited to approximately ±10 μm). Techniques such as nanophotolithography [115] and mechanical densification of VACNT forests [116] should therefore be explored, as they may enable larger (and possibly deterministic) control over CNT diameter, intra-CNT spacing, and VACNT feature alignment. Under a design perspective, additional geometrical layouts should be investigated for the functional nanoporous elements. In this thesis work, element layout was largely limited to cylindrical and rectangular geometries that mimicked extant solid designs. Incorporation of, e.g., aerodynamics considerations in microfluidic designs should however be pursued, as this could yield significant enhancements in both flow efficiency and bioparticle manipulation. As an example, in Figure 3-25 we present a new design that exploits airfoils to enable manipulation of flows in the microfluidic channels. The device consists of a hydrofoil-like VACNT element, and in Figure 3-25 we show the flow (streaklines) of 20μm cell-like particles around the nanoporous element at a flow rate of 20mL/min. Noticeably, several particles reach the element and contact its external surface, thus demonstrating the ability of this design to allow physical interaction between the functional elements and the particles in the flow.
Figure 3-25: Streaklines of 20μm cell-like particles flowing around an hydrofoil (aerodynamic NACA-7410 cross-section) nanoporous VACNT element.
Chapter 4

Conclusions and Recommendations

In this thesis work, two new MEMS approaches were developed that overcome some critical impediments of current micro-technologies. On one hand, a new approach to MEMS fabrication was demonstrated that enables the creation of three-dimensional (3D) micro-features for functionalities such as 3D sensing and actuation. Distinct from state-of-the-art fabrication methods that are largely limited to the creation of planar (2D) features, the technique here presented exploits residual stress-induced buckling phenomena to create functional elements that lay outside the wafer plane. The approach makes use of an analytical model for the non-linear buckling of multilayered beam structures developed in this thesis, that can be applied to both device design and thin-film characterization. Several three-dimensional MEMS architectures were experimentally demonstrated, notably also working within the confines of CMOS, including a 3D platform for acceleration sensing using thermal effects (thermal accelerometer). On the other hand, nanoporous forests of vertically aligned carbon nanotubes (VACNTs) were introduced as a new functional element in microfluidic applications. Microfluidic integration of nanoporous VACNT elements was experimentally demonstrated, with the forests’ structural properties preserved even under flow-through conditions. Most importantly, the nanoporous technology was proven capable of overcoming some limitations of state-of-the-art designs that use solid materials for their functional elements. Experimental results show a significant tightening of streamlines when transitioning to nanoporous designs, thus enhancing physical in-
teraction between the particles in the flow and the functional elements. A ~7X improvement in capture efficiency by VACNT designs was also demonstrated, as well as simultaneous multiphysics, multiscale isolation of multiple particle sizes on a single device. The nanoporous VACNT technology is also unique in that it enable access to smaller, sub-micron particles (e.g., exosomes) that escape the size limitations of current micro-scale devices, thus fostering the extension of microfluidic platforms to fields such as HIV diagnostics.

4.1 Contributions

Major contributions from this work are as follows:

4.1.1 3D MEMS via (Post-)Buckling of Micromachined Elements

Analytical model for the non-linear (post-)buckling of multi-layered thin film materials

A new analytical tool for analyzing the post-buckling of micromachined beam structures was developed. The model takes into account non-linear structural mechanics, residual stresses (mean and gradient) as well as boundary flexibility to describe the post-release evolution of multi-layered MEMS structures. The model overcomes the limitations of state-of-the-art models that assume boundary ideality for the structures (i.e., perfectly clamped or perfectly simply-supported structures), thus providing a flexible tool that can be used for both design and characterization of MEMS elements.

Thin-film characterization using the developed analytical tools

Current thin-film characterization techniques are based on structural models that are found to provide inaccurate estimates for the stress state of thin-film materials. In particular, current models assume that the structures' boundaries are infinitely stiff, thus incorrectly eliminating the effect of gradient stresses on the mechanics of clamped structures and making their post-release deformation dependent on mean stress effects only. As a consequence, more than one type of test structure is currently required to fully character-
ize the stress state in a thin-film material (e.g., microbridges for mean stress extraction, and cantilevered beams for gradient stress extraction). Here, a new approach to multi-layered thin film characterization was developed that uses analytical results to provide significantly reduced uncertainty on the extracted stresses. The method enables simultaneous extraction of both residual stresses (mean and gradient) and boundary flexibility based solely on experimental measurements of microbridge test structure out-of-plane deformations. The technique eliminates the need for both multiple microbridge lengths and cantilevers, thus significantly simplifying the characterization process and possibly lowering its overall cost by minimizing the wafer area that needs to be allocated for test structures. The technique was also demonstrated in combination with cantilever gradient measurements, and shown to provide an additional ~25% decrease in gradient uncertainty plus an additional five-fold decrease in mean stress uncertainty when cantilever test structures are used. Overall, the analytical approach gives more than an order of magnitude enhancement in uncertainty than prior techniques using the same number and type of test structures.

Extension of CMOS processes to 3D MEMS fabrication

The capabilities of CMOS processing were extended beyond 2D fabrication by combining CMOS, a bulk micromachining release step, and buckling control to achieve three-dimensional microfabricated elements that operate in the post-buckled regime. Four device architectures (patches, step-up's, runners, tethers) that enable control over the post-release deformation of micromachined elements were developed and experimentally demonstrated, thus further overcoming the design limitations of CMOS processes.

Experimental demonstration of 3D MEMS for thermal accelerometer applications

The analytical design approach was applied to a 3D architecture for thermal accelerometer applications. The design exploits buckling of microbridges and highly curved tethers to achieve significant device height, thus improving 2D resolution and also enabling 3D sensing capability. An analytical design procedure was presented, and the experimental results show very good agreement between the analytical predictions and the final device
geometry. In summary, the findings in this work demonstrate the possibility to create 3D MEMS functional elements that are designed to operate in the post-buckled regime, an approach that could be extended to several other applications including, e.g., flow sensors, load sensors and MEMS switches.

4.1.2 Integration of Bulk Nanoporous Elements in Microfluidic Devices

Microfluidic integration of patterned VACNT forests

A new approach to the microfluidic integration of nanoporous VACNT elements was developed that preserves the CNT forests' structural properties even under flow-through conditions. The method combines standard microfabrication techniques, chemical vapor deposition (CVD) and soft lithography of polymer materials. The method enables definition of the nanoporous microfluidic elements independent of channel boundaries, with the elements' in-plane layout defined using lithography while the out-of-plane geometry (height) is tailored through control of the CNT growth conditions.

Analysis of the fluidic properties of ultra-porous VACNT forests

The fluidic properties of VACNT forests were investigated and compared to state-of-the-art porous microfluidic platforms. Permeability levels comparable to or higher than that of other micro-/nano-scale materials were experimentally demonstrated for the VACNT forests ($k = 5.4 \times 10^{-14} \text{m}^2$). An analytical discussion on the effect of porosity on the permeability of porous materials (Ergun's formula) was used to explain the significant decrease/increase the permeability of microfluidic elements when designing in the very small and very large structural porosity regions. The ability to manipulate the permeability of VACNT forests through control of both material and CNT growth parameters was experimentally demonstrated as well, yielding ~100% enhancement in permeability for the nanoporous elements demonstrated here.

Design and fabrication of nanoporous VACNT biomedical platforms for simultaneous multiphysics, multiscale bioparticle isolation and manipulation
Isolation of particles over 3 orders of magnitude in size (from cells to viruses) was experimentally demonstrated, with the nanoporous VACNT devices yielding ~7X enhancement in capture efficiency compared to similar solid (PDMS) designs. This result is due to the ability of the nanoporous technology to allow flow both around and through the VACNT elements, thus modifying flow streamlines and increasing physical interaction between the particles in the flow and the functional elements. Allowing flow inside the nanoporous elements, VACNT designs result in a significant enhancement in active surface area (~200-400X for some geometrical layouts considered in this work). Simultaneous isolation of three distinct particle types using a single device was also demonstrated, combining mechanical filtration and chemical biomolecular recognition to enable bioparticle capture both on the external and on the internal surfaces of the nanoporous VACNT elements. Application of the nanoporous technology to bioparticle filtration, depletion, and concentration was experimentally demonstrated as well.

### 4.2 Recommendations for Future Work

Given the limitations of state-of-the-art MEMS platforms and the results presented in this work, future research efforts should include:

#### 4.2.1 3D MEMS via (Post-)Buckling of Micromachined Elements

**Design of device layouts beyond beams**

The post-buckling approach presented here should be extended to device layouts other than microbridges and cantilevers. As an example, the analytical tool of Section 2.3 and the design procedure of Section 2.6 could be extended to membranes and shells, thus moving to higher dimensional elements. Buckling of membranes and plates has been extensively analyzed during the second half of last century, and many works are present in the current literature that focus on this topic (see, e.g., [12, 59]). Devices that exploit membrane elements operating in the post-buckling regime are however extremely rare.
in the MEMS community (examples include, [72, 73]), as buckling is typically considered as failure. In addition, future work on 3D thermal accelerometers should combine the analytical design tool with multiphysics FE techniques to characterize the interaction between the working fluid and the compliant structural elements and hence to predict any non-linear performance (e.g., sensitivity) of the devices. Fabrication processes should also be selected that minimize variability in boundary flexibility across structures/wafers, as this work demonstrated that even small variations in boundary flexibility ($K$) can yield significant changes in the structural response of buckled structures (see Section 2.3.1).

**Tensile and package-induced stress extraction using analytical tools**

The possibility to extract both tensile and package-induced stresses was briefly introduced in Section 2.4.3. A more rigorous description of the protocol to extract these stress components using the analytical tool is however required in order for this technique to significantly benefit the MEMS community.

**Performance prediction using the developed analytical tool**

In this work we have demonstrated the application of the analytical method to the prediction of the post-release configuration of MEMS structures under the effects of residual stresses only. The analytical tool can however be easily extended to the analysis of other parameters such as transverse mechanical loads, thermal loads, and stress-induced material failure. As an example, inclusion of transverse loading into the analytical model is presented in Appendix C; for this application, key is the extraction of stresses using the analytical model to assess failure of the elements under operation. Future works should further investigate the capabilities of the analytical tool to enable the design of devices such as switches.

### 4.2.2 Integration of Bulk Nanoporous Elements in Microfluidic Devices

**Investigation of the fluidic properties of nanoporous VACNT structures**

Additional research efforts should be placed on further investigating the fluidic properties
of nanoporous VACNT forests beyond what was discussed in this work. As an example, properties such as tortuosity and fluidic drag [102] should be investigated and incorporated in future designs. A more exhaustive literature database on porous microfluidic and macroscopic materials should also be developed, which should identify additional key properties/parameters that need to be taken into account for future designs.

**Optimize control over VACNT forest morphology**

The possibility to tailor the permeability of VACNT elements by controlling both material (catalyst thickness) and CNT growth process (pre-treatment time) parameters was demonstrated in Section 3.4.3. However, the methods presented in this work allow control solely over the average properties of VACNT elements, and they do not enable large modifications in forest morphology (e.g., modification of intra-CNT spacing using our approach is limited to approximately ±10 μm). Techniques such as nanophotolithography [115] and mechanical densification of VACNT forests [116] should therefore be explored, as they may enable larger (and possibly deterministic) control over CNT diameter, intra-CNT spacing, and VACNT feature alignment. These properties were in fact demonstrated to determine the permeability of VACNT elements, thus constituting important design parameters that can be used to manipulate the fluid accessibility of nanoporous elements.

**Incorporation of aerodynamic considerations in future devices**

From a design perspective, additional geometrical layouts should be investigated for the functional nanoporous elements. In this thesis work, element layout was largely limited to cylindrical and rectangular geometries that mimicked extant solid designs. Incorporation of, e.g., aerodynamics considerations in microfluidic designs should however be pursued, as this could yield significant enhancements in both flow efficiency and bioparticle manipulation. A device example that uses an hydrofoil VACNT element to manipulate cell-like particle was presented in Figure 3-25.

**Control of forest morphology through CNT surface modification**
The vast literature on chemical and physical functionalization of CNTs represents an opportunity for further device tailoring and extension of functionality.

**Specific device designs and CNT sensors**

Future work also includes the exploration of a larger application spectrum for the CNT technology including, e.g., CTC isolation in whole blood using nanoporous designs. Next to this, the use of CNT elements as sensors should also be pursued, exploring the transition from nanoporous microfluidic elements to CNT sensing elements (e.g., electrodes) that could eliminate, e.g., the need for optical interpretation of the assay results.

To conclude, in this thesis we presented seminal work in two different areas: 3D MEMS and VACNT-based nanoporous microfluidic platforms. Both approaches have the potential to significantly enhance the capabilities and performance of current microsystem technologies, and are therefore attractive for uses in sectors and applications beyond those addressed in this work.
Bibliography


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Appendix A

Effective Properties of Multi-Layered Films

Modeling of composite materials to obtain effective properties is a common practice in a variety of fields. For instance, reinforced concretes are typically treated as homogenous materials in civil applications [117], and a related approach is usually adopted in the aerospace field to model advanced laminated composite materials [59]. We consider the layered beam of Figure 2-16(a) (length \( L \), width \( b \), and thickness \( H \)), formed by a total of \( n \) isotropic material layers. Each material layer is characterized by thickness \( h_i \), Young's modulus \( E_i \). The extensional and bending moduli for this structure are given by [59]:

\[
\begin{align*}
\bar{E}A &= \sum_{i=1}^{n} E_i A_i \quad (A.1) \\
\bar{E}I &= \sum_{i=1}^{n} E_i I_i = \sum_{i=1}^{n} E_i (I_i + A_i d_i^2) \quad (A.2)
\end{align*}
\]

where \( A_i = bh_i, \ I_i = bh_i^3/12 \), and \( d_i \) is the distance of the centroid of the \( i^{th} \) layer \( (z_{c,i}) \) from the centroid of the whole beam cross section \( (z_c) \):

\[
d_i = z_{c,i} - z_c = z_{c,i} - \frac{\sum_{i=1}^{n} z_{c,i} E_i A_i}{\sum_{i=1}^{n} E_i A_i} \quad (A.3)
\]

Assuming that the equivalent, homogeneous structure (see Figure 2-16(b)) has the same length
and width \((b)\) as the original layered beam, and that it is characterized by thickness \(\bar{h}\) and Young's modulus \(\overline{E}\), (A.1)-(A.2) lead to:

\[
\begin{align*}
\overline{Eb\bar{h}} &= \overline{EA} \\
\overline{Eb\bar{h}^3}/12 &= \overline{EI} \\
\Rightarrow \quad \overline{E} &= \frac{\overline{EA}}{b} \sqrt{\frac{\overline{EA}}{12\overline{EI}}} 
\end{align*}
\]

(A.4)

Equations (A.4) convert the layered cross-section properties \(\overline{EA}\) and \(\overline{EI}\) into equivalent \(\overline{E}, \bar{h}\). In Table A.1 we summarize the geometrical and material properties for the CMOS layered structures of this work:

Table A.1: Overview of the geometrical and material properties for the layered, thin-film CMOS materials analyzed in this work. \(\overline{EA}\) and \(\overline{EI}\) are computed from foundry-provided values for layer thicknesses and moduli.

<table>
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<th>(H)</th>
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<th>(\overline{E})</th>
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</thead>
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</tbody>
</table>

Note that Equations (A.1) to (A.4) hold for both beams and plates. Computation of \(\overline{EA}\) and \(\overline{EI}\) in (A.1) should therefore be performed based on the structural model under consideration. For example, when \(\overline{EA}\) and \(\overline{EI}\) are computed from plate values, \(E_i\) is replaced with \(E_i/(1-\nu_i^2)\), where \(\nu_i\) is the Poisson ratio of layer \(i\) and \(E_i/(1-\nu_i^2)\) is known as the plate bending modulus [118].
Appendix B

Test Structures Post-Release Deformation:

Experimental Results

In Table B.1 we present a summary of the experimental measurements for the post-release deformation of the test structures analyzed in this work. The out-of-plane displacement at locations \( x = \{L/6, L/3, L/2\} \) along the microbridge test structures’ length (Figure 2-23(a)) and the cantilevers’ radius of curvature (\( R \); see Figure 2-23(b)) are provided, respectively. All measurements were performed using non-contact profilometry (Zygo) as discussed in Section 2.4. .
Table B.1: Overview of test structure measurements for the CMOS layered thin-films of this work (b=40μm, h=3.3μm; ± indicates 1σ level).

### Polysilicon/dielectric bilayer

<table>
<thead>
<tr>
<th>Test structure type</th>
<th>Population size</th>
<th>Beam length</th>
<th>w(L/6)</th>
<th>w(L/3)</th>
<th>w(L/2)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[-]</td>
<td>[μm]</td>
<td>[μm]</td>
<td>[μm]</td>
<td>[μm]</td>
<td>[mm]</td>
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<tr>
<td>Microbridge</td>
<td>10</td>
<td>200±4.3</td>
<td>1.13±0.18</td>
<td>1.62±0.21</td>
<td>2.21±0.28</td>
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<tr>
<td></td>
<td>30</td>
<td>400±4.1</td>
<td>1.41±0.17</td>
<td>3.56±0.16</td>
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<tr>
<td></td>
<td>10</td>
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<td>1.72±0.19</td>
<td>4.23±0.27</td>
<td>6.27±0.26</td>
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</tr>
<tr>
<td>Cantilever</td>
<td>30</td>
<td>300±4.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12.26±1.01</td>
</tr>
</tbody>
</table>

### Dielectric bilayer/ILD/Oxide

<table>
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<th>Test structure type</th>
<th>Population size</th>
<th>Beam length</th>
<th>w(L/6)</th>
<th>w(L/3)</th>
<th>w(L/2)</th>
<th>R</th>
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<td>[-]</td>
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<tr>
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<td>3.89±0.22</td>
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<td>12.12±0.97</td>
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</table>

### Al/Poly/Dielectric bilayer

<table>
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<th>w(L/6)</th>
<th>w(L/3)</th>
<th>w(L/2)</th>
<th>R</th>
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<td>[μm]</td>
<td>[μm]</td>
<td>[μm]</td>
<td>[mm]</td>
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<tr>
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<td>2.81±0.21</td>
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<tr>
<td>Cantilever</td>
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<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>

### Al/Dielectric bilayer

<table>
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<tr>
<th>Test structure type</th>
<th>Population size</th>
<th>Beam length</th>
<th>w(L/6)</th>
<th>w(L/3)</th>
<th>w(L/2)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[-]</td>
<td>[μm]</td>
<td>[μm]</td>
<td>[μm]</td>
<td>[μm]</td>
<td>[mm]</td>
</tr>
<tr>
<td>Microbridge</td>
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<td>200±4.1</td>
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<td>-0.75±0.24</td>
<td>-1.01±0.28</td>
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<td>-1.66±0.24</td>
<td>-2.09±0.25</td>
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</tr>
<tr>
<td></td>
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<td>600±4.8</td>
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</table>
Appendix C

Governing Equations for the Post-Release Deformation of Micromachined Layered Structures Subjected to Residual Stresses

Figure C-1: Model of microbridge subjected to transverse distributed load per unit length $q$ and mean and gradient residual stresses $(\sigma_{\text{mean}}, \sigma_{\text{grad}})$, including key model inputs.

We consider the isotropic beam of Figure C-1, characterized by length $L$, width $b$, thickness $h$, effective Young's modulus $\bar{E}$, effective axial and bending moduli $\bar{EA}$ and $\bar{EI}$, and subjected to a transverse distributed load per unit length $q$ and to residual stresses in the form:

$$\sigma_{\text{residual}(z)} = \sigma_{\text{mean}} + \sigma_{\text{grad}} \frac{z}{h}$$

(C.1)

1As discussed in Appendix A, the model herein holds for both beams and plates. Computation of the structure's effective properties should therefore be performed based on the structural model under consideration.
Figure C-2: Loads and moments acting on a generic cross-section at location x for the structure of Figure C-1. The differential element has length dx and thickness dz.

We assume that the deformations occur in the x-z plane, and that this plane coincides with a principal axis of the beam's cross-section. We further assume that the out-of-plane (z-axis) deflections - \(|w(x)| - are much smaller than L, and that the beam thickness is significantly smaller than its radius of curvature [12,60,118]. Under these conditions, the equilibrium, strain-displacement and constitutive relations are given by [60] (see also Figure C-2):

**EQUILIBRIUM:**
\[
\begin{align*}
\sum F_z &= 0 \Rightarrow \frac{dS(x)}{dx} = -q(x) + \frac{d}{dx} \left( N(x) \frac{dw(x)}{dx} \right) \\
\sum M_0 &= 0 \Rightarrow S(x) = \frac{dM(x)}{dx}
\end{align*}
\]  
(C.2)

**STRAIN–DISPLACEMENT:**
\[
\varepsilon(x, z) = \frac{du(x)}{dx} - z \frac{d^2 w}{dx^2} + \frac{1}{2} \left( \frac{dw(x)}{dx} \right)^2
\]
(C.3)

**CONSTITUTIVE:**
\[
\varepsilon(x, z) = \frac{\sigma(x, z)}{E} + \varepsilon_{\text{residual}}(z) = \frac{\sigma(x, z)}{E} + \frac{\sigma_{\text{residual}}(z)}{E}
\]
(C.4)
where $\varepsilon_{\text{residual}}$ is the strain due the residual stresses in the structure\(^2\). Plugging (C.3) in (C.4), the following expression for the stress inside the structure is obtained:

$$
\sigma(x, z) = -E \left\{ \frac{d u(x)}{d x} - z \frac{d^2 w(x)}{d x^2} + \frac{1}{2} \left( \frac{d w(x)}{d x} \right)^2 \right\} - \sigma_{\text{residual}}(x)
$$

(C.5)

Given the equilibrium, stress-strain, and constitutive relations above, the axial force inside the structure - $N(x)$ - can be computed as:

$$
N(x) = -P = \int_{-h/2}^{h/2} \sigma(x, z) b dz = \frac{EA}{E} \left\{ \frac{d u(x)}{d x} + \frac{1}{2} \left( \frac{d w(x)}{d x} \right)^2 \right\} - A\sigma_{\text{mean}}
$$

(C.6)

where $P$ is the (assumed constant) axial force inside the beam. Integrating (C.6) over the beam length, and remembering that the beam boundaries are immovable in-plane (i.e., $u(0) = u(L) = 0$), we obtain:

$$
P = -N(x) = A\sigma_{\text{mean}} - \frac{EA}{2L} \int_0^L \left( \frac{d w(x)}{d x} \right)^2 dx
$$

(C.7)

Using a similar procedure, the moment - $M(x)$ - can be computed as:

$$
M(x) = -\int_{-h/2}^{h/2} \sigma(x, z) b z dz = \frac{EI}{h} \frac{d^2 w(x)}{d x^2} + \frac{I}{h} \sigma_{\text{grad}}
$$

(C.8)

Finally, combining the two equilibrium equations - (C.2) - and using the resulting relation in (C.8), the following non-linear governing equation can be obtained:

$$
\frac{E I}{h} \frac{d^4 w(x)}{d x^4} + \left[ A \sigma_{\text{mean}} - \frac{EA}{2L} \int_0^L \left( \frac{d w(x)}{d x} \right)^2 dx \right] \frac{d^2 w(x)}{d x^2} = -q(x)
$$

(C.9)

Equation (C.9) can be solved by combining it with the boundary condition equations for the

\(^2\)Note that residual stresses are conceptually similar to “thermal stresses”, in that they both arise only when the structure is constrained. Thermal mismatch between the substrate and the thin films is one of the main sources of residual stresses in micromachined structures. The reader is referred to, e.g., [119] and [60] for a thorough review of the effects of thermal loads on both MEMS and large-scale aerospace structures.
problem under consideration and by solving the resulting system of nonlinear equations. A solution example is provided in Section 2.3.1, where we analyze the problem of a microbridge structure that is constrained at both its ends by torsional springs and that is subjected to residual stress loading in the form of Equation (C.1) (transverse loading, \( q \), is not considered in this example). Note that solution of (C.9) requires the assumption of a post-release shape for the structure, and in this work a symmetric, sinusoidal shape was assumed for the CMOS microbridge (Section 2.3.1 and specifically Equation (2.13)). Depending on the application, the post-release shape could also be assumed as the combination of multiple shapes (e.g., a symmetric shape plus an antisymmetric shape), although such a formulation would require solution using, e.g., energy-based approaches [12]. Incorporation of asymmetric deformation shapes in the solution is relevant, e.g., when transverse loads are considered, as transverse loads could cause structural instability via either bifurcation or limit-point buckling. Finally, using (C.7) and (C.8) in (C.5), the stress inside the beam can be expressed in the following, well-known [118] form:

\[
\sigma(x, z) = \frac{P}{A} - \frac{M(x)z}{I}
\]