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OBSERVATION OF ANALYTE-INDUCED DEFLECTIONS FOR UNCOATED MICROCANTILEVERS USING THE FOCUSED ION BEAM PROCEDURE

A Thesis
Presented for the
Master of Science Degree
The University of Tennessee, Knoxville

Jacques Stephan Stacco
May 2008
DEDICATION

To the creator and to my parents Carolle Murad and Lesly Stacco, I dedicate this thesis to you in light that I am because of your love.

To my family, I dedicate this thesis to you in light that I have become more because of your love.

To Brigit Rivera, I dedicate this thesis to you in light that I saw beyond my potential because of your love.

To Michelle Nored, I dedicate this thesis to you in light that I manifested my inspirations because of your love.
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ABSTRACT

It has been found that structural modifications, involving the creation of submicron scale grooves on uncoated silicon nitride microcantilevers, allow microcantilevers to display analyte-induced deflections which have not been previously observed. The submicron grooves were created through the use of a focused ion beam procedure to mill deep and narrow grooves without the subsequent deposition of a chemically reactive coating. These modifications significantly increase (by approximately 400%) an uncoated microcantilever’s ability detect analytes such as water vapor, ethyl alcohol, acetone vapor, argon, and 1-monorotolune. The intention of the experiment was to achieve greater microcantilever deflections by increasing an uncoated microcantilever’s surface energy and surface area through the least amount of surface modifications. Accordingly, one to three grooves with a depth greater than the thickness of the microcantilevers were achieved by milling the grooves at a maximum angle of 45 degrees. One microcantilever, with a 100 nm wide groove (milled at an angle of 45 degrees relative to the surface normal and to a depth of 1.3 micrometers) deflected by 400 nm in the presence of an argon-ethanol mixture. The same microcantilever also exhibited a deflection magnitude which increased with gas concentration. When comparing the set of milled microcantilevers used in this experiment, deflections were found to increase as the width of the grooves decreased and the depth and number of grooves increased.
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1.1 Preparing for Nanotechnology

The development of electronic devices is presently adhering to a trend of miniaturization. The prefix “nano,” which represents the minute number $10^{-9}$, can be found in commercial advertisements as a keyword used to associate novel consumer products with ones conception of advanced technology. The introduction of the term “nano” into mainstream parlance heralds, to the consciousness of a mainstream audience, the arrival of a technological era ushered in by the availability of smart materials harvested from the agriculture of individual atoms into arrays of molecular devices called nanomachines.

The present state of the art finds itself at the archetypal stage of its ability to harness the nuances of individual atoms into these heralded nanostructures. Today, researchers are able to image, pick up, and move individual atoms using Scanning Tunneling Microscopes (STM) and Atomic Force Microscopes (AFM) [1, 2]. During the process of refining the AFM’s susceptibility to thermal and viscous influences from its environment, the AFM’s silicon microcantilever probe was observed to deflect in a predictable manner to these external factors. Thus in the early 1990’s, the AFM’s microcantilever was modified to produce a new genre of silicon based sensors, several hundred micrometers $(10^{-6} \text{ m})$ in length, called microcantilever (MC) sensors [3, 4].
Presently, microcantilever sensors are in the prototypical stage of their introduction into electronic devices. The integration of microcantilever sensors into microprocessors will provide an investigator with a hand-held electronic device which will be able to discern the identity of minute quantities of organic and inorganic compounds. A microcantilever sensor may be modeled as a one-dimensional mechanical oscillator with one fixed end characterized by a resonant frequency, spring constant, and mass [1]. The reduction of a cantilever’s length to less than several hundred nanometers (10^{-9} m) produces nanocantilevers, which display resonant frequencies in the megahertz range (10^6 Hz). At these frequencies, nanocantilevers will be able to detect masses smaller than 10^{-21} g [5].

Following the trend of device miniaturization, the goal of detecting a single molecule has motivated the development of nanocantilevers with resonance frequencies in the terahertz (10^{12} Hz) range as can be seen in figure 1 [3]. By monitoring chemical reactions between individual molecules, nanocantilevers will shed light onto the nuances of real-time chemical bonding mechanisms. Ultimately, it is projected that individual molecules will function as cantilever sensors. In understanding these aforementioned mechanisms, the template for the assembly of individual atoms into nanomachines will have been formed.

1.2 Hypothesis

It is believed that analyte-induced deflections of uncoated microcantilevers will increase with the depth of the grooves, by creating narrow grooves, and with the number of milled grooves.
Reducing the scale of cantilever sensors increases their resonant frequency and allows smaller particles to be detected. In the terahertz range microcantilevers display energies commensurate with large molecules.

**Figure 1**
This thesis will discuss the observation of analyte-induced deflections for uncoated silicon nitride microcantilevers which have been modified by using a focused ion beam (FIB) procedure to mill a small number of grooves into one side of the microcantilevers. Deflections were induced by exposing the milled microcantilevers to analytes including water vapor, air, ethanol, acetone, argon, and 1-mononitrotoluene. Analyte-induced deflections, of magnitudes which have not been previously observed were measured. In describing the mechanisms of analyte-induced deflections, the atomic origins of microcantilever surface expansion, surface-to-volume ratio, surface energy, and differential surface stress between the milled and unmilled sides of the microcantilever will be discussed. Upon analyzing the experimental results, the magnitude of microcantilever deflections are discussed in terms of the geometric parameters of the milled grooves, which are groove depth, width, and number of milled grooves.

1.3 Objective

This thesis reports on a method which allows uncoated microcantilevers to display a response, in the form of an analyte-induced deflection, when exposed to analytes such as water vapor, acetone vapor, and argon. Uncoated microcantilevers are comprised of a silicon nitride surface. In 2000 Betts et al. observed that uncoated microcantilevers produced no analyte-induced deflections [4]. In 2004 Pinnaduwage et al. were able to use uncoated microcantilevers to detect analytes through analyte-induced resonance frequency shifts [6].
In the experiments regarding this thesis, the Focused Ion Beam (FIB) milling procedure was used to mill deep and narrow grooves onto one of the uncoated microcantilever’s sides, prior to the introduction of the analytes [7] (see figures 2 and 3). The focused ion beam procedure uses ions focused through lenses to mill the surface of submicron samples, which are placed on a stage in a high vacuum chamber [8]. The presence of milled grooves on one of the microcantilever’s side’s created differential surface stress between the milled and unmilled sides. As the analytes adsorbed onto both sides of the uncoated microcantilever, the differential surface stress between the milled and unmilled sides resulted in the analyte-induced deflection of the uncoated microcantilever.

For an atomically pure surface under ultra high vacuum conditions (UHV) conditions, surface energy (and thus surface stress) is increased by the presence of dangling bonds which exist due to the absence of molecules above the surface [9, 10]. The dangling bonds increase surface energy by attracting surface atoms closer towards one another and reducing the interatomic spacing between surface atoms. In the ideal case of an atomically pure microcantilever surface (under UHV), the focused ion beam milling process creates a differential surface stress through the removal of bulk and surface atoms on the milled side. The removal of bulk and surface atoms increases surface area and exposes additional dangling bonds to the surface. The newly exposed dangling bonds will attract the surface atoms closer towards one another. The reduction of the interatomic spacing between the microcantilever’s surface atoms will subsequently increase the surface stress on the milled side, resulting in a differential surface stress between the milled and unmilled sides.
Figure 2 A microcantilever array. Each microcantilever is 400μm long, 100 μm wide and 1 μm thick.
Figure 3 A close-up view of a milled microcantilever. One groove was milled into the upper surface of the microcantilever. The width of the groove near the microcantilever’s lower surface was estimated to be 100 nm. In considering the cross-section of the milled grooves (where the surface of the groove wall was defined by a line rather than a two-dimensional area) and looking at the right wall of the milled groove, it was noticed that the surface of the groove wall was defined by a white line which extended about 300 nm into the groove. It was then assumed that the left wall of the milled groove also extended about 300 nm into the groove. Because the groove wall extended into the groove, when looking at the width of the groove near the base of the microcantilever, the actual groove width was assumed to be commensurate to the width of the shaded region between the two white walls. From the micron bar, the width of the shaded region and thus the width of the groove was estimated to be about 100 nm.
In the case of microcantilevers which are exposed to air, as in this experiment, the microcantilever’s dangling bonds are occupied by the atoms of a silicon oxide layer, and thus do not participate in the creation of a differential surface stress. In this case, the milling process creates a differential surface stress between the milled and unmilled sides, mainly by increasing the surface area (and thus the surface stress) on the milled side. Upon the creation of a differential surface stress, the milled and unmilled sides expanded at different rates upon analyte adsorption, resulting in measurable microcantilever deflections.

The response to the added mass of the adsorbed analytes onto the microcantilever’s surface is the mechanism by which uncoated microcantilevers have previously been utilized in order to detect analytes through resonance frequency shifts measurements. Analyte-induced deflections and resonance frequency shifts both rely on the adsorption of the analytes onto the microcantilever. In most experiments, a receptive coating is deposited onto one of the microcantilever’s sides in order to allow a selected analyte to adsorb onto the microcantilever. Therefore, it has been observed that a microcantilever’s selectivity to a particular analyte depends on the analyte receptive coating being used.

Along with providing an area for analyte adsorption, the deposition of a coating on one of the microcantilever’s sides produces differential surface stress between the microcantilever’s two sides which allows the microcantilever to deflect in the presence of analytes. We find that the production of a differential surface stress, on coated or
uncoated microcantilevers, is the greatest contributing factor which allows microcantilever’s to deflect in the presence of analytes.

In an effort to understand the other factors that affect the sensory and deflection responses of microcantilevers, this experiment monitored the responses of uncoated microcantilevers to a variety of analytes. With regard to the uncoated microcantilevers milled using the FIB procedure, analyte adsorption occurs due to several reasons. On the unmilled side, analyte adsorption resulted from van der Waals forces which induced attracting dipoles within the analyte and surface atoms. The attracting dipoles resulted in reversible analyte adsorption, or physisorption, onto the microcantilever’s unmilled surface. On the milled side, along with van der Waals forces, the increased surface area created by the milling process produced an excess surface energy due to the removal of bulk and surface atoms. As a result, analytes spontaneously adsorbed onto the milled side in order to minimize the excess surface energy.

Previously, analyte receptive coatings such as gold, polymeric films and gelatin [11] were used to detect analytes at concentrations as low as 50 parts-per-billion (ppb) [3]. Using a more intricate trimaterial coating, comprised of a silicon nitride substrate, a gold coating and a calixarene coating, Lavrick et al. were able to detect analytes at concentrations as low as 520 ppt (parts-per-trillion) [12]. By depositing an analyte receptive coating onto a microcantilever, which has initially been physically modified with nanoscale grooves, further increase in microcantilever sensitivity is predicted, see section 2.2.
1.4 MEMS Devices

Microcantilevers form a subset of a group of microscopic devices developed in the 1980’s referred to as Micro-Electro-Mechanical-Systems, (MEMS). The dimensions of these devices range from 1 mm to 100 μm. MEMS devices convert electrical, mechanical, and optical stimuli into mechanical deformations and vibrational changes, which are subsequently converted into electronic signals [13-21]. MEMS transducers are used in detecting gases, infra-red photons [22-29], small mechanical forces [30-33], and electric charges [34-37], and are found in optical and thermal imaging [38, 39], data storage [40, 41], and in telecommunications applications [42, 43]. Depending on the particular measurements being taken, MEMS shapes may be quite intricate.

Microcantilevers, on the other hand, have the relatively simple shape of a diving board, and are operationally distinguishable from other MEMS devices by the fact that while both microcantilevers and other MEMS share the ability to respond to chemical and biological stimuli through resonance frequency shifts, microcantilevers display the added ability to respond to stimuli through induced deflections [40, 45]. Microcantilevers are able to simultaneously provide deflection and resonance frequency shift measurements [46]. Microcantilevers are found to be lighter and to display faster signal response times [15] when compared with relatively larger MEMS sensors, such as quartz crystal microbalances (QCM) [47, 48], and surface acoustic wave devices [49-53]. Microcantilever deflections in the range of $10^{-6}$ m to $10^{-12}$ m have been measured for a wide range of analytes in aqueous, gaseous, and vacuous environments [3, 54-57].
There are many fields that will benefit from the development of microcantilever sensors. The ability to detect analytes in both the air and in a solution makes microcantilevers ideal for biological, medical, and environmental research [46]. Being silicon based, microcantilevers are able to be integrated into microprocessors [58-61]. Currently, microcantilever arrays are being combined with artificial neural networks (ANN) in order to develop electronic noses (olfactory mimicking) [62, 63] and electronic tongues (gustatory mimicking) [64], which will be able to detect a variety of analytes through their unique molecular signatures.

1.5 Properties of Micro-Scale Sensors

As a device’s size is decreased from 1 millimeter to 1 micrometer along one of its dimensions, the device’s surface-to-volume ratio increases by a factor of one thousand. This implies that surface dependent forces, such as surface stress, become a thousand times larger than volume dependent forces, such as inertial and electromagnetic forces [65].

A microcantilever is a leaf spring device with a thickness, of 1 μm or less, that is much smaller than its length or width. As a result, microcantilevers exhibit large surface-to-volume ratios and surface stresses [67]. It is their large surface to volume ratio which allows microcantilevers to synergize nanoscale surface effects into measurable deflections [68, 69].
By milling deep narrow grooves with FIB on one side of an uncoated microcantilever, analyte induced deflections arise as a result of two complementing factors. First, a differential surface stress is created between the milled and unmilled sides. Second, the microcantilever’s surface-to-volume ratio is increased. Both of these factors contribute to microcantilever deflection by increasing the microcantilever’s surface energy and surface stress prior to analyte adsorption. With a heightened surface stress, the microcantilever is more readily able to deflect upon analyte adsorption. In chapter 5 of this thesis, it is shown (through graphs which plot microcantilever deflection versus time) that the marked increase in differential surface stress for a milled microcantilever is large enough to convert nanoscale surface forces due to analyte interactions into measurable deflections.

The experiment regarding this thesis milled one to three grooves into eleven microcantilevers. It was found that the microcantilever with the narrowest groove, 100 nm in width, displayed the largest deflections which ranged between 100 nm to 400 nm for water vapor, acetone, ethanol, argon, 1-mononitrotoluene and combinations of these analytes. The other ten microcantilevers, (including one which had up to sixty shallow grooves with wider dimensions) displayed deflections less than 100 nm for all analytes.

Using a focused ion beam procedure to mill a large number of 800 nm wide grooves into a microcantilever, which was subsequently coated with an organic film, Headrick et al. [67] also reported on the production of 400 nm deflections. As a result, one is led to consider that grooves with widths around 100 nm or less allow uncoated microcantilevers
to produce deflections which are comparable to the deflections of coated microcantilevers. In applications, deflections larger than 100 nm are required in order to clearly distinguish an analyte signal from background noise, therefore it is conclusive that deflections were analyte-induce rather noise related [3].
CHAPTER 2 REVIEW OF LITERATURE

2.1 Historical Framework

Two of the most notable analytical models in the study of mechanical deformations in plates and in elastic beams which led to the development of MEMS transducers were developed by G. Gerald Stoney [70] in 1909 and Stephen Timoshenko [71] in 1940. In 1924, Meehan observed the reversible expansion of yellow pine charcoal upon the adsorption of carbon dioxide [72], while in 1954 Yates observed a similar reversible expansion for a porous glass substrate upon the adsorption of various nonpolar gases [73]. One of the first measurements involving microcantilevers as chemical sensors was performed by Thundat, using gold coated microcantilevers to detect mercury vapors [74].

Observing that the majority of a microcantilever’s flexion occurs at its base, it was concluded that a microcantilever’s spring constant is largely defined at its base. The mechanisms of analyte adsorption onto an uncoated microcantilever were described by Pinnaduwage et al. in an experiment where Trinitrotoluene was deposited in pulses of varied durations onto a silicon microcantilever [75, 6]. Islands of Trinitrotoluene adsorbates were observed to form on the uncoated microcantilever (see figure 4). Pinnaduwage stated that because the experiment was performed in air, oxidation of the silicon surface formed a 1.5-1.7 nm silicon oxide (SiO₂) layer prior to adsorption [76].
Figure 4 Atomic force microscope image of TNT samples deposited on a silicon substrate for various durations. (a) 50 sec, (b) 100 sec, (c) 300 sec, (d) 400 sec. The number of islands initially increases, while the height of the islands remains constant. Over longer exposures, the number of islands remains constant, while the height of the islands increases.
With regard to this thesis, all microcantilever deflection experiments were performed under ambient conditions, thus it is assumed that a SiO$_2$ layer with hydroxyl groups residing on the surface and in the oxide film [77] were present on the surface of the milled microcantilevers during the experiment. The sole contribution of the SiO$_2$ layer to the deflection of the milled microcantilevers is assumed to be negligible, based of prior experiments with uncoated, unmilled microcantilevers in ambient conditions. It is assumed that a SiO$_2$ layer was also present on these uncoated microcantilevers, yet the uncoated, unmilled microcantilevers displayed no analyte-induced deflections [4]. In the case of the milled microcantilevers used in this thesis, the combination of the silicon oxide layer within the narrow grooves of the milled microcantilever is thought to have led to large capillary forces between the microcantilever and the analytes within the groove, which in turn lead to large analyte-induced deflections. The large capillary forces arise from the microcantilever surface becoming very hydrophilic (adsorbing water from the air) due to the presence of hydroxyl groups on the SiO$_2$ layer [77, 78]. It was noted that water molecules in the air acted as a force of attraction between the oxygen atoms in the microcantilever’s SiO$_2$ layer and the oxygen atoms in the TNT molecules. It was therefore concluded by Pinnaduwage that the presence of water vapor greatly influences the analyte-to-surface and analyte-to-analyte interactions. [6].

### 2.2 Reference Experiments

In 2003, Headrick et al. [67] used the focused ion beam (FIB) method to mill approximately 80 grooves along the width of two microcantilevers.
The depth of the grooves was milled to 200 nm for the first microcantilever, and 400 nm for the second microcantilever. The width of the grooves was 800 nm wide for both microcantilevers, as seen in figure 5.

In one experiment, milled microcantilevers were coated with a thick permeable organic film in order to detect 2, 3-dihydroxynaphthalene (2, 3-DNH) [67]. It was reported that the microcantilevers’ analyte-induced deflections increased with the depth of the grooves, due to the reduction of the microcantilever’s spring constant.

From figure 6 we are able to compare the deflections of an unmilled microcantilever to the deflections of a milled microcantilever with 200 nm deep grooves, and a milled microcantilever with 400 nm deep grooves, upon exposure to 2, 3-DNH at concentrations ranging from 1000 to 25 ppm. For the microcantilever with the 400 nm deep grooves, the magnitude of the microcantilever deflection was observed to be 400 nm. In the case of the milled microcantilevers used in this thesis, a 400 nm deflection was also observed for a microcantilever with one milled groove, 1300 nm deep and with a minimum width of 100 nm. This shows that milling one deep and narrow groove into an uncoated microcantilever produces deflections comparable to a coated microcantilever with 80 shallow grooves. Upon depositing a permeable coating onto the microcantilevers with the 80 grooves, the interlocking interface between the grooves and the receptive coating was found to increase the efficiency with which analyte induced swelling of the
Figure 5  A milled microcantilever with 800nm wide and 400 nm deep grooves. [67]
Figure 6  The deflection of a modified microcantilever upon exposure to 2,3-DNH at concentrations ranging from 1000 ppm to 25 ppm. (A) Unmilled, (B) 200 nm deep grooves, (C) 400 nm deep grooves. [67]
permeable coating was transferred to the microcantilever’s surface, further increasing the microcantilever’s deflection. A sevenfold increase in sensitivity was also reported upon thinning the microcantilever with the 400 nm deep grooves.

It has been previously noted by Jensenius et al. [80] that microcantilever deflections depend on the analyte’s rate of evaporation. Jensenius et al. noted that polymer coated microcantilevers reacted identically to different alcohols, and only monitored the concentration of the alcohols. An example of the dependence of microcantilever deflection on analyte concentration can be seen in figure 7, where a gold coated microcantilever’s deflection is shown to increase linearly with the concentration of 2-mercaptoethanol [45, 81].

2.3 Rational for Pursuing Research

The benefits and efficacy of micro and nanocantilever sensors upon applications which monitor and remediate adverse chemical effects to the health of our environment, and its biological organisms, will manifest from the orders of magnitude increase in analyte sensing capabilities. By singularly depositing a variety of semi selective coatings onto individual microcantilever elements of an array, and connecting analyte response signals from the microcantilever array to pattern recognition software such as artificial neural networks (ANN) [81-86], electronic noses are currently being developed.
Figure 7 Microcantilever deflection as a function of the concentration of 2-mercaptoethanol. [45]
which will be able to identify of multiple species of analytes in a gas mixture. Electronic noses have been reported to discern between alcohol mixtures and natural flavors [5].

The implementation electronic noses will require the design of numerous pattern recognition algorithms in order to accommodate quantitative and qualitative requirements such as high identification accuracy, fast identification time, simple training algorithms, and low memory requirements [87]. The use of these electronic noses is one of the key components for the fruitful implementation of these sensors in our environment.

Another component of the implementation of microcantilevers in our environment is the use of nanostructured coatings, which are analyte receptive coatings that have nanoscale crevices. Using microcantilevers with nanostructured coatings, researchers are able to produce deflections which are as much as three orders of magnitude higher than smooth coated microcantilevers. The development microcantilever sensor capabilities which utilized nanostructured coatings and artificial neural networks (ANN), will provide more effective methods of converting weak chemical stimuli from biological organisms [88-91], volatile organic compounds [92-96], heavy metals [95, 98], and sulfurs [45] into measurable signals [99-101].

The optimization of microcantilever sensing capabilities for specific analytical applications encompasses numerous parameters, which are still in the prototypical stages of development. The basic sensing parameters which require optimization are sensitivity, selectivity, linearity in signal response, repeatability, the identification of the most
sensitive coating and the most effective microcantilever design. The analytical aspects which require optimization include readout mechanisms, noise reduction, and the development of signal processing algorithms, such as artificial neural networks [5, 82].

### 2.4 Challenges to Microcantilever Implementation

Current models for microcantilever deflections are projections of the behavior of macro scale phenomena into the micro scale. The quantification of a microcantilever’s deflection is based on Stoney’s equation (see section 3.4), which initially described the deflection of a millimeter scale metal film. This model does not account for nanoscale morphology or the mechanisms of analyte induced stresses.

Along with developing a more accurate model of microcantilever deflection, the implementation of microcantilever sensors will require the optimization of microcantilever sensors, the development of proper analyte delivery systems, the ability to package the sensors and their read out components onto a single microprocessor, and the development of pertinent computer-aided designs [5, 44]. Microcantilevers which are introduced into industrial settings will have to be resilient to high frequency acoustic fields and other mechanical impacts present during operation [5].

Due to a microcantilevers diminutive dimensions and mass, a microcantilever is able to withstand high accelerations. Juxtaposed with a microcantilever’s resilience to large accelerations, the optimization of microcantilevers for operation in industrial settings is
achievable. Another challenge faced in the implementation of microcantilever sensors arises from the adsorption of nonspecific analytes, which cause changes in surface stress that can continue for many hours after the initial analyte injection [5, 102].
CHAPTER 3 MICROCANTILEVER OPERATION

3.1 Cantilever Fabrication

Microcantilevers are carved into a single crystal silicon substrate using vapor deposition, photolithographic patterning, and reactive ion etching, as can be seen in figure 8. Fabrication begins with the deposition of an oxide sacrificial layer above a prepatterned substrate, followed by the deposition of structural layer of silicon dioxide, silicon nitride, or polycrystalline silicon [44]. A structural layer then is deposited through low pressure chemical vapor deposition (LPCVD) and plasma enhanced chemical vapor deposition (PECVD) [13], in order to define the microcantilever’s thickness. Microcantilever fabrication is based on the traditional approaches for micromachining solid state electronic devices, producing microcantilevers with dimensions ranging between 100-500 μm long, 20-100 μm wide and 0.2-1 μm thick [5, 103]. The lateral dimensions are defined in most cases through photolithographic patterning of the structural layer.

Reactive ion etching is then applied to remove the sacrificial layer in order to form a free standing rectangular or delta shaped microcantilever [3, 5]. Upon fabricating standard rectangular or delta shaped microcantilevers, the focused ion beam method may be used to modify the microcantilever (see section 4.2), or an analyte receptive coating may be deposited onto the microcantilever through physical vapor deposition.
The steps for fabricating a microcantilever:

1. Substrate patterning and etching
2. Sacrificial layer deposition
3. Planarization
4. Structural layer deposition
5. Structural layer patterning
6. Sacrificial layer removal

- single crystal Si - sacrificial layer - structural layer

**Figure 8** The steps for fabricating a microcantilever: Beginning with a prepatterned substrate, a sacrificial layer is deposited onto the substrate, followed by the deposition of a structural layer. The shape of the microcantilever is defined by photolithography and reactive ion etching.
3.2 Analyte Adsorption

Analyte adsorption results from interfacial forces which include van der Waals, chemical forces, capillary condensation, and electrostatic forces [77]. Lander states that an analyte may interact with a surface in three ways, which are strongly dependent upon coverage [104 page 26]; in the first two, the analyte may be elastically or inelastically scattered off the surface, in the third way, if the analyte remains in contact with the surface long enough, it may come into equilibrium with and adsorb onto the surface. Lander goes on further stating that there are four possible ways for an analyte to adsorb onto a surface [104 page 28]. First, van der Waals forces can cause adsorption by inducing attracting dipoles within the analytes and surface atoms. Second, induction forces in the form of an electric field on the surface of the substrate can attract an analyte’s permanent or induced dipole and cause adsorption. Third, charge-transfer forces can cause adsorption by transferring charge between the analytes and the surface. Fourth, the analytes may covalently bond to the surface.

The first two forces of analyte adsorption referred to above by Lander give rise to relatively weak physical adsorptions, characterized by binding energies less than 0.1 eV. The first and weakest force is a nonspecific intermolecular force which is defined as physisorption [104 page 28]. In physisorption, energetic equilibrium between the analytes and the surface is attained rapidly, and is defined by the mass transfer rate of the gas [105]. Vapor condensation arises due to physisorption, thus the heats of adsorption associated with physisorption are on the same order as the heats of condensation [105,
Since van der Waals forces are relatively weak, physisorption can be reversed by decreasing pressure.

The last two forces of analyte adsorption give rise to stronger chemical adsorptions (or chemisorptions), characterized by binding energies larger than 0.3 eV [3]. In chemisorption, adsorptions are irreversible or reversible with a large input of energy. The energies associated with chemisorption are large enough to induce chemical bonding, and structural changes on the surface of refractory solids, such as metals. Physisorption, on the other hand, is strong enough to cause surface reconstruction of molecular solids such as ice and polymers [105 page 492]. Microcantilevers experience both physisorption and chemisorption [102, 107]. The degree of chemical specificity for chemisorption is much higher than that of physisorption [105]. Along with sensitivity and selectivity, a microcantilever’s ability to regenerate itself at the end of an experiment through analyte desorption defines one of its most important qualities. If there is a large interaction energy between the analytes and the coating, the analytes may not spontaneously desorb at room temperature, requiring the microcantilever to be heated in order to desorb the analytes from its surface [46]. Since microcantilever sensors are comprised of a silicon substrate and a coated layer, a microcantilever is considered to be a bi-material structure whose deflection is susceptible to temperature changes. Because microcantilevers have masses on the order of a few nanograms, they display low thermal masses, thus are able to be ramped from 22 °C to 40 °C within a few milliseconds in order to induce analyte desorption [12, 46, 108]. As analytes exothermically adsorb onto a bi-material cantilever, the heat released is able to induce a deflection. It has been found that
microcantilevers are able to detect analytes more directly through stress induced
deflections, rather than through thermally induced deflections [109, 110].

In the case of the uncoated, milled microcantilevers researched for this thesis, analyte
adsorption onto the uncoated microcantilevers is due to van der Waals forces [105 page
492]. Due to the presence of the micron-scale grooves in ambient conditions, forces
arising from capillary condensation also contributed to changes in the microcantilever’s
surface energy, which in turn affects the magnitude of microcantilever deflections.
Capillary condensation is a process where adsorbed gases condense into a liquid at a
pressure (P) that is less than the saturation pressure of the gas (P^S). Capillary
condensation has been observed to occur at a relative pressure of P/ P^S \approx 0.3 [111]. As
the gases adsorb in the grooves, they are able to condense into a liquid at a lowered
pressure relative to the saturation pressure [112, 113, 114].

Capillary condensation may also be understood in terms of a reduction of the critical
temperature of the gas-liquid phase transition [115, 105]. A decrease in the temperature
at which the gases condense into a liquid are observed to occur within the narrow
grooves, which gives rise to capillary condensation. The driving force behind adsorption
has been sited to be the reduction of surface energy [113]. Capillary condensation has
been observed to lead to decreases in surface energy within pore walls; based on these
observations, capillary condensation was assumed to lead to decreases in surface energy
within the walls of milled grooves [116].
The combination of the reduction of surface energy within the milled grooves due to capillary condensation, and the different rates of expansion of the milled and unmilled sides on the uncoated microcantilevers are assumed to be the main mechanisms which allow the milled, uncoated microcantilevers to display analyte-induced deflections. The widths of the milled grooves ranged between 100 nm to 1 micrometer. Consequently, aside from capillary forces, van der Waals forces between the groove walls and electrostatic forces due to ion milling are also assumed to be present within the milled grooves [77].

In microcantilever sensors, analytes adsorb onto a chemically selective coating through a process of molecular recognition which induces the coating to expand. The resultant expansion establishes a differential surface stress between the coated and uncoated sides of the microcantilever, causing the microcantilever to deflect [117]. The use of an analyte receptive coating provides an area for analyte adsorption and creates a differential surface.

In this experiment, no analyte receptive coating was used. A differential surface stress was achieved by using a focused ion beam (FIB) procedure to mill grooves onto one side of the uncoated microcantilevers. The area for analyte adsorption onto the uncoated microcantilevers was established by the microcantilever’s large surface-to-volume ratio, which makes them more sensitive to analyte adsorption [114, 118]. The fact that the temperature of the analyte vapors was below their critical temperature also contributed to analyte adsorption. Upon adsorption, changes in the analyte’s internal energy and
entropy induced the analyte to convert part or all of its rotational energy into vibrational energy [105 pages 503-504]. At room temperature and atmospheric pressure, the adsorbed analytes are assumed to behave as a two-dimensional gas [104 page 30, 106 page 42]. As coverage is increased, the two-dimensional analyte gas is assumed to condense into a two-dimensional liquid [104 page 29]. Pinnaduwage et al. goes on further in observing the formation of islands after a deposition time of 400 seconds for the deposition of Trinitrotoluene analytes onto an uncoated microcantilever [6].

3.3 Surface Energy and Surface Stress

At the onset this experiment it was assumed that an uncoated microcantilever would be able to deflect upon analyte adsorption, if a large differential surface stress were able to be created between the microcantilever’s two sides. Lavrik et al. noted that larger the initial surface stress on substrate, the larger the change in surface stress will be upon analyte adsorption [3]. As a result, a Focused Ion Beam procedure (under ambient conditions) was used in order to mill deep grooves into one side of an uncoated microcantilever. It was assumed that by milling deep grooves into one of the microcantilever’s sides, a large differential surface stress would be created. This assumption is based on the ability of the FIB procedure to increase of surface energy by increasing the microcantilever’s surface area.

In the general case of a surface under UHV conditions, surface energy arises from the difference in the electronic structure of surface atoms compared to the electronic structure
of atoms within the bulk where atoms are surrounded with neighboring atoms that occupy all available electronic bonds. On the other hand, atoms on the surface reside at the interface between the bulk and the environment and have on average only half of their available bonds occupied by neighboring surface and bulk atoms. The unoccupied (dangling) bonds exert an attractive force between neighboring surface atoms and pull the surface atoms closer together. This compression of the surface atoms increases free surface energy (or Gibbs free energy) and surface stress; where free surface energy is defined as the reversible work per unit area to create a surface [119], and surface stress is defined as the reversible work per unit area to elastically stretch a surface [120, 121]. The excess surface energy allows spontaneous adsorption to occur in order to reduce surface stress [5].

When analytes with a high electronegativity adsorb onto the surface, charge is transferred from the dangling bonds to the analyte, consequently decreasing the attractive force between the surface atoms, reducing surface energy, and finally causing the surface to expand. Adsorption will then continue until free surface energy reaches a minimum value [106]. The accompanying decrease in surface stress is frequently defined as a compressive (negative) stress due to the possibility of the surface returning to its initially compressed state in the absence of the analytes [3, 5, 67, 119]. When analytes with a low electronegativity adsorb onto the surface, charge is transferred from the analyte to the substrate, resulting in an increased surface stress [67, 119]. The increase in surface stress is defined as a tensile (positive) surface stress, causing the surface to expand under its own stress.
The process of milling grooves in ambient conditions on one side of an uncoated microcantilever increases the free surface energy on the microcantilever’s milled side by increasing the surface area on the milled side. Analytes adsorbing onto on the milled side enter a region of higher surface energy, while the analytes on the unmilled side adsorb into a region of lower surface energy. Therefore, the analyte-induced surface expansion on either side of the milled microcantilever will be different causing the microcantilever to deflect [3, 45].

3.4 General Description of Microcantilever Bending Mechanisms

A Microcantilever’s deflection is directly proportional to three factors, the force acting on the microcantilever, the change in free surface energy, and the analyte concentration [46]. Assuming that the microcantilever deflection is much smaller than its length, Shuttleworth’s equation [46, 122], relates a microcantilever’s surface stress to its free surface energy through

\[ \sigma = \gamma + \frac{\partial \gamma}{\partial \varepsilon} \]  

(1)

where \( \sigma \) is the surface stress, \( \gamma \) is the free surface energy, and \( \partial \varepsilon \) is the surface strain defined as the relative change in the surface area, \( \partial \varepsilon = \partial A/A \). In most cases, the surface strain term can be neglected. Therefore, the surface stress is approximately equal to the free surface energy,
Changes in free surface energy are the primary initiators of changes in surface stress \[46\]. The basic mechanisms which lead to microcantilever deflection can be described by considering the temperature-induced bending of a bimetallic strip. In the case of a bimetallic strip formed by fusing two homogenous metallic strips along their length, bending arises due to the two different rates of thermal expansion of the homogenous strips \[123\]. Extrapolating this idea to a microcantilever, the process of coating or milling the top side of a microcantilever establishes a surface energy, \( \gamma_{\text{top}} \), on the top side of the microcantilever, and a surface energy, \( \gamma_{\text{bottom}} \), on the bottom side of the microcantilever. From Shuttleworth’s equation, this difference in surface energy produces a differential surface stress

\[
\delta \sigma = \sigma_{\text{top}} - \sigma_{\text{bottom}} \quad (3)
\]

between the two sides of the microcantilever, where \( \sigma_{\text{top}} \) is the stress on the top surface and \( \sigma_{\text{bottom}} \) is the stress on the bottom surface. In establishing a differential surface stress, the microcantilever’s top and bottom sides will exhibit different rates of expansion when exposed to an analyte, resulting in an analyte induced deflection, as can be seen in figure 9 for a coated microcantilever. In the absence of an analyte, these two stresses balance one another \[45\]. The differential surface stress created by milling grooves on the top side of a microcantilever by focused ion beam milling is expressed as

\[
\delta \sigma_{\text{FIB}} = \sigma_{\text{milled}} - \sigma_{\text{unmilled}} \quad (4)
\]
Figure 9  The process of coating a microcantilever establishes surface stresses $S_1$ on top and $S_2$ on the top and bottom sides of the microcantilever. In the absence of analyte these two stresses balance each other and generate a radial force ($F_r$) which keeps the microcantilever from deflecting. Upon analyte adsorption, the coating expands, and generates a force, $F_z$, which induces the microcantilever to deflect.
where $\sigma_{\text{milled}}$ and $\sigma_{\text{unmilled}}$ represent the surface stresses on the milled and unmilled sides. The sensitivity of a microcantilever is quantified by the magnitude of its deflection. The microcantilever’s deflection can be directly related to its differential surface stress, $\delta\sigma$, using Stoney’s equation

$$z = \frac{3L^2(1-\nu)}{Et^2} \delta\sigma$$  \hspace{1cm} (5)$$

where $z$ is the microcantilever’s deflection, $L$ is the microcantilever’s length, $t$ is its thickness, $E$ is the Young’s modulus for the microcantilever, and $\nu$ is Poisson ratio for the microcantilever [46, 95 101]. Using a focused ion beam to maximize the surface stress ($\sigma_{\text{milled}}$) prior to the deposition of a coating significantly increases a microcantilever’s sensitivity. Expressing the differential surface stress created by analyte adsorption onto a coated microcantilever as $\delta\sigma_c = \sigma_c - \sigma_{si}$, where $\sigma_c$ is the surface stress on the coated side and $\sigma_{si}$ is the surface stress of the uncoated silicon surface [4, 98]; when an analyte receptive coating is deposited onto a microcantilever which has been physically modified with a focused ion beam, the total differential surface stress will be the sum of the differential surface stresses created by the focused ion beam milling and by the coating.

In calculating a microcantilever’s deflection, Stoney’s equation provides an accurate model for smooth coated surfaces or if the coating’s thickness is much smaller than the cantilever’s thickness [5, 69]. In the case of a thinly coated microcantilever, signal amplification implies increasing differential surface stress, increasing the
microcantilever’s length, and decreasing its thickness. The matter of optimizing a microcantilever’s dimensions becomes more complex when the microcantilever is coated with a film that is comparable in thickness to that of the microcantilever.

3.5 Microcantilever Dynamics

From figure 9, we see that, prior to the introduction of an analyte, a microcantilever’s surface stresses \( S_1 \) and \( S_2 \), generate a radial force \( F_r \), which is expressed as

\[
F_r = (S_1 + S_2)L
\]  

(6)

where \( L \) is the microcantilever’s length [124]. Since microcantilevers are very thin, a microcantilever under surface stresses \( S_1 \) and \( S_2 \) may be modeled as a taught string with one fixed end, with a uniform linear mass density \( m_1 \), stretched by a tensile force \( F_r \). This assumption leads to a wave equation for a microcantilever’s transverse vibration, expressed as

\[
\frac{\partial^2 z}{\partial^2 y} = \frac{m_1}{F_r} \frac{\partial^2 z}{\partial^2 t}
\]  

(7)

where \( z \) is the microcantilever’s transverse displacement, \( y \) defines the microcantilever’s longitudinal direction along its length, and \( t \) is time. The tensile force and linear mass
density are combined in order to describe the speed of wave propagation $v$ [124], expressed as

$$v = \sqrt{\frac{F_r}{m_i}} \quad (8).$$

The speed of wave propagation ($v$) through a microcantilever is then related to its wavelength ($\lambda$), and its frequency of vibration ($f$), by $v = f \lambda$. Using the boundary condition for a vibrating string with one fixed end, we arrive at an expression for the microcantilever’s fundamental wavelength, given by $\lambda = 4L$. Combining these two equations, the microcantilever’s fundamental resonance frequency can be expressed as [124]

$$f = \frac{v}{\lambda} = \frac{1}{4L} \sqrt{\frac{F_r}{m_i}} \quad (9)$$

The microcantilever’s resonant frequency can then expressed in terms of its surface stresses, $S_1$ and $S_2$, as

$$f = \frac{1}{4} \sqrt{\frac{S_1 + S_2}{n_1m_b}} \quad (10)$$

where $m_i = n_1m_b$, $n_1 = 0.24$ for a rectangular microcantilever and $m_b$ is the mass of the suspended beam [125]. From Hooke’s law, the microcantilever’s spring constant is then expressed as
\[ K_{i} = \frac{\pi^2 n}{4 n_i} (S_1 + S_2) \] (11)

where \( n = 1, 2, 3 \ldots \) [124]. The microcantilever’s spring constant is also expressed in terms of its elastic properties as

\[ k = \frac{Ewt^3}{4L^3} \] (12)

where \( k \) is the spring constant, \( E \) is the Young’s modulus, and \( w, t, L \) are respectively the microcantilever’s width, thickness, and length [3, 126].

A microcantilever’s spring constant characterizes the microcantilever’s stiffness and sensitivity. When deflection measurements are performed, the microcantilever’s spring constant is decreased in order to reduce its stiffness and to allow larger deflections. When resonance frequency shifts are measured, the spring constant is increased in order to produce a large resonance frequency prior to analyte adsorption, thus increasing the resolution of resonance frequency shift measurements [46, 66].

**3.6 Microcantilever Detection Mechanisms**

Microcantilevers are able to detect analytes using two different transduction modes initially developed for use in Atomic Force Microscopy. First, in static mode analytes are
detected by measuring deflections associated with analyte-induced changes in surface stress. Second, in dynamic mode analytes are detected by measuring resonant frequency shifts associated with analyte-induced changes in the microcantilever’s mass [98, 99]. The sensitivity of static mode measurements increases with the microcantilever’s deflection and flexibility.

In order for a microcantilever to perform as a useful sensor, deflections and resonance frequency shifts must be able to be converted into real-time electronic signals and with at least nanometer scale signal resolution. In terms of the microcantilever’s spring constant \((k)\), the sensitivity of static mode measurements increases with smaller spring constants. The sensitivity of dynamic mode measurements increases with the microcantilever’s resonance frequency and spring constant. Whether operating in static or dynamic mode, analyte adsorption always induces changes in the microcantilever’s resonance frequency and spring constant [127]. In most cases though, changes in the spring constant are assumed to be negligible [124, 128].

In terms of the FIB milling procedure, the process milling of grooves into a microcantilever reduces a microcantilever’s spring constant. As a result, the FIB milling procedure is more suitable for static mode/deflection measurements. Both static and dynamic mode measurements are able to detect analytes with picogram sensitivity [74, 128]. In general though, when static and dynamic mode measurements are obtained from the same microcantilever, the measurements will display different sensitivities [3]. In detecting 2-mercaptoethanol analytes, microcantilevers operating in static mode produced
measurements which were at least one order of magnitude larger than dynamic mode measurements [45, 81]. In static mode, measurements are more suited for the use of microcantilevers in detecting microsized analytes, while dynamic mode measurements are more suited for the use of nanocantilevers in detecting nanosized analytes.

As analyte adsorption increases, dynamic mode measurements begin to provide more information [45]. Dynamic mode measurements are unaffected by thermal vibrations, but are greatly damped in a liquid [129]. Microcantilevers operating in a liquid in static mode are unaffected by viscosity, but are susceptible to changes in flow rate and pressure [3, 5, 82]. These changes in flow rate cause the microcantilever to drift from its equilibrium position.

3.7 Static Bending Mode

Microcantilevers are most often operated in static mode. Static mode measurements are the most effective mode of operation for the detection of analytes in a liquid because microcantilever deflections are unaffected by the viscous properties of a relatively static fluid [3, 82]. A microcantilever’s free surface energy changes with the analyte to coating affinity. As a result, a microcantilever will deflect by different amounts upon exposure to different analytes.

The deflections of coated microcantilevers are described by three different models which arise from the use of three different coatings. In the first model, a microcantilever is
coated with a thin film which expands upon analyte adsorption. This model can be used to describe surface-confined phenomena associated with physisorption and chemisorption, as seen in figure 10. The second model is appropriate in cases where a permeable coating thicker than a monolayer is deposited onto a microcantilever. In this model, a thick nanoporous coating establishes an effective surface stress on the microcantilever by allowing analytes to be absorbed into the coating. Upon absorption, electrostatic, steric, and osmotic forces induce the coating to swell, as can be seen in figure 11 [12, 20, 44, 68, 69, 92, 117, 130, 131].

The third model involves the deposition of a nanostructured coating onto a microcantilever. Nanostructure coatings are comprised of narrow crevices and grain boundaries that lead to large electrostatic and steric forces between the nanoscale gaps and the adsorbed analytes [69, 79-82, 107, 132]. Analyte-induced deflections arise from bulk, surface, and interstitial interactions with the coating [68], as seen in figure 12. Nanostructured coatings have been shown to increase microcantilever deflections by three orders of magnitude compared to the smooth gold coated microcantilevers [44, 101]. The presence of nanoscale gaps on the microcantilever’s coating also presents the advantage of an increased number of adsorption sites, and an increase surface-to-volume ratio.

In regard to the milled region of the uncoated microcantilevers, the milling process sputters the milled region. It is thus assumed that within the milled region, nanoscale gaps similar to those of a nanostructured coating are created. As a result, electrostatic and
Figure 10 Thin film coating (model one). As analytes adsorb onto the thin film, the thin film expands at a different rate than the uncoated side, causing the microcantilever to deflect.
Figure 11 Permeable Coating (Model Two). The absorption of analytes into the bulk of a thick nanoporous coating induces the coating to swell. This swelling establishes a differential surface stress which allows the microcantilever to deflect.
Figure 12  Nanostructured Coating (Model Three). The dealloyed gold and silver coating. After removing the silver atoms, a granulated gold surface with nanoscale gaps remains. Analytes entering into the interstices experience large steric forces, which increase microcantilever deflection by several orders of magnitude.
steric forces similar to those that occur in a nanostructured coating occur within the milled region of the uncoated microcantilevers. Therefore, just as the electrostatic and steric forces within the nanostructure coating lead large analyte-induced deflections, the electrostatic and steric forces within the milled region of the uncoated microcantilevers lead to large analyte-induced deflections.

3.8 Dynamic Mode

In most cases it is assumed a microcantilever’s vibrational amplitude will be much smaller than its length [5]. Therefore, a microcantilever can be modeled as a one-dimensional harmonic oscillator with an effective mass \( m^* \), spring constant \( k \), and resonant frequency expressed as [21, 134]

\[
f_o = \frac{1}{2\pi} \sqrt{\frac{k}{m^*}} \quad (13)
\]

The spring constant typically ranges from 0.1 to 0.01 N/m for a rectangular microcantilever. The effective mass is expresses as \( m^* = 0.24m_b \), where \( m_b \) is the mass of the rectangular beam [15]. In most cases the microcantilever’s spring constant is assumed to remain constant upon analyte adsorption. Therefore, a microcantilever’s resonant frequency shift from \( f_o \) to \( f_1 \) upon the adsorption of a mass \( \Delta m \) is expressed as [5, 15, 99]
\[ \frac{1}{f_i^2} - \frac{1}{f_o^2} = \frac{\Delta m}{4\pi^2 k} \quad (14). \]

where \( k \) is the microcantilever’s spring constant. Equation (14) displays an inverse relation between the fundamental resonance frequency and the adsorbed mass. Therefore, high fundamental resonant frequencies are required in order to detect minute quantities of analytes. With resonant frequencies in the megahertz range, nanocantilevers most efficiently operate in dynamic mode. Lavrik and Datskos were able to detect \( 5.5 \times 10^{-15} \) g of 11-mercaptoundecanoic acid vapor using a 6 \( \mu \)m long by 2 \( \mu \)m wide gold coated cantilever operating at 2.25 MHz [107]. Etching procedures which are normally used in the fabrication of microcantilevers are able to produce cantilevers with lengths as small as 10 \( \mu \)m. The focused ion beam procedure, nano FIB, and FIB combined with etching have been used to produce cantilevers of lengths less than 1\( \mu \)m [133].

3.9 Noise in Static and Dynamic Modes

The characterization of noise present during microcantilever operation helps to determine the limits of detection [3]. Sources of noise in microcantilever signals can be extrinsic and intrinsic. Intrinsic sources occur as thermal drift in the microcantilever’s equilibrium position and resonance frequency [45, 102], and extrinsic noise sources occur in the signal read out mechanism [3]. Thermal drift, due to laser heating, is the main mechanism by which noise contributes to the detected signals.
In static mode, a microcantilever’s sensitivity to surface stress changes increases with the length of the microcantilever, as seen in equation (5). In increasing a microcantilever’s length, the microcantilever’s spring constant \(k\) is resultantly decreased [3] see equation 12. With a low spring constant, microcantilevers are more susceptible to a thermal drift in position due to laser heating and the attainment of a thermal equilibrium between the microcantilever and its environment.

In dynamic mode, decreasing the microcantilever’s initial mass and increasing its spring constant, equation (13) implies a higher resonant frequency and sensitivity. The reduction of a microcantilever’s mass also leads to thermal drift due to a dynamic exchange of energy between a microcantilever and its environment. The amplitude of a thermal drift in position for static and dynamic mode measurements is expressed as

\[
\delta_n = \sqrt{\frac{2k_BT}{\pi Q f_o k}}
\]  

(15)

where \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature, \(B\) is the bandwidth of the measurements, \(Q\) is the quality factor which characterizes the dissipated energy, \(f_o\) is the microcantilever’s resonant frequency, and \(k\) is the microcantilever’s spring constant [21].

In dynamic mode, microcantilevers also experience a temperature induced resonance frequency shift, expressed as
\[ \delta f_v = \frac{1}{z_{\max}} \sqrt{\frac{2\pi f_v k_B T_B}{Q_k}} \] (16)

where \( z_{\max} \) is the microcantilever’s amplitude of oscillation [3]. The noise magnitude in static mode measurements has been determined to be approximately 10 nm [12, 79]. These disturbances can decrease a microcantilever’s sensitivity by an order of magnitude [124]. The effects of thermal drift on deflection and resonance frequency measurements can be minimized by: using a calibrated reference microcantilever in order to subtract thermal motion from the measurements [5], driving the microcantilever to oscillate at its highest amplitude, and annealing the microcantilever in order to relieve residual stresses.
CHAPTER 4 EXPERIMENTAL

4.1 Focused Ion Beam History and General Information

A focused ion beam (FIB 200, FEI Co., Hillsboro, OR, USA) was used to mill grooves along the entire width the microcantilevers. The FIB 200 can also be used for scanning electron microscope (SEM) and transmission electron microscope (TEM) for grain structure analysis, MEMS fabrication and cross section preparation [8]. For the focused ion beam procedure, a strong electric field is used to extract gallium ions (Ga+) from a liquid metal ion source and to accelerate the ions to an energy of 30 kV. The electric field then directs the ions into an optical column where a series of lenses and deflectors focus the ions into a beam, which is then scanned onto the microcantilever’s surface [8]. A spot diameter is defined as the diameter of the beam as the sample surface. A spot diameter of 30 nm or less is able to be achieved. The ion beam is maintained in a high vacuum (less than $7 \times 10^{-7}$ millibars) in order to avoid interference between the ion beam and gas molecules. As the ion beam is scanned over the microcantilever’s surface, atoms are ejected from the surface by physical sputtering, with an average removal rate of 12 $\mu$m$^3$/min [135]. Secondary electrons and ions are then ejected from the surface, and are detected in order to form an image of the milled sample.

The separation between the milled grooves can reach a minimum separation of 0.1 $\mu$m [136]. The aspect ratio, which is defined as the ratio of the depth of the milled groove to the smallest width of the milled groove, has been reported to be 3:1, and can be increased.
to 6:1 by combining gas-assisted etching with the FIB process. The steps taken in operating the FIB 200 are described below.

4.2 FIB Milling Procedure Utilized for this Experiment

Begin by using a pair of latex gloves and viewing the microcantilever array through a microscope, the microcantilevers are held in one hand with a pair of tweezers. With the other hand, another pair of tweezers is used to lift a thin metallic clamp, which is fastened at one end to an FIB sample holder. The microcantilever array is then manually inserted between the clamp and the sample holder. In order to place the sample holder into the FIB sample stage, the FIB monitor is turned on, along with a picoammeter (Keithley 485 auto ranging picoammeter) which monitors the beam current. The button labeled “high tension” located on the workstation control panel is turned off.

The main FIB screen is separated into three parts, the menu bar, the image window, and the control window. The image widow displays an image of the FIB stage and sample. The control window (which is located on the right side of the menu bar) is divided into three parts: the system page, the work page, and the image processing page. In order to place the sample holder in the FIB sample chamber, the sample chamber is ventilated by selecting the system page from the menu bar and pressing the “vent” button. The stage’s tilt is set to 0° by turning the lever on the stage door and locking the stage’s tilt by turning the lock lever to the locked position.
Once the sample chamber is ventilated, the stage door automatically unlatches, and is fully opened. The sample holder is then inserted into a stub holder located at the center of the sample stage. The FIB stage door is then shut and the stage door is locked by turning the lock lever. The high vacuum conditions are then reestablished within the FIB chamber by selecting “pump” from the system page’s control area, and awaiting the “vacuum ok” message on the system page.

In order to establish the ion beam current, the button labeled “high tension” (located in the workstation control panel) is pressed. Then, the button labeled “operate”, located on in the system page, is pressed. The magnitude of the FIB current is then observed from the monitor and is allowed to stabilize to a constant value of 2.2 μA. In the instances when the ion beam does not stabilize, the “suppressor” and “extractor” voltages located in the system page are adjusted in order to stabilize the beam current to 2.2 μA. The “suppressor” voltage should be approximately 1 kV, while the “extractor” voltage is allowed to range between 6.00 to 8.00 kV. From system page, the “30 kV” button is then selected.

In order to view the microcantilever array, the “beam” is selected from the menu bar, and “Low Mag” is selected from the pull down menu. Then, “! image start” is selected from the menu bar. The contrast, brightness, magnification, focus, and stigmation dials are then adjusted from the manual user interface in order to view the sample stage. A joystick is then used to position the microcantilevers at the center of the screen. The image resolution is then increased by selecting “beam” from the menu bar and setting the beam
current to 11 pA. “Magnification” on the menu bar was then selected, and “calibrate micron bar” was then selected. A reference particle was selected in order to calibrate the micron bar. This step was repeated twice in order to compensate for beam movements.

In order to mill a particular microcantilever, a test area beneath the base of the microcantilever is used to increase magnification and to adjust the beam focus without overexposing the microcantilever to the damaging ion beams. Using the joystick, the sample stage is moved in order to position the microcantilever’s base on the image window. The joystick is then used to move the image window beneath the microcantilever’s base, to a position where the microcantilever is outside the image window. A small structure with visible edges, usually a dust particle or a defect, is then identified within this region and is used as a reference in order to increase magnification to 10,000. “beam” is selected and the ion beam current is increased to 70 pA. Next, “image stop” is selected. By pressing the function key F12 to “capture one frame,” a snapshot of the microcantilever is taken.

In order to view different parts of the microcantilever in “image stop” mode, the joystick is moved in incremental amounts, and F12 is subsequently pressed after each increment in order to take a new snapshot. Taking a snapshot of the microcantilever rather than a continuous image, while operating with the large beam current of 70 pA, reduces the damages produced on the microcantilever by the intensified ion beam.
The “contrast” was then increased. Using the “focus” and “stigmator” dials located on the manual user interface, fine adjustments to the ion beam’s focal point are made in order to produce an image which allows the sharp edges of the reference particle to be observed. First, the image is brought into focus and then brought slightly out of focus. Then the “stigmation” in the x direction is then adjusted to bring the image back into focus. The “stigmation” in the y direction is adjusted to increase the focusing, and finally the “focus” dial is adjusted to make the sharpest possible image.

In order to verify how finely the ion beam will mill the surface, a test mill is performed at a spot near the test particle. From the menu bar, “patterning” is selected, then “spot mode”. While in “spot mode”, a spot is continuously milled. By selecting “grab,” a snapshot of the milled spot is taken. If the milled spot is observed to circular, the spot milling process is stopped. In the instances when the milled spot is not circular or does not display sharp edges, the “focus”, and “stigmator” dials on the manual user interface are adjusted in order to produce a circular spot. Magnification is then decreased, and the microcantilevers are then positioned with the tips pointing downward along the image screen’s vertical +y direction. Magnification is increased until the width of one microcantilever fills up as much of the image screen’s area as possible. The microcantilever’s length was then aligned with the image screen’s vertical (y) axis, by selecting “stage” from the menu bar, and selecting “X-Y align”.

In order to mill straight grooves into the microcantilever, “line” is selected from the pattern toolbox, and the mouse is used to trace out a line along the width of the
microcantilever, and extending the traced line a few micrometers outside the edge of the microcantilever in order to allow the entire width of the microcantilever to be milled. The mouse is then used to position the traced line at the preset distance of the groove from the base of the microcantilever. The milling icon located on the pattern toolbox is then selected in order to mill a groove into the microcantilever. While the grooves were being milled the depth of the milled grooves were displayed on the Pattern Status dialogue box. When the depth of the milled grooves reached the calculated depth, the milling process was stopped by pressing “esc.”

After the milling process is finished, the value of the beam current is returned to 11 pA, and “image start” is selected from the menu bar in order to return to continuous imaging mode and to allow an image of the milled surface to be taken. In order to take an image of the milled microcantilever, select “image utilities” from the menu bar. From the pull down menu, “graph photo frame” is selected, and the scanning speed is set to 24 µs.

4.3 Experimental Assembly

The experiment is performed atop a vibration-isolated optical breadboard table (Newport Corp., RS2000). A stage, comprised of two 65 mm steel stage x side mount (Optosigma, Santa Ana, California), a 65 mm steel stage z pivot drive (Optosigma, Santa Ana, California), and a 65 mm rotating stage (Optosigma, Santa Ana, California) was assembled in order to mount the flow cell used to house the microcantilever array during the experiments. The flow cell was a 100 µl Teflon flow cell, which had an input port for
carrier gas and analyte delivery, an output port, and a removable glass window. Situated behind the flow cell’s glass window was a circular, indented area for placing the microcantilever into the flow cell. The two ball-bearing linear stages were oriented atop one another in order to allow the flow cell to be moved along the plane of the vibration isolation table, in two perpendicular directions labeled x and y. The lifting stage was then placed atop the linear stages in order to allow the flow cell to be moved upwards and downwards along the z direction. The rotating stage was then placed atop the lifting stage to allow the flow cell to be rotated along the z axis. A 5 mW diode laser (Coherent Laser Corp., Auburn, CA), operating at 635 nm was then lined up along the x axis and directed onto the center of the flow cell. A lens was placed in front of the laser, in order to focus the laser beam onto the microcantilever. A quad-cell position sensitive photodetector (PSD), built in house, was then lined up along the y axis, and directed towards the flow cell. A Watec CCD camera (Edmund Industrial Optics, Barrington, NJ) equipped with a zoom lens, was the placed between the laser and PSD, and directed towards the flow cell.

At this point the carrier gas, and analyte delivery system was assembled. First, a device comprised of a 2-way valve with six ports was used to mix the analytes and the nitrogen carrier gas before the gases were injected into the flow cell. port #1 was connected to a gas cylinder which contained the nitrogen carrier gas, port #2 was connected to the flow cell’s injection port, ports # 3 and 6 were formed a 10 mL gas loop which was used to mix the analyte and nitrogen gas, port #4 was used as an exhaust, and port # 5 was connected to an automated 10 mL syringe (Model 5020, Rheodyne, Inc. Cotati, CA, USA), within which the analyte liquid was poured into. Upon injecting the analyte vapors
into the 10 mL loop, the 2-way valve was switched from a direct connection of the nitrogen carrier gas into the flow cell, to an indirect connection into the flow cell which combined the analyte and carrier gas through the 10 mL gas loop before the analytes entered the flow cell. A digital mass flow controller (MKS Instruments, Inc., Andover, MA, USA) was then connected to the output port of the flow cell in order to monitor flow rate. After the carrier gas and analyte delivery system was assembled, the analytes which were liquid at room temperature (ethanol, acetone, 1-monorotolene, and water vapor) were poured into the automated syringe for their particular experiments. Argon, being a gas at room temperature, was supplied to the flow cell from a compressed gas cylinder.

4.4 Optical Alignment and Calibration

Upon assembling the analyte delivery system, the microcantilever array was placed into the flow cell. Microcantilever deflections were measured by reflecting the 5 mW diode laser beam from the surface of the microcantilever and into the position sensitive photodetector (PSD) using the optical lever read out method developed by Meyer and Amer for use in atomic force microscopy [137] (see figure 13). Other read out methods such as optical interferometry [138], piezoresistive method, and capacitive method [3] have also been used in microcantilever sensors. The position sensitive photodetector (PSD) used in this experiment was a quad-cell photodiode, which consisted of a quadrant of four photosensitive cells labeled A, B, C, and D. The cells’ output voltages, $V_A$, $V_B$, $V_C$ and $V_D$ are proportional to intensity of reflected light impinging on the respective cells.
Figure 13 Optical lever method. A laser is reflected off of the microcantilever’s tip, and into a PSD. As the microcantilever deflects, the position of laser on the PSD proportionality varies.
The differential output voltage ($V$) was then calculated from the output voltages, and is expressed as

$$V = \frac{(V_B + V_D) - (V_A + V_C)}{V_A + V_B + V_C + V_D} \quad (17).$$

The differential voltage varies linearly with the displacement of the laser beam across the position sensitive photodetector. Optical lever method is one of the simplest and most sensitive readout mechanisms due to its linear responses, its ability to be used in liquid environments, and the absence of electronic connections. The application of optical lever method is limited by interference with ambient light, by the bandwidths of the PSD’s, and to low opacity media. Optical lever method is also limited by the size of the cantilever’s reflective area. The minimum reflective area for the efficient conversion of optical signals into electronic measurements is in the range of $10 \times 10 \, \mu m^2$. In using optical readout methods for cantilevers of lengths less than $20 \, \mu m$, the dimensions of the cantilever’s reflective area becomes commensurate with the laser’s wavelength, resulting in the scattering of the reflect laser prior to the laser being detected [46]. As a result, optical lever method performs less efficiently for nanocantilevers. The nanocantilever’s small size, also limits the accuracy of other signal read out methods such as piezoelectric, and capacitive methods [139]. Electron transfer read methods, such as electron tunneling and electron shuttling [140] have been found to be more suitable for nanocantilever sensors.
4.5 The Technical Procedure for the Optical Lever Method

First, the diode laser, PSD, CCD camera, and the camera’s video monitor were turned on. A sheet of paper was placed in front of the flow cell, and the position of the diode laser and lens were adjusted in order to place the beam’s focal point onto the sheet of paper, and subsequently onto the tip of the microcantilever. By viewing the video monitor, the linear, lifting, and rotating stages were moved in order to position the diode laser’s focal point onto the tip of the microcantilever.

In order to more finely position the laser’s focal point onto the tip of the microcantilever, a sheet of paper was placed this time in front of the PSD. The steel stages were shifted and rotated, and the intensity and shape of the diode laser impinging on the sheet of paper was observed. When the laser beam was located at the tip of a microcantilever (with the tip of the microcantilevers pointing downwards), the laser beam as observed on the sheet of paper would disappear if the microcantilever’s position was shifted to the left, right, or beneath the tip of the microcantilever. The size of the laser beam on the sheet of paper also changed as the laser beam moved across the microcantilever. A secondary light was observed on the sheet of paper due to the laser beam reflecting off of the flow cell’s glass window. As the microcantilever’s position was moved, the laser beam reflected off of the glass window retained the same shape and intensity. Once the laser beam was positioned onto the tip of the microcantilever, the PSD was then shifted in position in order to center the diode laser onto the PSD. A sheet of paper was used an indicator of the beams position on the PSD.
4.6 Electronic Assembly

A BNC “T” connector was connected to channel 1 of a TDS 220 digital oscilloscope (Tektronix, Beaverton, OR). A second BNC “T” connector was connected to “auxiliary input 1” of an SRS 850 DSP lock-in amplifier (Stanford Research Systems, Sunnyvale, CA). The differential voltage output from the PSD was connected to one end of the oscilloscopes “T” connector. A cable was then used to connect the oscilloscopes “T” connector to the lock-in’s “T” connector. The lock-in amplifier was used to record and store the PSD signals, while the oscilloscope was used to facilitate optical alignment. An SR 760 FFT spectrum analyzer (Stanford Research Systems, Sunnyvale, CA) was then connected to the lock-in’s “T” connector in order to measure resonant frequency (see figure 14).

To center the reflected laser beam onto the quad-cell detector, the position of the PSD was adjusted so that the oscilloscope voltage corresponding to position in the horizontal direction was equal to zero, and voltage corresponding to position in the vertical direction was equal to zero. When the laser beam is centered onto the quad-cell, shifting it in any direction will cause the magnitude of the differential voltage to increase. Also, any clockwise or counterclockwise rotation of the microcantilever array will cause the magnitude of the differential voltage to increase.

When the laser beam was centered onto cell A, the differential voltage was increased to the maximum value +10 V, and decreased to the minimum value –10 V for cell B. Also,
Figure 14 A schematic diagram of the experimental instruments used during the experiment.
when the laser beam was centered onto the quad-cell, the total voltage read a maximum value of 10V. The quad-cell PSD’s dynamic range, defined as the fullest extent of the detected signal range that occurs without excessive distortion [8], was then measured by displacing the PSD in order to displace the reflected laser beam from the center of cell A to cell B. It was observed that when the PSD’s position was moved by turning the micrometer from 5.4 mm to 7.9 mm, the PSD’s voltage increased from -10 volts to +10 volts.

The conversion factor between the microcantilever deflection and the corresponding the differential output voltage was then determined to be 470 nm/volt by rotating the microcantilever stage by fixed amounts, within the PSD’s dynamic range, and measuring the resultant change in differential output voltage from the oscilloscope. This conversion factor was then used when calculating microcantilever deflections. Figure 15 illustrates how the rotation of the microcantilever and the corresponding shift in the position of the reflected laser beam across the PSD were used to calculate the conversion factor for a microcantilever of length $l$, and a position sensitive photodetector of width $D$, separated by a distance $h$.

The rotation of the microcantilever corresponds to the microcantilever deflection depicted in figure 15. As the microcantilever is rotated, the reflected laser beam travels across the position sensitive photodetector by a distance $d$. The position and movement of the laser beam across the position sensitive photodetector is measured from the
Figure 15 Optical lever method. The geometrical factors $l$, $h$, $d$, and $D$ are used in calibrating microcantilever deflections to the output voltages from the PSD.
magnitude and sign of the differential output voltage. With the tip of the microcantilevers pointing in the –z direction, microcantilever deflections in the +x (up) or –x (down) directions were distinguished from one another by moving the PSD in the +z direction (which corresponded to microcantilever deflection in the –x direction). Upon shifting the PSD in the +z direction, a positive voltage on the oscilloscope implies a downward microcantilever deflection, and a negative voltage implies an upward microcantilever deflection. Deflections of $10^{-14}$ m have been reported in various papers, using this method [3, 21, 23, 45, 81].

4.7 Experimental Procedure

First the laser, detector, oscilloscope, camera and television screen were turned on. The nitrogen carrier gas was introduced into the flow cell by first opening the main valve on the nitrogen gas cylinder, and then opening the gas cylinder’s regulator valve. By monitoring the flow meter, the gas regulator valve was adjusted in order to set the nitrogen gas’s flow to a rate of $\leq 5$ ppm. Then the aqueous analyte solution was poured into the syringe. The syringe was connected to the 10 ml gas loop. The laser beam was the directed onto the microcantilever array. The laser beam was then directed onto the tip of one microcantilevers. When the laser beam was positioned onto the microcantilever, the reflected beam became brighter, and changed its shape in a fluid manner as the beam moved across the microcantilever.
The microcantilever’s position in the x, y, and z directions were adjusted in order to obtain the brightest circular reflected spot. The PSD’s position was then adjusted in order to center the reflected beam onto the quad-cell so the respective voltages which corresponded to the beam’s position in the horizontal and vertical directions were equal to zero. The detector’s polarizer was adjusted in order to set the total voltage less than or equal to \( \leq 10 \) V.

The microcantilever’s resonant frequency was then measured from the FFT spectrum analyzer. The 2-way valve was set to direct flow into the flow cell to allow the carrier gas into the flow cell. A lock-in trace was taken for 1 minute. During this time, the lock-in baseline voltage was verified to be flat. The baseline voltage corresponds to the reflected laser beam centered onto the PSD. The 2-way valve was set to indirect flow to introduce the analytes (water vapor, air, ethanol, acetone, argon, or 1-mononitrotoluene) into the flow cell.

As the analytes entered the flow cell lock-in trace was monitored for any change in position. The lock-in trace was expected to display a shift in position from its baseline value, which is proportional to the analyte induced deflection. As the analyte supply began to deplete with the flow cell, the lock-in voltage trace was observed to decrease in height, returning to the baseline voltage. At this point the 2-way valve was switched to direct flow in order flush the analytes out of the flow cell more rapidly. A second lock-trace experiment was performed after the baseline voltage returned to its initial value. The lock-in trace was then saved onto the lock-in amplifier.
4.8 Description of Microcantilever Grooves

A small number of grooves, between one and three, were milled into ten uncoated microcantilevers of a sixteen microcantilever array. The ninth microcantilever in the array was initially found to have a shallow grating of sixty grooves milled into its surface, and was not modified any further. In total, eleven microcantilevers were used in this experiment, and are numerically labeled from 1 to 11. Since the silicon microcantilevers were exposed to air prior to performing the analyte-induced deflection experiments, a silicon oxide layer was assumed to be present on the surface of the microcantilevers. Figure 3 shows the focused ion beam image of the most responsive microcantilever (microcantilever 1), figure 16 shows one of the least responsive microcantilevers (microcantilever 3), and figure 17 shows one the microcantilevers which displayed an intermediate response (microcantilever 5).

Some of the microcantilevers were milled at an angle (relative to the surface normal) to increase the depth of the grooves to a value greater than the microcantilever’s thickness. The dimensions of the grooves were estimated from the focused ion beam image. The grooves were milled approximately 15 micrometers from the base of the microcantilever, and it is assumed that the effective length of the microcantilever begins after the location of the grooves.

A feature that distinguishes microcantilever 1 from the other ten microcantilevers is observed by taking a side view of microcantilever 1 to view the groove’s cross-section.
Figure 16 **Focused** ion beam image of microcantilever 3 displays a wide and shallow groove.
Figure 17 Focused ion beam image of microcantilever 5 displays two deep and wide rectangular grooves.
From figure 3 we see that the groove cross-section for microcantilever 1 displays a conical profile, with the vertex terminating at the microcantilever’s lower surface. The groove’s conical profile is a direct imprint of the focused ion beam’s conical profile (see figure 18). Therefore, figure 3 shows that the FIB’s focal point was located at the microcantilever’s lower surface during milling. As a result, a 100 nm groove width was produced at microcantilever 1’s lower surface.

Figure 16 shows that the FIB’s focal point was located several 100 nm above microcantilever 3’s lower surface during milling. A rectangular groove cross-section is observed in figure 17, and implies that the FIB’s focal point was located beneath microcantilever 5’s lower surface during milling. The fluctuation in the position of the FIB’s focal point for the milling of microcantilever 3 resulted in its wide and shallow groove, and in microcantilever 5’s wide rectangular grooves.

The cross-sectional dimensions of a groove are comprised of the depth of the groove, the width of the groove at the microcantilever’s upper surface (where the focused ion beam first intersects the microcantilever), and the width of the groove at the microcantilever’s lower surface. Table 1 lists the cross-sectional dimensions of the grooves, the number of grooves milled, the angle at which the grooves were milled, and the resonant frequencies for eight of the eleven microcantilevers used in this experiment. Microcantilevers 4, 6, and 10 are omitted from Table 1 because they were not imaged with a focused ion beam. Tests were also performed on a second array of microcantilevers, which were milled at about 30 degrees and had 10 or more grooves milled to a depth larger than a micrometer.
**Figure 18** Energy profile of the focused ion beam as a function of the radial distance from the beam’s axis.
Table 1 Dimensions of Milled Grooves

<table>
<thead>
<tr>
<th>MC</th>
<th>Resonance Frequency (kHz)</th>
<th>Groove width at lower surface (nm)</th>
<th>Groove width at upper surface (nm)</th>
<th>Depth of grooves (nm)</th>
<th>Number of grooves milled</th>
<th>Milling angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.62</td>
<td>100</td>
<td>750</td>
<td>1300</td>
<td>1</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>9.24</td>
<td>500</td>
<td>500</td>
<td>1300</td>
<td>1</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
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<td>250</td>
<td>600</td>
<td>250</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>9.50</td>
<td>250</td>
<td>250</td>
<td>500</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
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<td>500</td>
<td>1</td>
<td>45</td>
</tr>
<tr>
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<td>500</td>
<td>1400</td>
<td>500</td>
<td>2</td>
<td>45</td>
</tr>
<tr>
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<td>500</td>
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</tbody>
</table>
Most of the microcantilevers from the second array were found to be bent along the groove’s axis after milling or easily broke off when handled.
CHAPTER 5 DISCUSSION

5.1 Analyte-Induced Deflections of Uncoated Microcantilevers

The process of altering an uncoated microcantilever’s physical structure by milling grooves into one of its sides produces a differential surface stress that allows the microcantilever to deflect upon analyte adsorption. The alteration of the microcantilever’s physical structure increases the microcantilever’s sensitivity by reducing its spring constant, without providing the microcantilever with the chemical specificity offered by an analyte receptive coating.

A question then arises pertaining to the presence of stress induced deflections prior to the introduction of the analyte which is to be assayed. Analytes adsorb onto uncoated microcantilevers through nonspecific intermolecular forces. Therefore, the nonspecific adsorption of ambient molecules onto the microcantilever is able to induce microcantilever deflections prior to the introduction of the analyte which is to be analyzed. Since all deflections are measured relative to the microcantilever’s position immediately preceding the adsorption of the analyte onto the microcantilever, deflections due to nonspecific adsorption are automatically subtracted from the measurements.
5.2 The Deflections of the Milled Microcantilevers

Based on the deflection magnitudes, the eight microcantilevers used in the analysis were partitioned into three groups. The first group contained the most responsive microcantilever, microcantilever 1, which displayed deflections as large as 400 nm upon exposure to an argon-ethanol mixture, as seen in figure 19. The second group contained the moderately responsive microcantilevers: microcantilevers 5, 8, and 9, which were characterized by deflections as large as 90 nm. The third group contained the least responsive microcantilevers: microcantilevers 2, 3, 7 and 11, which were characterized by deflections as large as 70 nm.

Figure 20 shows deflections upon exposure to water vapor for microcantilever 1 (repeated twice) microcantilevers 5, 8, and 9, and microcantilevers 2, 3, 7, and 11. Table 1 shows an association between the geometry of the milled grooves and the induced deflections. Microcantilever 1 is the only microcantilever with a 100 nm groove width. In comparing the moderately responsive microcantilevers to least responsive microcantilevers, we notice that the moderately responsive microcantilevers have 2 milled grooves or a shallow grating of 60 grooves. The least responsive microcantilevers have one milled groove, with the exception of microcantilever 11 which has 3 milled grooves, but microcantilever 11 also had very wide and shallow grooves which decreased the microcantilever 11’s sensitivity. The moderately responsive and least responsive microcantilevers both display a minimum groove width of 250 nm. Thus we conclude that deflections increase with the number of milled grooves, and with the reduction of
Figure 19 Deflection of microcantilever 1. Upon exposure to argon, ethanol, and an argon-ethanol mixture, the largest deflection of 400 nm was exhibited by microcantilever 1 upon exposure to the argon-ethanol mixture. The 400 nm deflection is attributed to the increased density of the binary mixture within the flow cell. The positively sloped peak to the argon-induced deflection may be due to thermal drift which shifts the deflections upwards. The ethanol deflection is taken from another trial of this experiment.

(Note that for figures 19 through 24, the lock-in traces which display more than one analyte or more than one microcantilever were sequentially positioned along the time axis in order to allow the deflection magnitudes to be conveniently compared, the actual lock-in trace measurements of different analytes, or different microcantilevers, were not taken sequentially.)
Figure 20 Water vapor induced deflections of the most sensitive cantilever, microcantilever 1 (which was repeated twice); the moderately responsive microcantilevers 5, 8, 9; and the least responsive microcantilevers 2, 3, 7, and 11.
groove widths to the nanometer scale. Microcantilever 11 stands apart from this trend because it had three grooves and yet displayed a maximum deflection of 70 nm. Microcantilever 11’s grooves were also very wide (with a width of 1.9 μm) and very shallow (with a depth 0.5 μm). The fact that microcantilever 11 had very wide and shallow grooves is noted to have reduced the sensitivity gained by milling three grooves.

When exposed to water vapor, microcantilever 13 from the second array of microcantilevers had ten deep and wide grooves milled on its surface, and produced 40 nm deflections, immediately followed by an erratic deflection pattern with a noise amplitude of 60 nm. Also, microcantilever 13 displayed no measurable deflections when exposed to argon. The inconsistencies in microcantilever 13’s deflection patterns were shared by the remaining microcantilevers in the second array. It is therefore assumed that for a 1μm thick microcantilever, the process of milling multiple grooves whose widths are larger than a micrometer, and whose depth is larger than 500 nm, damages the microcantilever.

Headrick et al. successfully obtained 400 nm deflections after milling 800 nm wide grooves to a depth of 400 nm into a 1.5 μm thick microcantilever, which was subsequently coated with an organic film [67]. Thus it is assumed that multiple wide grooves are able to be milled into a microcantilever without damaging the microcantilever, by keeping the depth of the grooves to a value less than half the microcantilever’s thickness. In order to mill multiple grooves to a depth of 500 nm or larger into a 1μm thick microcantilever, the ideal groove width would be 100 nm or less.
5.3 Comparison of Microcantilever Deflections

All the coated microcantilevers used in the analysis exhibited large and measurable deflections when compared to uncoated microcantilevers which were not physically modified. Uncoated microcantilevers which were also physically modified by the creation of milled grooves on one of their sides displayed deflection magnitudes which were comparable to the coated microcantilevers. Large deflections are representative of the microcantilevers’ reduced spring constant. The microcantilevers’ spring constants are reduced by several factors. First, the fact that the grooves were milled near the microcantilever’s base, where Pinnaduwage stated that the microcantilever’s spring constant is largely defined, significantly reduces the spring constant [6]. Second, the compressive (or negative) stresses created by analyte adsorption further reduces the spring constant, as can be seen in the expression for the surface stress contribution to the spring constant

\[ K_i = \frac{\pi^2 H (S_{\text{top}} + S_{\text{bottom}})}{4 n_1} \] (18)

where \(S_{\text{top}}\) and \(S_{\text{bottom}}\) are respectively the surface stresses on the top and bottom sides of the microcantilever, \(n=1, 2, 3, \ldots\), and \(n1 = 0.24\) for a rectangular microcantilever [124].

The microcantilevers’ reduced spring constants can be inferred from their low resonant frequencies, as seen in Table 1. Using Hooke’s law, we can compare the spring constants
of two microcantilevers, $k_1$ and $k_2$, by expressing them as a ratio, written in terms of their resonance frequencies $f_1$ and $f_2$ and their volumes $V_1$ and $V_2$

$$\frac{k_1}{k_2} = \left(\frac{f_1}{f_2}\right)^2 \frac{V_1}{V_2} \quad (19)$$

where the microcantilever masses have been rewritten in terms of the density of silicon, and the respective volumes of the microcantilevers. The resonant frequency of microcantilever 1 is 9.62 kHz while its volume was calculated to be $4.0 \times 10^4 \, \mu m^3$. The resonance frequency of an unmilled microcantilever coated with 2, 3 DNH was reported to be 61.4 kHz, while its volume was calculated to be $1.5 \times 10^4 \, \mu m^3$. The resonance frequency of an uncoated and unmilled microcantilever was reported to be 300 kHz, while its volume was calculated to be $4.5 \times 10^4 \, \mu m^3$ [6, 67].

In comparing microcantilever 1’s spring constant to that of the unmilled microcantilever, we find that microcantilever 1’s spring constant is 15 times smaller than the unmilled microcantilever. Also, in comparing microcantilever 1’s spring constant to that of the uncoated and unmilled microcantilever, we find that microcantilever 1’s spring constant is 1100 times smaller. Microcantilever 1’s reduced spring constant is the source for the uncoated microcantilever’s large analyte induced deflections.

Along with displaying large deflections, the microcantilevers exhibited a degree of chemical selectivity by deflecting by different amounts for different analytes. The uncoated microcantilever’s selectivity arises due to two factors. First, as mentioned by
Jensenius et al., the different rates of analyte evaporation induce the microcantilevers to deflect by different amounts [80]. The second factor which provides the microcantilevers with a degree of chemical selectivity occurs upon the adsorption of analytes within the grooves.

Jones et al. used a scanning tunneling microscope to image regions that were milled with FIB and observed defects 2 nm in diameter distributed throughout the milled region [22]. Therefore, as different analytes adsorb within the grooves, strong short range electrostatic forces between the analytes and the nanoscale interstitial spaces within the milled region may also contribute to the varied magnitudes of analyte induced deflections. Figures 20 and 21 allow us to compare microcantilever deflections upon exposure to ethanol and water vapor. Microcantilever 1 displayed the largest deflection for different analytes due to capillary condensation within its 100 nm groove. The moderately and least responsive microcantilevers exhibited a smaller change in deflection upon exposure to different analytes due to their wider grooves.

The largest deflection was observed when microcantilever 1 was exposed to a binary mixture of argon and ethanol, see figure 19. Thus, it seems that Microcantilever 1’s sensitivity increases upon exposure a gas mixture which is comprised of multiple analyte species. This increased sensitivity may be due to heightened vapor concentrations of the gas mixture. Microcantilever 1 also exhibits a dependency on the vapor concentrations of acetone and 1-mononitrotoluene, as seen in figures 22 and 23. During the experiments, the effects of thermal drift were observed in the form of baseline shifts in the
microcantilever’s deflection. Microcantilever 1 exhibited a thermal drift which shifted the magnitude of its deflection upwards, as can be seen in figure 24 when exposed to air.
**Figure 21** Deflection of microcantilevers 1 and 5, 8, and 9 and 2, 3, 7, and 11 upon exposure to ethanol.
Figure 22 Deflection of microcantilever 1 when exposed to 40%, 30% and 15% acetone. Here we are able to observe that microcantilever deflections increase with analyte concentration.
Figure 23 Deflection of microcantilever 1 when exposed to 1-mononitrotoluene at 10%, 20%, 40%, and 60%.
Figure 24 Deflection of microcantilever 1 in air. Toward the end of the experiment, thermal drift, perhaps due to laser heating, causes the microcantilever to shift upwards from its equilibrium position.
CHAPTER 6 CONCLUSION

There are four main claims resulting from the experiment related to this thesis. The first claim is that uncoated microcantilevers are able to display analyte-induced deflections which have not been previously observed. The second claim is that by reducing the width and increasing the depth of the grooves that the magnitude of microcantilever deflections would increase. The third claim is that the analyte induced deflections of the milled and uncoated microcantilever’s increased with analyte concentrations. Finally, the fourth claim is that microcantilever deflections increased with the number of grooves.

Claim One: Uncoated microcantilevers are able to display analyte-induced deflections (which have not been previously observed) by using the focused ion beam procedure to mill at least one deep and narrow groove into one of the microcantilever’s sides. This claim was supported by the deflection measurements obtained from a lock-in amplifier trace that showed a voltage change (which was then interpreted as the magnitude of the microcantilever’s deflections) upon exposure water vapor, air, ethanol, acetone, argon, and 1-monomitrolooluene. The uncoated microcantilevers were able display analyte-induced deflections by creating a differential surface stress between the two sides of the microcantilever using the focused ion beam procedure to mill deep and narrow grooves into one of the microcantilever’s sides. Upon the creation of the deep and narrow grooves, the microcantilever’s surface area and surface energy (on the milled side) increased while the surface energy on the unmilled side remained the same, thus creating a differential surface stress between the milled and unmilled sides. Upon analyte
adsorption onto the microcantilever, the energies transferred between the analytes and the microcantilever surface during adsorption caused the two sides of the microcantilever to expand at different rates due to the differential surface stress. By respectively experiencing two different rates of expansion between the milled and unmilled sides, the uncoated microcantilever was able to deflect in the presence of analytes.

Claim Two: By reducing the width and increasing the depth of the grooves, the magnitude of microcantilever deflections will increase. In order to create grooves with a depth that is larger than the microcantilever’s thickness, the grooves were milled at an angle relative to the microcantilever’s surface normal. This claim was supported by the observation that the microcantilever (microcantilever 1) with the 100 nm wide and 1.3 nm deep grooves displayed analyte-induced deflections as large as 400 nm (see figure 19), while the remaining microcantilevers with the wider (greater than 250 nm) and shallower grooves (less than nm 500) displayed analyte-induced deflections as large as 90 nm. Along with the decrease in surface energy which leads to microcantilever surface expansion upon analyte adsorption, microcantilever 1 experienced a second form of surface energy decrease upon analyte adsorption due to the larger capillary condensation forces within its narrower groove.

Claim Three: Analyte-induced deflections of the milled and uncoated microcantilever’s increased with analyte concentrations. This claim was supported by lock-in amplifier traces where the deflections of microcantilever 1, when exposed to acetone decreased from 140 nm to 80 nm as the acetone concentration decreased from 40 % to 15 % (see
Also, in an experiment with 1-mononitrololuene, microcantilever deflections were observed to increase from 60 nm to 140 nm as the analyte concentration was increased from 10% to 60% (see figure 23). Microcantilever deflections were observed to increase with analyte concentration due an increase in the number of analytes which adsorb and participate in the reduction of the microcantilever’s surface energy.

**Claim Four:** *Microcantilever deflections increased with the number of grooves.* This claim is not as clearly interpreted from the microcantilever deflections, due to the likeliness that microcantilever deflections are dependent on the cumulative effects of groove width, depth, and number of grooves. Future experiments will be performed to further substantiate this claim. During the milling process, the FIB beam’s current was observed to fluctuate during the milling process, which resulted in grooves whose depth and width fluctuated from one milling cycle to another. Without being able to mill multiple grooves with the same dimensions, only microcantilevers from the moderately and least responsive set are used to support this claim. Claim four is supported by the lock-in trace in figure 20, where the microcantilever array was exposed to water vapor. In this trace it was observed that microcantilevers 5, 8, and 9 (which had two milled grooves) displayed 90 nm deflections while microcantilevers 2, 3, 7 (which had one milled groove) displayed 70 nm deflections. Microcantilever 11, which had three wide grooves, would be expected to display deflections larger than 90 nm, but actually only displayed 50 nm deflections. The reduced sensitivity of microcantilever 11 is attributed to the fact that the three milled grooves were shallow and wide, opposed to the most sensitive microcantilever which had deep and narrow grooves. It is therefore also claimed
that microcantilever deflections depend on the combined effects of groove depth, width, and number of grooves.

The existence of a deflection for all milled microcantilevers in this experiment provides microcantilever sensors with an additional means of increasing chemical sensitivity through nanoscale surface modifications. Taking as a starting point the fact that a microcantilever’s spring constant is primarily defined at its base, an empirical survey of the relations between deflection magnitudes and a range of simple modifications such as: the distance of a groove from the base, the depth and width of a groove, the number of grooves, and the spacing between the grooves could provide a quantitative analysis of how various geometrical modifications increase a cantilever’s sensitivity. The main challenge faced in performing an empirical survey arises during the milling process, where the width of the focused ion beam and fluctuations in the position of the beams focal point reduces the repeatability of producing nanoscale grooves.

In creating nucleation sites for quantum dots, Nano FIB has recently been used to create 10 nm-wide and 3 nm-deep holes onto an aluminum indium arsenide (AlInAs) substrate [141]. As a result of Nano FIB’s ability to produce 10 nm surface modifications, it may be possible to consistently produce grooves of widths less than a 100 nm onto a microcantilever, because as observed from the experiment relating to this thesis, the microcantilever with the most narrow groove width of 100 nm produced the largest deflections. By increasing the duration of milling process or the beam energy, the nanoscale grooves can mill a significant distance into the microcantilever. Future
optimization of microcantilever sensors will be achieved by creating multiple nanometer wide grooves which extend into a microcantilever to a depth larger than half the microcantilever’s thickness, and reducing the microcantilever’s thickness, because the most sensitive microcantilever was observed to have the deepest groove. Upon physically modifying the microcantilever, a coating may be deposited onto the microcantilever for chemical, biological, thermal and optical sensing applications.
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VITA

Stephan Stacco was born on the island of Haiti on September 12, 1977. As a child living on this tropical island, he was surrounded by the love of his family and by the artwork of numerous Haitian painters. His gaze was enveloped by the island’s green mountains, shimmering aqua shores, and the spectral reflections of the islands fruits and flowers. In recalling the encouraging compliments given to me by my family, Stephan remembers hearing their voices saying to me, and to one another, that he was born with the gift of drawing. Along with being able to draw, as a child he began to ponder upon the existence of new colors in other universes, and what was the color of the universe before anything existed.

Stephan came to the America in 1987, at the age of nine. Throughout his adolescence and teenage years he planned on becoming a cartoonist and a painter, until one day when he watched a car pass by and wondered if there was a way to use the car’s own weight to increase the car’s fuel efficiency. From that moment on I began to ponder upon numerous inventions and to research my scientific interests, as well as artistic inspirations. He continued to study art and obtained an Associate of Arts (A.A.) in Commercial Arts from Miami-Dade College in 1999.

Around this time, Stephan began researching wave interference in resonant cavities, and found an inspiration in their nodal patterns which gave me the desire to learn the
fundamental nature of the universe, in order to understand the ubiquity of these nodal patterns. From this desire to learn about nature from its most fundamental level, he chose to study physics and obtained a Bachelor of Science (B.S.) from Florida International University in 2005, and a Master of Science (M.S.) from the University of Tennessee in 2008.

During Stephan’s graduate studies, where he developed his scientific nature, he also found my artistic voice in painting. Now, his artistic and scientific inspirations compliment and nurture one another. The inspiration which he received while researching wave interference in resonant cavities has remained the most vivid form of scientific interest for him throughout my undergraduate and graduate studies. As a result, he has chosen to pursue a Doctor of Philosophy in Electrical Engineering, where he will specialize in fiber optics in order to understand electromagnetic wave interference in resonant cavities.