Analysis and preliminary characterization of a MEMS cantilever-type chemical sensor

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Analysis and preliminary characterization of a MEMS cantilever-type chemical sensor

by

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SUMMARY

This Thesis relates to the continually advancing field of microelectromechanical systems (MEMS). With MEMS technology, there are many different areas of concentration available for research. This Thesis addresses analysis and preliminary characterization of a cantilever-type MEMS chemical sensor for detection of chemicals and organic components operating at room temperature (20°C and sea level pressure of 1 atm). Such sensors can be useful in a wide variety of applications.

There currently exist several different types of MEMS chemical sensors. Each is based on a different detection method, e.g., capacitive, thermal, resistive, etc., and is used for specific tasks. Out of all currently available detection methods, the most common is the gravimetric method. The gravimetric sensor works by absorbing the chemical in a special material, usually a polymer, which alters the overall mass of the sensing element that can then be measured, or detected, to identify the chemical absorbed.

One of the more exciting developments in the field of gravimetric chemical MEMS has been with the advancement of cantilever-type sensors. These cantilevers are small and usually on the order of only about 300 µm in length. In order to utilize the gravimetric method, a cantilever is coated with a polymer that allows an analyte to bond to it and change its mass, which in turn changes the resonant frequency of the cantilever. The change in frequency can then be measured and analyzed and from it, the amount of absorbed mass can be calculated. Current research in the cantilever-type resonating sensors for the detection of hydrogen is developing measurement capabilities of 1 ppm (part-per-million).
In this Thesis number of sample cantilevers were qualitatively assessed and their dimensional geometry measured. Based on these measurements, frequency data were obtained. In addition, the overall uncertainty in the resonant frequency results was calculated and the contributing factors to this uncertainty were investigated. Experimental methods that include laser vibrometry, optoelectronic laser interferometric microscopy (OELIM), and atomic force microscopy (AFM), were utilized to measure the frequency responses of the samples. The analytically predicted natural frequencies were compared to the experimental data to determine correlation subject to the uncertainty analysis.

Parametric analyses involving chemical absorption processes were also conducted. Such analyses considered different parameters, e.g., damping and stiffness as well as changes in their values, to determine contributions they make to the quality of the frequency data and the effect they have on sensitivity of the MEMS cantilever-type chemical sensors. Once these parametric analyses were completed, it was possible to estimate the sensitivity of the cantilever, or the ability for the cantilever to detect frequency shifts due to absorption of the target chemical. Results of the parametric analyses of the fundamental resonant frequency were then correlated with the sensitivity results based on the chemical absorption.

This Thesis correlates many results and ideas and probes problems revolving around the analysis and characterization of a MEMS cantilever-type chemical sensor.
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NOMENCLATURE

\begin{itemize}
\item $b$: width of the cantilever
\item $b_1$: width of the end of cantilever
\item $b_2$: width of point of cantilever
\item $b_t$: total width of cantilever
\item $c$: concentration of gas, damping coefficient
\item $c_c$: critical damping coefficient
\item $c_o$: initial concentration of gas
\item $c_{gas}$: concentration of gas at the surface
\item erf: Gaussian error function
\item $f$: resonant frequency
\item $f_i$: initial resonant frequency
\item $f_1$: initial resonant frequency
\item $f_2$: final resonant frequency
\item $f$: frequency
\item $h$: thickness of the cantilever
\item $h_t$: total thickness of the cantilever
\item $h_{Ti}$: thickness of the titanium layer
\item $h_{Pd}$: thickness of the palladium layer
\item $h_{\Delta}$: change of thickness constant
\item $k$: spring constant
\item $m$: effective, or dynamic, mass
\item $n$: effective mass constant
\item $n_r$: effective mass constant for a cantilever coverage at value $r$
\item $n(x)$: effective mass constant in terms of $x$
\item $p$: pressure
\item ppm: parts-per-million
\item $r$: frequency ratio, percent coverage of cantilever with polymer
\item $s$: Sievert’s constant, solution to differential equation
\item $s_{1,2}$: solution to differential equation with two roots
\item $t$: time
\item $v$: velocity
\item $v_{max}$: maximum velocity of a body
\item $w_o$: distributed load
\item $x$: position along the cantilever
\item $y$: displacement
\item $y(x)$: displacement in terms of $x$
\item $y_{max}$: maximum displacement
\item $z$: position across the cantilever
\item $A$: amplitude
\item $A$: area of shaped tip of cantilevers
\item $C_{1,2,3,4}$: constants
\end{itemize}
$D$ diffusion rate  
$E$ modulus of elasticity  
$E_{eq}$ equivalent modulus of elasticity  
$E_{Ti}$ modulus of elasticity of titanium  
$E_{Pd}$ modulus of elasticity of palladium  
$E_{Si}$ modulus of elasticity of silicon  
$F_{max}$ maximum force acting on a body  
$F$ force  
$F(y,t)$ time dependent forcing function  
$FEM$ finite element method  
$H$ thickness of damping fluid  
$I$ moment of inertia  
$K$ sensitivity vector  
$K_{1}$ direction of illumination vector  
$K_{2}$ direction of observation vector  
$KE$ kinetic energy of a system  
$L$ displacements vector  
$L$ length of the cantilever  
$L_{t}$ total length of the cantilever  
$L_{1}$ length of shaped end of cantilever  
$L_{2}$ equivalent length of the shaped end of cantilever  
$L_{3}$ length of side point of cantilever  
$M$ mass  
$M_{x}$ bending moment along the cantilever  
$MEMS$ microelectromechanical systems  
$PZT$ piezoresistive transducer  
$S_{e}$ sensitivity for an end loaded cantilever  
$S_{d}$ sensitivity for a distributed load cantilever  
$S_{m}$ mass sensitivity  
$T$ temperature  
$V_{Pd}$ volume of palladium coating  
$V_{Si}$ volume of silicon cantilever  
$V_{Ti}$ volume of titanium coating  
$V_{t}$ total volume of cantilever with coatings  
$X$ amplitude  
$X(x)$ general solution to a differential equation  
$\zeta$ damping ratio  
$\theta$ phase angle  
$\mu$ viscosity  
$\nu$ poisson’s ratio  
$\xi$ percentage area coverage by the polymer layer  
$\rho$ density  
$\rho_{eq}$ equivalent density  
$\rho_{Ti}$ density of titanium
\( \rho_{Pd} \) density of palladium
\( \rho_{Si} \) density of silicon
\( \omega \) angular frequency
\( \omega_n \) natural angular frequency
\( \omega_d \) damped angular frequency
\( \Omega \) fringe-locus function
\( (\cdot) \) matrix
\( (\cdot)^T \) transpose
\( \delta(\cdot) \) uncertainty
\( \delta m \) uncertainty in mass
\( \delta k \) uncertainty in stiffness
\( \delta f \) uncertainty in frequency
\( df \) infinitesimal change in frequency
\( dm \) infinitesimal change in mass
\( \Delta f \) finite change in frequency
\( \Delta m \) finite change in mass
\( \Delta k \) finite change in stiffness
1. OBJECTIVES

The objectives of this thesis were to design, analyze, and perform preliminary characterization of MEMS cantilever-type chemicals sensors for operation at 20°C and 1 atm pressure, using ACES methodology.
2. INTRODUCTION

To understand the methodology and processes used in this Thesis it is important to have background information on the MEMS cantilever-type chemical sensor. Many different aspects will be covered, some just for completeness, in this chapter. Each section will cover some facet of the multidisciplinary technology of these microsensors, which can be considered to be a part of a broad category of micromachines.

2.1. Micromachine beginnings

Ignoring science fiction roots, the impetus towards micromachines was inspired by Prof. Richard P. Feynman of the California Institute of Technology in Pasadena, California in 1959 (Feynman, 1992). In the late 1950’s, Prof. Feynman initiated a new area of research that is currently expanding at unprecedented rates. Technology has gone from making macrosized machines to millimeter sized to more recently, within less than two decades, micrometer sized devices as is shown in Fig. 2.1 (Pryputniewicz, 2002a). Figure 2.2 compares a micro gear with a human hair for a visual understanding of their relative scale. While nanotechnology is still largely not of everyday application at the nanometer size, the size of the new microdevices continues to decrease (Pryputniewicz, 2002b).
The most researched area of micromachines is with microelectromechanical systems (MEMS). These systems are a combination of mechanical and electrical components built into incredibly small devices that are fabricated using sophisticated integrated circuit (IC) batch processing technologies (Pryputniewicz, 2002a). MEMS began in the mid 1980’s and some of the first products were accelerometers. MEMS are intricate devices that can have several different moving parts and coupled together with
other MEMS can sense, analyze and perform complex operations in addition to being able to control and actuate motion on the microscale (Hilbert et al., 2000).

MEMS have been labeled one of the most promising and relevant technologies of the 21st century (Hilbert et al., 2000). Revolutionizing industrial and consumer products and processes, their steady infiltration into everyday life has begun to dramatically improve and change the way we live (Madou, 2002).

2.2. MEMS foreword

The acronym MEMS is used today to define both the fabrication processes and the devices resulting from these processes (Pryputniewicz and Furlong, 2003). The processes are a result of merging of advanced micromechanical and integrated circuit (IC) technologies. The methods used for making MEMS are similar to those used in the silicon wafer/chip market (Baltes et al., 2002). They are in fact mostly fabricated using silicon wafers or some variation of them. The packaging of MEMS devices also still is, for the most part, based on how chips are made (Pryputniewicz, 2003a). Packaging is a technological barrier that must be worked out, at this time, for each specific application of MEMS.

Adaptation of chip fabrication processes allowed development of bulk and surface micromachining and high-aspect ratio micromachining (HARM) (Gormley et al., 2000). Advancements in these fabrication processes allowed construction of three-dimensional devices in the micrometer scale, Fig. 2.3.
The first true MEMS using current fabrication methods appeared around 1988 as gear trains and tongs (Hsu, 2002). These relatively complex devices were the product of the fabrication techniques such as lithography and etching. Even though the technology for lithography was around for about 200 years, this was the first time it was applied at a micrometer scale. With the continued advancement of the fabrication techniques, more and more complex devices could be made. Today’s gears are capable of rotating at one million revolutions per second (Pryputniewicz et al., 2000), a giant leap from the early versions. Beginning with accelerometers and pressure sensors, development of humidity, temperature, and chemical sensors soon followed. In addition to sensors, complex devices such as micro turbines, motors, steam engines, RF switches, optical devices, and actuators have been since made, to name a few (Hilbert et al., 2000). Most of these devices have gone from research to actual commercial products. An example of this occurred in 2002. After about a decade of research, one of the most complex MEMS devices became a commercial product known as the DMD-DLP™ (Digital Micromirror Device - Digital Light Processing) (TI, 2003).
The DMD chips are used, e.g., in digital projectors capable of displaying high-resolution images by utilizing and rapidly moving some 1.3 million tiny mirrors characterized by 20 µm diagonals, each representing a single pixel, comprising a single MEMS DMD. This MEMS device utilizes a multidisciplinary approach (mechanical, electrical, optical engineering, etc.) simultaneously to produce digital images that are among the best in the world (TI, 2003). Details of construction of the DMD are shown in Fig. 2.4.

![Fig. 2.4. Details of a DMD chip (TI, 2003): (a) graphic illustration of the construction of the DMD, (b) close up on the DMD array, (c) close up with one mirror removed from the surface, (d) all the mirrors removed from the DMD, (e) close up of a single element of the DMD without mirrors.](image)

While it may seem that the only advantage for MEMS are their small size, there are indeed many additional benefits (Madou, 2002). Small sizes imply that less material
is used and less energy is consumed. Their small size allows for the construction of arrays of hundreds of them on a single chip. Many sensors are also breaking records of sensitivity with some chemical sensors having the capabilities to detect presence of individual molecules and atoms (Britton, Jr., et al., 2000).

Perhaps the most prominent advantage to MEMS is the financial factor. By being able to produce thousands of devices on each individual silicon wafer, the cost per unit can be driven down to affordable prices. This can also allow development of disposable devices, which opens entirely new product markets.

MEMS devices are rapidly making their way into every aspect of modern life. The future is getting smaller, more accurate, and quicker, and MEMS technology is aiding in the development of NEMS (Nanoelectromechanical Systems) technology (Feynman, 1992; Pryputniewicz, 2002b). NEMS, true nanotechnology, is similar to MEMS only that it deals with devices three orders of magnitude smaller in dimensions, or in the nanometer scale. At this scale, individual molecules can be moved to make devices only a few atoms in dimension.

### 2.3. Sensors

MEMS typically contain the following components: mechanical microstructures, microsensors, microactuators, and microelectronics, Fig. 2.5. These are the general components that make up MEMS as we know them today.
One of the most common applications of MEMS is by utilizing them as sensors. In fact, the original use for MEMS was as a sensor (Madou, 2002). They have become varied in their applications and can be found almost everywhere in everyday life. The popularity of these sensors is mostly due to the great advantages that they possess. In addition to their small size, MEMS sensors consume very little power and are capable of delivering accurate measurements, which are unparalleled with macro-sized sensors.

Fig. 2.5. A schematic illustration of MEMS components and their interdependence (Madou, 2002).

Perhaps the most appealing factor to MEMS sensors is that they also are very inexpensive to make. With each wafer producing thousands of sensors affordably, these sensors can now be utilized in areas that were cost prohibitive before with other means.

Regardless of application, all MEMS sensors work on the principle of measuring some form of a change, just as any macro sized sensor (Hilbert et al., 2000). Some utilize
common sensor methods while others take advantage of the benefits of the small scale. While methods may alter, MEMS sensors are able to detect a multitude of different measurable changes. These include, but are not limited to, mechanical, thermal, chemical, radiant, magnetic, and electrical changes.

Methods of operation of MEMS sensors are different depending on the use. While there are many methods along with many types of sensors there are a few mechanisms that are common among them. All sensors measure a change and MEMS devices do it with either one or a combination of the following four methods: mechanical, optical, electrical, and/or chemical. These methods are generalizations for the basic system in which a MEMS device gathers information from the surrounding environment. While measurements by MEMS sensors are not limited to these four methods, they are among the most commonly used. It should be noted that each of the methods also depends on electrical interconnections between different components of the MEMS sensor in order for it to function. Sections 2.3.1 through 2.3.4 describe these methods in more detail.

2.3.1. Mechanical detection

Certain MEMS sensors measure changes based on mechanical displacement or movement. These are some of the most appealing and intricate of the sensors. This motion is caused, or accented, by relevant external force(s). It can then be detected either externally with optics or internally with electrical electrodes. One of the most common is
the MEMS accelerometer (Bernstein et al., 1999; Hsu, 2002). A sample accelerometer is shown in Fig. 2.6.

In the MEMS accelerometer, Fig. 2.6, there is a proof mass that is suspended on springs and allowed to move in one or two directions, but because of operational requirements of the device, out-of-plane motion is limited. External forces act upon the proof mass causing it to displace. This motion, in turn, changes relative positions between stationary and moving parts of capacitive pickups in the microaccelerometer (represented by long finger-like protrusions in Fig. 2.6), which can be measured electronically as changes in capacitance. These changes in capacitance are interpreted into usable data.

![Fig. 2.6. A view of the “sensor” part of a dual-axis accelerometer where the proof mass can be seen with all the perforations in the middle and a quarter-view close up on one of its corners (AD, 2003).](image)

Another common type of mechanically actuated sensor is the pressure sensor, which also is one of the oldest type of MEMS sensors. There are several different
designs for MEMS pressure sensors, but they all can be classified as either one of the following three types: absolute, gage, and differential pressure (Pryputniewicz et al. 2002a; Johari, 2003). Typically, they are constructed as a cavity covered with a diaphragm. When an external pressure is applied to the diaphragm, it deforms, due to stresses produced by applied loads. These stresses are picked up by electrical piezoresistors on the diaphragm, which in turn produce an electrical signal. By measuring this signal and interpreting it, the pressure is determined.

2.3.2. Optical detection

While most of the applications for MOEMS (micro-optoelectromechanical systems) are in communications there are a number of uses in other areas (Madou, 2002). Sensing differences in incoming light compared to the outputted light is the basis for optical detection outside of communication purposes. Light is usually passed through, reflected off, or altered by some space containing a medium in question. Some of these sensors are for the detection of chemicals. This shows the multidisciplinary aspect of these devices. Infrared spectrometry is an example of a method that can be used for optical detection (Wang et al., 1999; Wuttig et al., 2002). Another example is the Fabry-Perot optical sensor (Han et al., 1996). Simply said, this sensor works by introducing a gas into a chamber and then passing light through the chamber. Due to changes in the chemical composition the light passing through will be different than without the gas.
This light is analyzed and from the results a determination can be made about the type of
gas being tested. This sensor works similarly to a test tube experiment.

2.3.3. Electrical detection

The bulk of all MEMS sensors rely on electrical connections for power and as
means of transferring data from the device into the macro world where they can be
accessed and analyzed.

Piezoresistors are used for the production of electric currents. Piezoresistors are
components that convert mechanical energy into electrical and vice versa (MS, 1998).
By attaching a piezoresistor to a mechanism that moves, an electrical signal can be
produced and measured. From the signal measurements, parameters defining the motion
of the body can be calculated.

2.3.4. Chemical detection

The detection of chemicals using other chemicals is the basis for the chemical
detection method. It is based on calculated and known reactions between certain
chemicals. When specific chemicals interact a reaction occurs. Effects of these reactions
are known and can be used to determine what chemical caused the reaction. These
effects are often exploited by, but not limited to, the use of polymers. In the broad sense,
a polymer is a laboratory made chemical that can be used for a variety of purposes including controlled, calculated reactions (Lange et al., 2001; Thundat et al., 2000). Polymers for MEMS can be engineered to be sensitive only to specific types of chemicals. When these chemicals are present near the polymer, they get absorbed (or adsorbed) onto it and change one or a few of the properties (e.g., illuminescence, color, opacity, conductivity, resistivity, etc.) of the polymers. This effect is particularly useful and is utilized in several different ways.

One way of utilizing this selective polymer sensitivity is with the artificial tongue sensor, or Fabry-Perot sensor (Yoo et al., 1997). Micro storage wells are filled with tiny beads of a polymer designed to attract a specific chemical, as shown in Fig. 2.7, and are illuminated from behind.

![Fig. 2.7](image)

The analyte is released over the wells and the polymer beads absorb the selected chemical. Once the polymer absorbs the suspect analyte, there is a chemical reaction that causes a change in color or luminescence in the bead. Because of the illumination from behind, it is possible to detect these shifts in color. This change is detected with a CCD
(Charge Coupled Device) array, and means that the sensor identified the suspect chemical. Since each well is very small, it is possible to make many wells, each with a different polymer designed for detecting a different chemical. By having many wells filled with different polymers it is possible to measure complex analytes quickly as well as being able to detect multiple analytes simultaneously.

A far more robust method of using polymers, however, is with cantilever sensing elements. Cantilever elements also rely on polymer absorption, but utilize it differently. A micron sized cantilever, Fig. 2.8, is coated with the polymer of choice that is then exposed to the suspect analyte (Ilic et al., 2000, 2001).

When the polymer absorbs the desired chemical, it changes the mass of the cantilever, which in turn changes the fundamental frequency of the cantilever. With the cantilever attached to piezoresistors, this change can then be measured and the analyte can be identified.

Fig. 2.8. Micron sized cantilevers developed at IBM for research purposes (IBM, 2002).
2.4. MEMS cantilever chemical sensor

Detection of chemicals is required for many industries. MEMS sensors bring a novel solution for that requirement in small devices with high sensitivity. One aspect of these sensors is that they be customized for most applications. While they seem like the perfect solution, they are not without flaws.

There are many aspects to chemical sensors. They can be simple or highly complex. In most cases, they are very accurate. It is possible, for example, for a cantilever sensor to detect mass changes in picograms (Madou, 2002). Many different technologies must come together in order to allow development of MEMS (Pryputniewicz, 2002b). Sections 2.4.1 through 2.4.16 discuss some of the aspects of MEMS cantilever chemical sensor technology and while not all of them will pertain directly to this Thesis they were inserted for completeness and future work.

2.4.1. Material

The most commonly used material for fabricating MEMS devices is silicon and silicon compounds (Madou, 2002). Although there are many other materials that can also be used, the overall properties of silicon are very good at small scales (Petersen, 1982; Pryputniewicz, 2002b). Combination of the yield strength and modulus of elasticity (among other properties) of silicon is especially useful for the life and durability of small devices. Some other materials, such as silicon carbide or diamond, offer better properties
but they also cost many times more than silicon making them uneconomical except for
the most demanding and specific purposes (Thaysen et al., 2002).

For the fabrication of MEMS and CMOS (complementary metal-oxide semiconductor) chips alike, silicon is first processed into ingots of about 4 feet in length. Ingots are bars of silicon (or of any other chip materials) with 99.99% purity. Purity is essential to making consistent flawless devices. The ingots are specially made with the crystallographic orientation of the silicon arranged into either [100] or [111] as these are the most commonly used (Madou, 2002). Silicon ingots and wafers are shown in Fig. 2.9 during fabrication and after slicing.

Fig. 2.9. Initial steps in fabrication of MEMS and CMOS chips: (a) preparation of a silicon for slicing, (b) visual inspection of silicon wafers (MEMC, 2003).

This crystallographic orientation of silicon allows MEMS to have well defined and sharp edges and shapes with perpendicular angles resulting from etching as described
in Section 2.4.2. The ingots are then sliced into wafers usually ranging from 100 mm to 300 mm in diameter and about 1 mm in thickness. These wafers act as the substrate or foundation for all MEMS devices.

2.4.2. Fabrication

The fabrication of MEMS is an entire field of research on its own (Pryputniewicz, 2002a). It is extremely diverse and still expanding (Madou, 2002). With the growing number of companies that fabricate MEMS, the technology is continually improving. With each breakthrough, MEMS technology becomes more affordable, better, and easier to fabricate in ever increasing quantities. The technology is also pushing the size envelope and continually working towards the development of smaller devices such as NEMS (Madou, 2002).

There are several different processes for producing MEMS; most prominent of these, however, is lithography. Lithography currently produces the smallest and most exact features available in MEMS (Pryputniewicz, 2003a). It is comparable to dry etching, which has many different sub-methods. Surface micromachining and dry etching have an advantage over other techniques such as bulk micromachining and LIGA (German acronym for x-ray lithography, electrodeposition, and molding) in the size of the features made.

MEMS devices are fabricated in a manner similar to making a cake. Layers are deposited on one another, patterned, and the components are released to form 3D
structures. Depending on the process, the number of layers, and the complexity of the design, the fabrication process can take up to a few months.

MEMS devices are fabricated on wafers made usually of silicon, as described in Section 2.4.1. Using one of the processes available, a MEMS is built up one layer at a time. In most cases, the layer is grown in a vapor filled environment. This growth can be time consuming, but there have been improvements in it. These improvements include automation of the steps. This automation has allowed the price of MEMS to be reduced while improving quality of the devices that are produced. One place of such improvement is at Sandia National Laboratories (SNL) in Albuquerque, New Mexico (SNL, 2001). SNL has developed an automated process known as SUMMiT™-V (Sandia’s Ultra-planar MEMS Multilevel Technology), which is capable of fabricating MEMS devices out of up to 5 structural layers in complexity, Fig. 2.10 (Pryputniewicz, 2002a). SNL is the only place in the world, at this time, capable of fabricating a 5 layer MEMS using a sacrificial surface micromachining process. The rest of the world is limited to 3 layer fabrication processes.

Fig. 2.10. Examples of SUMMiT™-V process: (a) a ratchet gear, (b) a clutch activated transmission, (c) a thermally actuated motor, (d) example of the 5 structural layers of deposition (SNL, 2001).
While it may seem simple, the fabrication of each layer is quite complex. Using lithography, for example, a series of steps are required for each layer (Hsu, 2002; Madou, 2002; Pryputniewicz, 2002a). Starting with the deposition of the first structural polysilicon layer onto the wafer, the polysilicon is exposed to masks, light, and chemicals to etch holes and/or dimples. The next layer is sacrificial and it is also exposed to masks, light, and chemicals to continue with the fabrication. Masks somewhat resemble cookie cutters cutting out shapes in a layer of cookie dough. The light used is to harden, or soften, certain parts of a given layer so that when they are exposed to specific chemicals, they will etch away leaving the desired shapes. The deposition and etching steps alternate between the structural polysilicon layers and the sacrificial SiO₂ layers making shapes in each layer and continuing until the desired device is fabricated.

2.4.3. Packaging

One of the biggest hurdles in MEMS technology is with packaging, Fig. 2.11. The development of MEMS devices has come a long way and new boundaries have been reached (Pryputniewicz, 1986; Pryputniewicz et al., 2001a; Hsu, 2002; Pryputniewicz, 2002b; 2003). A problem still remains however in being able to communicate efficiently with these devices. While MEMS are small, the packages that contain them are still considerable in size to facilitate their handling and assembly. Packaging of MEMS is application specific. It is too vast for the scope of this Thesis and will not be addressed herein.
2.4.4. Sensing types and methods

As discussed in Sections 2.3.1 through 2.3.4, MEMS sensors are used for a variety of purposes. Most of the different types of chemical sensors available are targeted for the detection of specific chemicals. These can either be regular, simple composition chemicals or complex biological agents. Chemical sensors have even been used for the detection of DNA strands with different base sequences (Fritz et al., 2000a) and are also capable of measuring pH values in analytes (Bashir et al., 2002). With so many different types of sensors, it is necessary to categorize the chemical detection methods to better understand MEMS.

Of the different types of sensors, there are two basic methods of operation to detect chemicals. The two methods could be called contact and non-contact methods.
Contact methods include any system in which the analyte is physically touched or altered. In non-contact mode, the analyte is observed from a distance and its behavior and/or characteristics are measured and studied.

The contact method uses polymers deposited on cantilever sensing elements to absorb the specific chemicals and thus produce a change in mass, stress, electrical, or thermal properties of the element. For a change in mass, an increase in mass can be detected by measuring the change in frequency of the resonating cantilever, which has mass as one of its parameters, Fig. 2.12. The second way is by measuring change in stress in the element, which occurs when mass is absorbed into the polymer. This stress (or surface stress) change can then be measured by piezoresistors on the surface of the sensing element. The other way to detect the suspect chemical is to use a thermocouple to measure the change in temperature due to heat produced from the absorption of the analyte by the polymer. All of these methods have been successfully incorporated into chemical sensors (Koll et al., 1999; Lang et al., 1999; Jensenius et al., 2000; Kerness et al., 2000; Thaysen et al., 2001; Subramanian et al., 2002; Baselt et al., 2003).

Two other methods of interest are SAW (Surface Acoustic Wave) and BAW (Bulk Acoustic Wave) sensors, Fig. 2.12 (Ivanov, 2000). They function when the analyte comes in contact with the polymer “containing” either a surface or a bulk wave that travels through the material. A change in these waves can be measured with sensors. The downside of these methods is that they have a much lower accuracy when compared with the methods described earlier in this section.
Fig. 2.12. Operation of different gravimetric sensors: (a) graphic illustration of a cantilever bending under the load of analytes attaching to the polymer coating, (b) illustration behind the principles of BAW and SAW (Ivanov, 2000).

2.4.5. Resonance frequency

The main principle behind cantilever sensors is with the measuring of change in the resonance frequency (Betts et al., 2000). Resonance frequency is the frequency that produces the largest amplitude that a vibrating body can achieve. This frequency is dependent on the spring constant of the body and its dynamic mass. Should one or the other of these parameters change, the resonant frequency will also change. This is the basis behind using change in resonance frequency as means of detection. Alteration in the mass of a vibrating cantilever changes the total mass, which in turn shifts the resonant frequency to some other frequency. By measuring this shift, one can determine the amount of mass that was added to the cantilever assuming the spring constant remained constant. If the cantilever is selective to the kind of analyte it absorbs, then in addition to detecting the chemical, if present, the sensor can also detect the concentration of it. This method of chemical detection is highly accurate. Some experiments have successfully
demonstrated the ability to detect a change in mass of as little as 0.7 picograms (Madou, 2002).

2.4.6. Cantilever actuation methods

In order for the MEMS sensor to function in dynamic, or frequency, response mode, it is necessary for the cantilever to be vibrating (Arecco and Pryputniewicz, 2003). There are several ways of actuating a cantilever into its resonance frequency, which can be classified as direct and indirect actuation methods (Cho and Ahn, 2002; Li et al., 2002; Stephan et al., 2002). Indirect methods include using acoustic vibration to shake the sensor much like a piece of paper in front of a speaker vibrates from the compression waves in the air. Another indirect method has a magnetic coat deposited on the cantilever and an inductance coil underneath it to generate magnetic fields that attract and repel the cantilever into vibration.

For direct methods, the most common is by the use of a PZT (Pb-Zr-Ti transducer or, as it is sometimes called, piezoelectric z-axis actuating transducer), which is capable of vibrating at different frequencies very accurately depending on the driving voltage (Harley, 2002; Mehta et al., 2001; Turner and Zhang, 2001). Another method that is less common, but of great interest, is by fabricating piezoresistive electrodes directly on the cantilever and bending it rapidly into vibration by bimorph actuation. Figure 2.13 shows some sample PZTs available commercially.
It is of interest to combine and use direct and indirect methods when conducting research. It is even possible to combine both direct methods into one package that allows for high-speed functionality (Kim et al., 2003).

2.4.7. Cantilever I/O

In order for the sensor to function it is necessary to have some means of communicating out the data it collects. There are several ways of accomplishing this and the most relevant to this Thesis will be discussed.
One of the most common ways of detecting frequency shifts is by optically inspecting the cantilever. Using a technique similar to those in AFMs (atomic force microscopes), a laser is reflected off the cantilever tip and into a position sensitive diode (PSD) (Raiteri et al., 2001; Kim et al., 2001a; Battiston et al., 2001). The reflected angle changes due to the bending of the cantilever. This change is detected by the PSD and it can be measured and analyzed, Fig. 2.14. While the technique is proven and quite reliable, it is too bulky for portable purposes.

Fig. 2.14. Graphical illustration of the operational principle for an AFM where different bend angles reflect the laser beam to different locations on the PSD.

Another method that is also quite popular is by using piezoresistive elements on the cantilever itself (Porter et al., 2003; Lange et al., 2002). Any changes in the surface stress due to bending will cause an electrical output from the piezoresistive electrodes.
This output can be analyzed and the frequency can be calculated. Figure 2.15 shows how a typical piezoresistor is used on a cantilever.

![Cantilever with integrated piezoresistors](image)

**Fig. 2.15.** Cantilever with integrated piezoresistors: (a) view of piezoresistive cantilever used for scanning probe microscopy (SPM) applications, (b) close up of the Wheatstone bridge piezoresistive elements (Gotszalk et al., 2000).

### 2.4.8. Polymer thickness

In fabricating cantilever sensors with special coatings it is important to take into account the thickness of this layer. The thickness affects several aspects of the sensor. Mostly, it affects the rate at which the polymer becomes saturated with the suspect analyte (Britton et al., 2000). The thicker the polymer, the longer it takes for the polymer to reach saturation. This is not really a problem unless time is a critical factor in the function of the sensor. It is generally preferred to make the coating as thin as possible, however, to minimize other effects. One of the most prominent of these effects is that of residual stresses which will be discussed in Section 2.4.14.1. A thicker layer of polymer
is more reactive to effects of different coefficients of thermal expansion and also it is more sensitive to pressure effects, which are discussed in Sections 2.4.16.

2.4.10. Fick’s law of diffusion

For any particle that is absorbed into another there is a rate at which the diffusion takes place (Hughes and Bastasz, 1988; Streeter et al., 1998; Hu, 2001). During diffusion, or mass transport, a gas (or liquid) with a higher concentration of a sample will move into an area of lesser concentration. Diffusion is usually an interstitial motion in that the sample gas travels to the voids in the lattice structure of a material. The diffusion can be modeled with Ficks’ laws. These laws address two specific conditions, steady state and nonlinear (non-steady) diffusion. During steady state diffusion (first law), the rate is constant, as it would be in an ideal condition with infinite volumes of gas passing through a membrane. The nonlinear state (second law) is a more accurate model for finite volume cases where the diffusion rate will change as the concentration gradient equalizes.

2.4.11. Reference cantilevers

In order to guarantee sensor functionality and reliability, the data quality must be high. Because of signal noise from a variety of different sources, such as thermal effects,
electrical noise, and others, it is important to include a parallel system to improve the signal. By incorporating a reference cantilever it is possible to minimize noise and improve the signal quality. Reference cantilevers function by having them react to only the noise producing effects, which means that they are not coated with the analyte-attracting polymer (Thaysen et al., 2000). The signals of the reference and coated cantilevers can then be compared and external forces (noise) can be removed computationally thus improving quality of data.

2.4.12. Quality factor

Most vibrating mechanical structures have a variable known as the quality factor, Q (or Q-value) (Yasumura et al., 2000). This value is a non-dimensional parameter for quantitatively assessing the ‘quality’ of a structure. In other words, the Q-value is a measure of how much energy is dissipated in a vibrating system. The higher the Q-value, the better the structure is capable to conserve energy. If the structure can conserve energy efficiently, the structure can operate longer and produce more data. It should be noted that Q has a great dependence on damping and thus the environment that the structure operates in. Structures in air usually operate much better than those in liquids and the Q will be the highest in a vacuum environment (Tamayo et al., 2001).

The quality factor is reflected in the shape of a resonance frequency peak. The narrower the peak of the frequency response curve, the higher the Q value is while the opposite is also true. The width of the peak is also sometimes referred to as the
bandwidth of the resonance frequency curve. This bandwidth is measured at half power points, though, for consistency and convenience.

2.4.13. Electrical aspects

Practically all MEMS devices collect measurements electronically. This means that there must be a mechanism for producing a signal to the macro world. The signal produced must be directly linked to the motion, or action, that the MEMS performs in order to determine quantitative results. This mechanical to electrical effect is accomplished with a phenomenon usually referred to as a piezoresistive effect (MS, 1998). The piezoresistive effect is the change in electrical resistivity that occurs with the application of mechanical stress, which allows conversion of stress into proportional, measurable electrical signals. The piezoresistive effect is observed in piezoresistive elements and materials.

One of the most common gauges used is a piezoresistive strain gauge (Chow et al., 2002; Thaysen et al., 2002). They are used for detecting the action, or motion, that is incurred in a sensor. The gauge is usually attached to, or built into, the device as that will produce the most accurate results. The operation is based upon measuring increasing stress/strain in an element of the MEMS. When a strain is produced in the gauge, an electric signal is generated. This signal can then be amplified and measured.
2.4.13.1. Wheatstone bridge

The basic and most commonly used method of gathering and measuring the electric signal generated from gauges is with a Wheatstone bridge circuit, Fig. 2.16. The Wheatstone bridge is a classic and common configuration for determining voltage differences in electrical circuits. Four resistors are connected together with a middle resistor, \( R_1 \), (usually the strain gauge or other measuring gauge) acting as a gate switch. Any variation in current in the middle resistor will cause a difference in voltage output from the circuit (Pauw, 1958). For MEMS applications, the middle resistor would be a piezoresistive element, which can change its resistance with mechanical changes.

![Wheatstone bridge diagram](image)

Fig. 2.16. Wheatstone bridge where changes, e.g., in \( R_1 \), alter the output voltage with a high accuracy and precision.

2.4.13.2. Feedback loop

Because the method of extracting data is usually electrical, there is typically noise present in the results. This noise and errors in the data can be reduced, however, with the
use of feed back loops (Abadal et al., 2001; Humphris et al., 2000; Sulcheck et al., 2000). Feed back loops is a post processing technique used to increase accuracy of the data in which the data are refined several times. It is utilized with computers and special circuit setups. Active feed back loops continuously correct the data being processed so that error is minimized. These can be very complex systems and require a lot of knowledge in electrical engineering. Because of time, equipment, and complexity concerns, feed back loops will not be incorporated into the experiments planned for this Thesis.

2.4.14. Inherent problems

In designing a MEMS device, there are a multitude of variables that must be accounted for. With so many variables, there are inherent problems that arise (Handel, 2001; Manias et al., 2001; Kassegne et al., 2002). Tweaking and adjusting of techniques and design can overcome most, however. There are two problems, though, that are reoccurring and of some concern: residual fabrication stresses and stiction.

2.4.14.1. Residual stresses

During the fabrication of a multi-layered MEMS device two or more dissimilar layers are deposited on top of one another depending on the process and design. Because of differences in coefficients of thermal expansion (CTE) of the materials, residual
stresses will be produced in these layers due to the fabrication processes (Fritz et al., 2000b; Lu et al., 2001; Pryputniewicz et al., 2002c, 2003b). A lot of the fabrication techniques involve depositing layers at high temperatures (600°C +). When the fabrication is over and temperatures return to room temperature (~20°C), different materials will shrink (or expand) by different amounts leading to stress gradients (Pryputniewicz, 2003a, 2003b). These gradients will manifest themselves as warping of structures, cracks, or other failure modes; Fig. 2.17 shows the effects of residual stresses on a MEMS component. This is a constant design problem that must be taken into account. One method of reducing and/or eliminating residual stresses is by annealing the device after the deposition process. Anneling is a process of heating the device at a certain temperature for a specific time in order to allow for any stress to dissipate. This is a proven process, but requires a lot of experimental verification and takes up valuable production time.

Fig. 2.17. Effects of residual stresses: (a) a MEMS device is bent after its release, (b) a close up on the device showing how extreme the bending is (Dartmouth, 2002).
2.4.14.2. Stiction

A very common problem that plagues devices with small thickness (1 to 4 µm) is a phenomenon known as stiction. Stiction is probably the most serious of problems that occur in micromachining (Buks and Roukes, 2001). Stiction occurs when two flat surfaces are near each other, Fig. 2.18. This close proximity along with forces such as van der Waals cause the components to tend to stick to one another.

![Diagram of Polysilicon beam, Constraint base, Sacrificial layer, and Possible Fracture](image)

Fig. 2.18. Collapse of a thin cantilever due to stiction.

In a cantilever type sensor, stiction can cripple a device making it useless. It is possible to fix stiction, but during that process excessive forces are required which can damage or destroy the device. Another major problem with stiction is that it can occur at any time and not just during fabrication. There are solutions for this problem. New organic modifiers (coatings) have been developed against stiction and have been tested and shown to lessen the effect (Kim et al., 2001b). With some limited solutions already in place and continued research, stiction will hopefully become a problem of the past in the near future.
2.4.15. Effects of temperature

Temperature has a critical effect on the functionality of the MEMS sensors (Hanson et al., 2001; Pryputniewicz, 2003a). Because the cantilever sensor is based on a bimaterial (e.g., substrate and polymer coating) there will be two materials and thus two coefficients of thermal expansion. Any temperature change in the environment will affect the beam (Gotszalk et al., 2000). Increase or decrease in the temperature will produce a surface stress on the cantilever due to different CTEs and thus create a pronounced bending as shown by Stoney (1909) and Pryputniewicz et al. (2003a). This bending can alter results of any detection system setup. If any temperature change will be expected it is necessary to include reference beams to allow for the compensation of this phenomenon (Hanson et al., 2001). For producing better results and data it would be desirable to reduce the temperature induced bending, as this would lessen the amount of compensation required from the reference beams. This means that the temperature of the sample should ideally remain as constant as possible. The effects of temperature have been, however, capitalized to create calorimeters with femto-range accuracy, Fig. 2.19 (Kerness et al., 2000).

2.4.16. Effects of pressure

The pressure of the environment in which the sensor is in can affect the results produced. If the pressure of the environment increases, the dynamic viscosity of the damping fluid increases. This increase in damping reduces the Q-value and can also
reduce the deflection of the cantilever which both, in turn, decreases the data quality and reliability. In addition to changing the damping, an increase in pressure will also alter the concentration of the gas in the environment, which can affect the absorption rate, and equilibrium giving shifted results.

Fig. 2.19. A femtocalorimeter utilizing thermal bending effects with piezoresistors (Gotszalk et al., 2000).
3. MEMS SAMPLES

This chapter describes the MEMS samples used in this Thesis and their characteristic parameters and includes information for the proposed MEMS chemical sensor.

3.1. MikroMasch USA cantilevers

Sample cantilevers used in this Thesis were purchased from MikroMasch USA (MM, 2003). The company is headquartered in Estonia, Spain, and their main product are atomic force microscope (AFM) chips. AFM chips are silicon-based cantilevers that have a high aspect ratio tip at the end. They are used for topographic surveying on the nanometer scale of the samples investigated. The samples used in this Thesis are actual AFM contact silicon cantilevers that are uncoated and also are without any tips, model number CSC12 (MM, 2003). They are micromachined cantilevers with the fixed ends being integral parts of a chip. It is important that the cantilevers be uncoated so that a special coating can be deposited on them without any other underlying layer. Figure 3.1 shows an AFM chip with cantilevers with tips from MikroMasch, while Fig. 3.2 shows the special samples purchased for this Thesis. The nomenclature illustration in Fig. 3.1 applies to the samples used in this Thesis. In fact, the labeling of the cantilevers (A-F) shall be used from here on to refer to each cantilever, as only the three longest cantilevers (D-F) shall be investigated in this Thesis. Table 3.1 lists the manufacturer’s specifications of the samples purchased. As can be seen from the photographs, the chips
contain 6 cantilevers of varying lengths, all listed in Table 3.1. The thickness and width of each of the cantilevers should be the same according to manufacturers specifications. The cantilevers and the chips are all made of single-crystal silicon with the dimensions and material properties listed in Table 3.1.

![Fig. 3.1. MikroMasch AFM chip: (a) SEM photograph of cantilevers (A,B,C) with tips, (b) dimensions of the chip and cantilevers as well as a standardized nomenclature (MM, 2003).](image)

Table 3.1. Characteristic dimensions, as supplied by the manufacturer, MikroMasch USA, and the corresponding material properties as listed by Madou (2002).

<table>
<thead>
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<th>Characteristics</th>
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<td></td>
<td>35</td>
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<td></td>
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</tr>
<tr>
<td>Thickness, $h \pm 0.3 \mu m$</td>
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<td>1.3</td>
<td>0.7</td>
<td>1</td>
<td>1.3</td>
</tr>
<tr>
<td>Resonance freq., $f$ kHz</td>
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<td>105</td>
<td>150</td>
<td>95</td>
<td>155</td>
<td>230</td>
</tr>
<tr>
<td>Force constant, $k$ N/m</td>
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<td>0.95</td>
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<td>0.45</td>
<td>1.75</td>
<td>5</td>
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<tr>
<td></td>
<td>D</td>
<td>E</td>
<td>F</td>
<td>D</td>
<td>E</td>
<td>F</td>
</tr>
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<td>350</td>
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<tr>
<td>Width, $b \pm 3 \mu m$</td>
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<td>35</td>
<td>35</td>
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<td>35</td>
</tr>
<tr>
<td>Thickness, $h \pm 0.3 \mu m$</td>
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<td>1.3</td>
<td>0.7</td>
<td>1</td>
<td>1.3</td>
</tr>
<tr>
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<td>7</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>Force constant, $k$ N/m</td>
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<td>0.1</td>
<td>0.01</td>
<td>0.03</td>
<td>0.08</td>
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<tr>
<td>Modulus of elasticity, $E \pm 3$ GPa</td>
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<td></td>
<td>2.33</td>
<td>2.33</td>
<td></td>
<td>2.33</td>
</tr>
</tbody>
</table>

Density, $\rho \pm 0.05$ g/cm$^3$ | 2.33
Fig. 3.2. Photographs of the AFM chips used in this Thesis: (a) a view of the entire chip from above with all the cantilevers visible. The cantilevers of interest are the ones on the right, (b) a top view of the primary cantilevers used in this Thesis (D,E,F), (c) a photograph of the underside of the cantilevers (D,E,F).

### 3.2. Chemicals used

This Thesis is based around a sensor that is capable of detecting a specific chemical. Thus it is important to select a chemical that is easy to detect and useful for research purposes. While it is possible to detect just about any analyte with the right polymer, some polymers are easier to make and are more accessible than others. Due to the focus of this Thesis and time/cost issues, availability played an important role in determining the polymer/analyte combination to use. In the process of coating, there are
many different types of materials that are fairly standard and can be found and used easily and quickly. Most are not used for a gravimetric chemical sensor, but there are a few that are. One of these materials is palladium (Pd). Palladium will, at room temperature, absorb 800-900 times its own volume of hydrogen (Lewis, 1967). This is a significant amount for a very reasonable condition. The process is also reversible. The palladium-hydrogen system is very well documented and very easy to conduct experiments with (Lewis, 1967). While there are other absorption systems, they are much more complex and can be very difficult to set up and maintain. Most systems are not reversible in absorption without some kind of treatment to the absorbing material.

3.2.1. Palladium

The element palladium (Pd) was selected as the absorbent layer for the cantilever because of its sensitivity to hydrogen (Darling, 1958). As mentioned in Section 3.2, it has an ability to absorb (not adsorb) great quantities of hydrogen. It is in fact a very unique ability in that there are few other materials that naturally behave as palladium does with hydrogen. Because of this phenomenon, palladium is often used as a filter of hydrogen as when it is heated; only hydrogen will diffuse through it. A true benefit of this interaction for the Thesis is that the absorption will occur at room temperature. The hydrogen then desorbs out of the palladium when the hydrogen source is removed. These are highly desired features that simplify the experiments. Properties of palladium are found in Appendix A.
3.2.2. Hydrogen

The element hydrogen (H$_2$) is the lightest and most abundant in the universe. It is a very versatile element and a very promising fuel. When it burns the only by-product is water. The one fact about hydrogen that limits its use is its explosive nature. Hydrogen is explosive from 4% - 40% concentration. This means that if the concentration is below or above that range, hydrogen will not burn. Because of this range, great care must be taken when setting up any experiment dealing in hydrogen to prevent a concentration greater than 4%. Pre-mixing a nitrogen-hydrogen gas with 1% and less hydrogen concentration reduces the risk factor. This would be acceptable since this Thesis will investigate a sensor for detecting the lower concentration limits (<<1% hydrogen). Nitrogen would be the inert gas carrier for this experiment as it is very stable and helps reduce humidity from the cantilevers. In the setup, special care will be used to ensure safety during the experiments. Properties of hydrogen can be found in Appendix A.

3.2.3. Titanium

There will be a small amount of titanium (Ti) used in the coating of the cantilevers. During the deposition process, a thin layer of Ti will be placed before coating the cantilever with palladium. The reason behind this thin layer is to help prevent delamination, or separation, of the palladium from the single-crystal silicon cantilever. It has been seen that palladium will delaminate in the presence of hydrogen if it is directly coated onto silicon. For this reason, a very thin layer (approximately 10 Å of Ti) will be
used as an adhesive layer between the silicon and the palladium. Even though the layer is very small, it will be accounted for in calculations. The properties of titanium can be found in Appendix A.

3.3. Coating process

Once all the materials have been selected for coating the cantilever, it is necessary to use a technique that will allow for the deposition of layers with accurate thickness. For this task, resources such as those at Case Western Reserve University (CWRU) in Cleveland, Ohio can be used. There, a sputtering machine can be used to coat layers of Ti and different, controlled thickness of Pd on the cantilevers. The thickness for palladium, as will be discussed in Chapter 4, only affects the length of time for the absorption process to complete. To verify this, it would be recommended to get two different Pd thicknesses: 1000 Å and 2000 Å.

For the calculations in this Thesis, it was assumed that the deposition process would be ideal in that there is a perfect bonding between the layers and there are no imperfections. This is a fairly safe assumption to make given the nature of the deposition process. It was also assumed that the properties of the layers (including the silicon substrate) are isotropic in nature.
3.3.1. Complete versus partial coating

Coating the cantilever with palladium can alter the results, quality, and sensitivity of the sensor. Therefore, it is important to consider the placement of the palladium coating. Calculations describing sensitivity and placement of the palladium on the cantilever are discussed in Chapter 4. As it will be shown in Section 5.8, coating the entire length of the cantilever is beneficial to the sensitivity. In addition to coating the entire length, all five sides (top, bottom, left and right sides, and tip) shall be coated. By doing this, bending effects due to any differences in the values of parameters characterizing coatings can be minimized, as there will be (ideally) equal and opposite bending moments and stress gradients. Figure 3.3 illustrates the differences between bending moments of a fully coated on both sides (i.e., top and bottom) and a one-side (i.e., top only) cantilever. It is assumed that the deposition of any titanium and palladium is uniform throughout and that this will also effectively minimize, or even eliminate, any bending effects.

Fig. 3.3. Bending moment comparison: (a) the bending moments of a fully coated cantilever where the moments cancel each other, (b) the moments of a one-side coated cantilever. where moments add to each other.
3.3.2. Effects of humidity

Once the cantilever is coated with palladium, it will be sensitive to humidity in the air (Baselt et al., 2003). Palladium will naturally start to form palladium oxide in the presence of water or oxygen, which will slow or prevent hydrogen absorption. This will cause the palladium to expand as well. As the palladium oxide is exposed to hydrogen, the oxide will slowly recede and the palladium will become pure again allowing for the hydrogen to absorb normally. For this reason, care should be taken to ensure that the cantilever experiments will be conducted in an oxygen free environment with as little humidity as possible. With the hydrogen being delivered in nitrogen–hydrogen mix, the relative humidity will be reduced, and potentially eliminated, as oxygen will be removed from the environment around the cantilevers. This would resolve any humidity problems that might arise.

3.3.3. Time limits

For the palladium to reach 100% saturation of hydrogen, the time required is exponentially high in that it will take an infinite amount of time for the hydrogen to reach complete equilibrium in the palladium. For this reason, the experiments should be run till the saturation level is only 90%. This diffusion process is described in more detail in Section 4.2.4.1. For desorption, the time is just as long, if not longer, taking up to days depending on the varying conditions of the system, which is unacceptably long for practical operation of the sensor. Because it is very hard to fully remove 100% of all the
hydrogen once it has been absorbed into the palladium, there would be some residual left over. This residual hydrogen will keep the palladium lattice permanently changed. Over the course of several runs, the absorption/desorption process will deteriorate the structure eventually leading the palladium to fail via cracks or delamination. Because of this limitation, the first few runs are the most important for data collection and the total number of experiments conducted on each chip should be minimized while increasing the total number of chips experimented on to help improve the quality of the information gathered.
4. METHODOLOGY

This Thesis conducts a study to optimize performance of a cantilever chemical sensor, which is to operate at the conditions of room temperature (~20°C) and sea level pressure (1 atm). Because of its nature, this study will be based on the analytical, computational, and experimental solutions (ACES) methodology (Pryputniewicz, 1997; Pryputniewicz et al., 2001a, 2003a).

4.1. ACES methodology

The methodology used in this Thesis is known as ACES (analytical, computational, experimental solutions), Fig. 4.1. This methodology uses analytical, computational, and experimental solutions to obtain results which otherwise might be difficult to obtain.

The analytical part of the solution is based on exact, close form solutions. These solutions are applicable when the boundary, loading, and initial conditions can be specified, or in other word, for the equations to be comprehensive to all the aspects of the problem. The information generated greatly facilitates any computational and experimental work that needs to be performed.

The computational solution is based on using finite element method (FEM) software to model the problem and to produce approximations of the solution. The
solutions are based on discretization of the governing partial differential equations (PDEs).

Fig. 4.1. Graphical representation of ACES methodology and the interdependence of each solutions category towards determining a final result.

Because of continued efforts to advance experimental capabilities, a number of different methods have been developed. Practicality of these methods, however, depends on the specific application. For example, in this Thesis, optoelectronic laser interferometric microscopy (OELIM), laser vibrometry, atomic force microscopy (AFM), and scanning electron microscopy (SEM) methodologies were used. Each method carries with it its own strength and weakness. However, comprehensive testing using several methods can improve the overall quality of the data. This is one reason for comparing the analytical and computational solutions to the experimental.
4.2. Analytical investigations

In order to commence calculations for the analytical investigation of the cantilever, it is necessary to understand what must be evaluated. There are a number of publications (Battiston et al., 2001; Bashir et al., 2002; Baselt, 1993; Britton et al., 1999; Brown and Pryputniewicz, 1992, 1995, 1996, 2000; Pryputniewicz, 1985a, 1988, 1991a, 1991b, 1995, 1996, 1998, 2003b, Pryputniewicz et al., 2001b, 2001c, 2002a, 2002b, Pryputniewicz and Stetson, 1990) listing different properties and characteristics of cantilevers. Some of the publications address issues that must be considered. For this Thesis, a sensor will be investigated that operates at room temperature and 1 atm pressure. Sections 4.2.1 through 4.2.11 describe some of the necessary issues that need to be considered in the calculations for this cantilever based chemical sensor.

Several different cases will be considered while analyzing a vibrating cantilever. They will take into account different combinations of parameters characterizing a vibrating body. These parameters describe damping, stiffness, external forces, and other characteristics of the cantilever-type MEMS sensor. Depending on the specific set of parameters used, the results might change. Once the different cases or scenarios are taken into account, the results of each will be compared. This will help in determining how each parameter affects the overall results.
4.2.1. Sensitivity

A way of measuring how well a sensor functions is by determining its sensitivity. It is important to determine the sensitivity of the cantilever, as there are different ways of coating the cantilever with palladium. By different ways, it is meant that by coating the entire cantilever versus just coating a small portion at the tip with palladium the sensitivity will change. It is also important to clarify the condition of the sensitivity. The cantilever will be exposed to hydrogen until the coating of palladium reaches 90% of saturation. This will allow mass of hydrogen to accumulate on the cantilever leading to a shift in frequency. The sensitivity can then be defined as the ability for the cantilever to detect shifts in the frequency. The higher the sensitivity of the cantilever, the better it will function.

Sensitivity, $S_m$, of this sensor can be defined as a function of the frequency shift and the absorbed analyte mass, (Madou, 2002) i.e.,

$$S_m = \lim_{\Delta m \to 0} \frac{1}{f_i} \frac{\Delta f}{\Delta m} = \frac{1}{f_i} \frac{\partial f}{\partial m},$$  \hspace{1cm} (4.1)

where $f_i$ is the initial frequency, $\Delta f$ and $\partial f$ are finite and infinitesimal, respectively, changes in the frequency, and $\Delta m$ and $\partial m$ are the changes mass (see Appendix B).

Additional Figure 4.2 illustrates the boundary conditions and equivalent system of the cantilever.

Calculating the sensitivity is important in determining the best location for the polymer coating. Changing the coverage of the cantilever by the polymer can alter the sensitivity of the sensor.
Fig. 4.2. Idealization and modeling of a cantilever.

If we cover the cantilever only at the tip or with just a small percentage compared to the entire cantilever we get sensitivity for an end loaded cantilever, \( S_e \), as (see Appendix B for derivation)

\[
S_e = \frac{-1}{2} \left( k \sqrt{\frac{k}{m}} \sqrt{\frac{k}{m+nr\Delta m}} \right)^2, \tag{4.2}
\]

where \( k \) is the spring constant of the cantilever, \( n \) is the effective mass constant, \( r \) is the percent area coverage by the polymer layer of the cantilever, \( m \) is the original effective mass (see Appendix B.3), and \( \Delta m \) is the change in mass of the cantilever. For simplification of the problem, it will be assumed that there is no change in the spring constant.

The percentage area coverage, \( r \), used was estimated from Fig. 5.16 of the dynamic mass effect on the cantilever. Derivation of the dynamic mass utilizing the boundary conditions of a cantilever, Fig. 4.2, uses the kinetic energy, \( KE \), equation

\[
KE = \frac{1}{2}mv^2, \tag{4.3}
\]
where \( m \) is the mass of the moving body and \( v \) is its velocity. If the equation is solved subject to the cantilever boundary conditions of a sensing element, the final solution is

\[
KE = \frac{v_{\text{max}}^2}{2} C_1 n(x) \ ,
\]

where \( v_{\text{max}} \) is the maximum velocity experienced by the body in motion, \( C_1 \) is a constant that is comprised of structural properties of the cantilever, and \( n(x) \) is a constant that varies with the position along the cantilever that describes the effective mass. From Eqs 4.2 to 4.4, the correct amount of coverage can be calculated to analyze the cantilever sensitivity.

If we now look at the case where the polymer covers the entire cantilever the sensitivity for a distributed load, \( S_d \), will be

\[
S_d = \frac{k}{2} \left[ \frac{1}{\sqrt{\frac{33}{140} M}} \right]^2 \left[ \frac{1}{\sqrt{\frac{33}{140} (M + \Delta m)}} \right]^2 \ ,
\]

where \( M \) is the mass of the cantilever. It is now possible to compare the two equations and determine which will produce the largest frequency shift. Increasing the sensitivity increases the detectable shift in frequency of the cantilever. In determining the sensitivity of the cantilever sensor it is important to maximize this response, as it will directly determine performance of the sensor (Hu et al., 2001; Lange et al., 2001; Hsu, 2002; Yu et al., 2002). High sensitivity can be defined as the ability to detect a very small frequency response.
4.2.2. Equivalent variables

In order to model the cantilever more accurately, it is necessary to account for all the layers and coatings on it. Each layer of the cantilever will have a different material, which in turn means that it has a different modulus of elasticity and density. When calculating the frequency shift it is necessary to use an equivalent value for both parameters. The equation for the equivalent modulus of elasticity is (Jones, 1975; Berthelot, 1999)

\[
E_{eq} = \frac{(E_{Si}E_{Ti}E_{Pd})V_i}{E_{Ti}E_{Pd}V_{Si} + E_{Si}E_{Pd}V_{Ti} + E_{Si}E_{Ti}V_{Pd}},
\]  

(4.6)

where \(E_{Si,Ti,Pd}\) are the moduli of silicon, titanium, and palladium, respectively, \(V_{Si,Ti,Pd}\) are the volume fractions for each element, and \(V_i\) is the total volume. Equation 4.6 is used along with the following equation for the equivalent density (Jones, 1975; Berthelot, 1999):

\[
\rho_{eq} = \frac{\rho_{Si}V_{Si} + \rho_{Ti}V_{Ti} + \rho_{Pd}V_{Pd}}{V_{Si} + V_{Ti} + V_{Pd}},
\]

(4.7)

where \(\rho_{Si,Ti,Pd}\) are the densities of silicon, titanium, and palladium, and \(h_{Si,Ti,Pd}\) are the thicknesses of each of the material layers, respectively.

4.2.3. Gas concentration

Since the hydrogen that is to be sensed would be in a gas form it is necessary to understand how to deal with any gas calculations. The two most common ways of
referring to gas concentrations are with percent concentration (%) and with parts-per-million (ppm). The relationship between the two forms is

\[ 0.0001\% = 1 \text{ ppm} \]

where the concentration of the volume of the analyte gas to the carrier gas is equated. To use concentration in equations, it is necessary to convert it into a more useful form such as density, i.e.,

\[ \frac{1 \text{ mg}}{m^3} = \left[ \frac{\text{ppm} \cdot (\text{molecular weight}) \cdot 273 \cdot p}{0.0224 \cdot \text{mol} \cdot T} \right] \]

where \( \text{ppm} \) is the gas concentration in parts-per-million, \( \text{molecular weight} \) is the molecular weight of the sample analyte, and \( p \) and \( T \) are the partial pressure (in atm) and temperature (in °K) of the gas, respectively. Using Eq. 4.9 it is possible to estimate the amount of mass that will be absorbed for a given volume of palladium. It is important to note though that the partial pressure is of the gas to be detected from a sample of a gaseous mixture, in this case hydrogen, and will play a vital role in the results.

### 4.2.4. Absorption

The main operating principle of the cantilever sensor is its ability to absorb an analyte and thus alter resonant frequency of the sensing element. To determine the maximum amount of hydrogen that can be absorbed into the palladium it is necessary to look at the steady state situation. The amount of hydrogen that is absorbed varies with
different pressures and temperatures. According to experimental results, reported in literature throughout the years, absorption of hydrogen is nonlinear at lower temperatures, Fig. 4.3. This figure shows the relationship between the partial pressure of hydrogen and the atomic ratio (at equilibrium) at different temperatures. The atomic ratio (H/Pd) is the volumetric, or mass ratio, between two elements in a given volume. In this case, the atomic ratio compares the hydrogen volume in palladium. While the figure is accurate, it does not list the temperature, ~20°C, or room temperature, that is of interest.

Since the hydrogen that is to be investigated will be in a mixture with nitrogen, we must look at the partial pressures of the hydrogen. The total pressure for the mixture will be at 1 atm (101kPa), so for a concentration of 1% hydrogen the partial pressure will be 0.01 atm (1.01kPa) and the figure indicates that the atomic ratio, or absorption of hydrogen, will be around 0.621 at 20°C. While this is not the specified temperature, it is fairly close and the atomic ratio listed for this temperature (20°C) will be used.

However, Fig. 4.3 does not have much information about very small pressures, which for this Thesis equals the small concentrations (<0.1% or <1000 ppm) that are of interest. There is very little information about the atomic ratio at such small concentrations available. Because of this, the atomic ratio at 1 ppm had to be approximated from the available information. Since the concentration is proportional to the partial pressure, which in turn is proportional to the atomic ratio, a square root relationship was used to relate the small concentrations with the atomic ratio. The square root proportionality comes from Sievert’s Law that states (Lewis, 1967)

\[ c = s \sqrt{p} \quad , \]  

(4.10)
where \( c \) is the hydrogen concentration in equilibrium in the palladium, \( s \) is the Sievert’s constant parameter, and \( p \) is the partial pressure of the hydrogen. Using Eq. 4.10, the atomic ratio was approximated at small partial pressures for equivalent concentrations. It is important to note that Fig. 4.3 is assumed as completely correct, as the uncertainty in the curves in the figure will be zero for isotropic conditions of palladium. Table 4.1 lists several steady state concentrations at different pressures along with several conversions of the atomic ratio.

Using information summarized in Table 4.1, it is possible to estimate the amount of mass that would accumulate on the cantilever and thus cause a shift in frequency.

Fig. 4.3. Concentration and pressure relationships based on experimental data of many research studies conducted throughout the years, where the concentration, \( AR \), is in units of atomic ratio (H/Pd) (Lewis, 1967).
4.2.4.1. Diffusion rate

It is of importance to determine how long it will take for the hydrogen concentration to reach equilibrium in the palladium. For this information, it is necessary to have the diffusion rate, $D$. This rate has also been experimentally found for steady state permeation rates and is $5.4 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$ at a temperature of 25°C for diffusion of hydrogen into palladium (Alefeld and Völkl, 1978a, 1978b). A graphical representation was developed by Lewis (1967) to illustrate the permeation rates and importance of flow at higher temperatures, Fig. 4.4.

Since the temperature at which the experiment should be performed at is around 20°C and with a static flow of hydrogen, the permeation rate will be fairly high according to Fig. 4.4. This is what is desired as it also simplifies the experiment by not having to set up mass flow controllers.
The diffusion rate of a sample concentration can be analytically found using Fick’s second law of diffusion (Streeter et al., 1998; Hu et al., 2001)

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2},
\]

where \( c \) is the concentration and \( D \) is the diffusion rate. Fick’s second law applies to systems that are not operating in an infinite volume condition, as is the case for this Thesis. If the boundary conditions of the experimental setup are implemented, including Sievert’s Law of square root proportionality (Hughes and Bastasz, 1988; Hu et al., 2001), the equation has a solution of the form
\[
\frac{\sqrt{c_{\text{gas}}} - \sqrt{c}}{\sqrt{c_{\text{gas}}} - \sqrt{c_0}} = \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right), \tag{4.12}
\]

where \(c_{\text{gas}}\) is the concentration of the gas at the surface of the absorbing layer (in this case palladium), \(c_0\) is the initial concentration within the layer, \(c\) is the concentration at a certain depth, \(x\), and \(t\) is time required for the sample at depth \(x\) to reach a concentration of \(c\). The term \(\text{erf}\) stands for the error function, which is a Gaussian error function that is tabulated in mathematical tables (Spiegel and Liu, 1999). If the initial concentration of the palladium is zero then Eq. 4.12 simplifies to

\[
\sqrt{c} = \sqrt{c_{\text{gas}}} \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right], \tag{4.13}
\]

where the error function is always a constant and thus the argument within the error function is constant. Therefore, Eq. 4.13 can be solved to show that the depth variable, \(x\), is proportional to the square of the time, i.e.,

\[
\left( \frac{x}{2\sqrt{Dt}} = \text{Const.} \right) \rightarrow \left( x = \text{Const.} \cdot 2\sqrt{D} \sqrt{t} \right) \rightarrow x \propto \sqrt{t}. \tag{4.14}
\]

Equation 4.14 shows that the thickness of the polymer layer (palladium) will only affect the length of time required for the layer to reach equilibrium. As was stated in Section 3.3, the desired thickness for conducting experiments shall be 1000 Å and 2000 Å. For the analytical calculations in Sections 4.2.5, a palladium thickness of 1000 Å will be used.
4.2.4.2. Volume increase

Because the hydrogen will be absorbing into the palladium interstitially, there will be an increase in the lattice structure size. Palladium metal has a lattice constant of 3.889 Å and can increase up to 3.893 Å with hydrogen absorption. This increase varies with the concentration. There currently are limited data on this lattice increase, but a graph was compiled over the years that displays several experimental data points from many different previous experiments and fits a line accordingly, Fig. 4.5 (Alefeld and Völkl, 1978a, 1978b).

From Fig. 4.5 it is possible to estimate how much the volume will be affected at any concentration of hydrogen. It is interesting to note, though, that the slope of the line is fairly steep at 1/5 so that when the concentration is at 1% or the atomic ratio is 0.621 H/Pd, the volume change will be approximately 12.4%. It was assumed that the data of Fig. 4.5 were accurate in that there is no uncertainty in the values generated from it. In order to account for this volume change, which can affect the modulus of elasticity, it should be included in the analytical calculations where possible. However, because the spring constant is dependent on individual geometric values (length, width, height) instead of volume and it cannot be simplified, this change in volume is assumed to affect only the height (thickness) of the cantilever. This will lead to results that will vary slightly from the true value.
4.2.4.3. Change in modulus of elasticity

While there are changes in the lattice volume, the absorption of the hydrogen in palladium will also affect the stiffness (and resonant frequency) because of changes in the modulus of elasticity. It has been documented and shown that the modulus of elasticity decreases as hydrogen is absorbed into the palladium (Lewis, 1967). This decrease is shown in Fig. 4.6, which was estimated from experimentally determined data by Krüger.
and Jungnitz (1936) at ambient room temperature (~20°C), which is the temperature condition for this Thesis.

Fig. 4.6. Estimated results from experimental data illustrating the change that occurs in the modulus of elasticity during absorption of hydrogen into palladium (Lewis, 1967).

From Fig. 4.6 it is clear that it will be necessary to include a changing modulus of elasticity in the analytical calculations in order to maintain accuracy. When the atomic ratio (H/Pd) is at around 0.621, the modulus of elasticity will decrease by about 10%, which is a considerable amount. Once again, the data from Fig. 4.6 were assumed as accurate and when conducting any calculations, no uncertainty was considered for it.
However, this change in modulus was only implemented in the analytical calculations when the spring constant was considered a variable. The condition for incorporating this changing stiffness will be described in more detail in Section 4.2.5.

4.2.5. Resonant frequency and frequency shift

In order to determine the amount of mass collected, the fundamental frequency must first be determined. Starting with the general equation for a vibrating body (Rao, 1995) we get

\[ F(y, t) = m \frac{d^2 y(t)}{dt^2} + c \frac{dy}{dt} + ky \quad , \]  \hspace{1cm} (4.15)

where if damping, \( c \), and external forces, \( F(y, t) \), are not included we get a function in terms of dynamic, or effective, mass, \( m \), and stiffness, \( k \), as

\[ 0 = m \frac{d^2 y(t)}{dt^2} + ky \quad . \]  \hspace{1cm} (4.16)

The homogeneous differential equation, represented by Eq. 4.16, can be solved for the fundamental frequency of vibration to obtain (Pryputniewicz, 2002b)

\[ f = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad , \]  \hspace{1cm} (4.17)

where \( k \) is the spring constant for the cantilever and \( m \) is its effective or dynamic mass. The effective mass was calculated for a cantilever and is 33/140, or about 0.24, of the total (i.e., static) mass for the cantilever. As Eq. 4.17 shows, any change in mass will
change the frequency of the cantilever, subject to modifications of the spring constant
(Furlong and Pryputniewicz, 1995). This equation was used for determining frequency of
the cantilever for the simplified case, discussed later in this section, which will be
compared against computational and experimental data. Uncertainty calculations will
also be conducted on this frequency, which will be described in more detail in Section
4.2.11. It should be noted that the calculation of the dynamic mass and all other
equations can be found in Appendix B.

The dynamic mass written in its explicit form is

\[ m = \frac{33}{140} \rho bhL \]  

where \( \rho \) is the density of the cantilever, while \( b, h, \) and \( L \) are the geometric dimensions of
the cantilever, as shown in Fig. 4.7.

Fig. 4.7. Representation of cantilever with geometric dimensions and a cross section
view through the middle with each of the layers of the cantilever labeled.

Several different cases of the resonant frequency shall be looked at in the
calculations. The first case will look at the simplest scenario where the only variable that
changes during the absorption process is the mass of palladium, as it increases. If the absorption of hydrogen does not change the spring constant of the palladium, the equation for calculating the frequency shift due to absorbed mass can be written as

\[ \frac{f_1^2 - f_2^2}{f_2^2} = \frac{\Delta m}{m}, \]  

(4.19)

where \( f_{i=1,2} \) are the initial and final frequencies of vibration, respectively, \( m \) the dynamic mass of the cantilever, and \( \Delta m \) the absorbed mass accumulated causing \( f_i \) to change to \( f_2 \).

Equation 4.19 can be rewritten in terms of the final frequency, \( f_2 \). Once that is determined, it is possible to calculate the shift in the frequency due to the absorption of hydrogen at any given concentration. In this Thesis, 1% hydrogen (in a 1 atm pressure nitrogen-hydrogen mix) will be used as the concentration of hydrogen for the calculations.

In this Thesis, in order to determine frequency shift, the gas concentration will be 1% hydrogen in a 99% nitrogen mix at a total of 1 atm pressure and 20°C and the palladium coating will be 1000 Å thick.

### 4.2.6. Spring constant consideration

Every oscillating, or vibrating, body has a parameter known as the spring constant, or stiffness, \( k \). The spring constant is the value that relates to the elastic energy that can be stored and released in a body for a given distance. It is defined as a ratio of force and the corresponding displacement, i.e., (Young and Freedman, 2000)
where $k$ is the spring constant, $F$ is the force acting on the spring, and $x$ is the displacement of the spring. It is possible to simplify the spring constant into a set of variables that pertain to the characteristics of the cantilever. Using the cantilever boundary conditions of the sensing element, the spring constant can be shown to be (Pryputniewicz, 2002b)

$$k = \frac{Eb h^3}{4L^3},$$

where $E$ is the modulus of elasticity, while $b$, $h$, and $L$ are the width, thickness, and length of the cantilever, respectively, Fig. 4.7. Equation 4.21 shows how important the structural dimensions of the cantilever are to the spring constant. Also, since the thickness and length are cubed, they significantly affect the value of $k$.

A varying spring constant is one variable that is usually not taken into consideration in studies dealing with cantilever type MEMS. Most publications simply calculate the static spring constant of the polymer-coated cantilever. However, it is important to note that as the palladium absorbs the hydrogen, the spring constant of the cantilever changes (Cherian and Thundat, 2002; Jericho and Jericho, 2002; Gibson et al., 2001). This dynamically changing spring constant will be included in the calculations. In Eq. 4.19, a change in frequency is determined based on a change in mass; this equation will have to be modified, however, if the absorbed mass changes the spring constant. The new equation where the spring constant changes as the mass changes is derived in Appendix B, i.e.,
\[ f_2 = \sqrt{\frac{f_1^2}{1 + \frac{\Delta k}{k}}} \left(1 + \frac{\Delta m}{m}\right), \]  

where \( \Delta k \) and \( \Delta m \) are the changes in the spring constant and effective mass, respectively, and \( k \) and \( m \) are the initial spring constant and effective mass, respectively. Substituting Eqs 4.18 and 4.21 into Eq. 4.17, the initial frequency \( f_i \) can also be expressed as

\[ f_i = \frac{1}{2\pi E} \sqrt{\frac{35 E}{33 \rho}}. \]  

If the spring constant value alters, it will be by a change of the parameters of Eq. 4.21 that, in turn, will affect Eq. 4.23. A change in stiffness will come from either a change of volume, a change of the modulus of elasticity, or a combination of both. Since it was shown in Sections 4.2.4.2 and 4.2.4.3, that the modulus of elasticity and the volume change with the absorption of hydrogen it is reasonable to state that there will be changes in the spring constant, which depend on these parameters. Stating again, however, the increase in the palladium volume will be considered to affect the thickness and, in turn, stiffness. The results of Section 5.11.5 will show that this is a reasonable argument.

### 4.2.7. Damping coefficient consideration

Damping is the phenomenon that reduces/absorbs energy of a vibrating system over a period of time. There is damping everywhere in the real world. It is present in all
applications with an exception of systems vibrating in vacuum environment. Damping helps bring everything to an equilibrium state and maintain it in a static condition.

When doing measurements and calculations, damping plays an important part in order to get accurate results. It is necessary to understand when and how damping will affect a given system. Even though the cantilever sensor is only on the order of 300 µm long, damping will alter results if it is not noticed and considered (Rast et al., 2000). Only if the cantilever is in vacuum there will be no damping due to the surrounding medium. However, when the analyte gas is released, it itself will damp the cantilever.

The most common place that damping occurs is in oscillating or vibrating bodies. Damping itself is a force dependent process that can be expressed as (Young and Freedman, 2000)

\[
c = -\frac{F}{v},
\]

where \( F \) is the force acting upon the body, \( v \) is the velocity of the body, and \( c \) is the damping coefficient, which for a specific set of parameters defining a vibrating body and its environment is a constant that describes the “strength” of the damping force. The negative sign in Eq. 4.24 indicates that the damping force acts against the body and attempts to reduce the total energy acting upon it.

The damping coefficient can also be written as a function of several parameters defining the damping fluid and the volume that it occupies, i.e.,

\[
c = \frac{2\mu Lb}{H},
\]
where $\mu$ is the dynamic viscosity of the damping fluid, $L$ and $b$ are the length and width of the cantilever, respectively, and $H$ is the nominal thickness of the fluid film that the object moves through. There are two items of importance to note when examining Eq. 4.25. One is that the thickness of the cantilever is not a variable in the relationship defining the damping coefficient. The other is the obvious relation of how the viscosity of a fluid alters the damping. This will play a role in the quality factor, which will be discussed in Section 4.2.8. For this Thesis, the damping coefficient will be calculated analytically and then it will be experimentally verified in order to ensure that the frequency shift calculations are being properly represented. The experimental determination of the damping coefficient will be discussed in Section 4.4.4.

### 4.2.8. Free vibration system

If we look at Eq. 4.15 defining motion of a free vibration system, based on discussion in Section 4.2.5, i.e.,

$$0 = m \frac{d^2 y(t)}{dt^2} + c \frac{dy(t)}{dt} + ky,$$

(4.26)

where there are no external forces, it demonstrates that damping and the spring constant need to be considered in any calculations for the free vibration system. If this homogeneous equation is solved for an underdamped system characterized by where

(Young and Freedman, 2000)
with $\omega$ being the angular frequency, the solution will be

$$y(t) = Ae^{-\left(c/2m\right)t} \cos\left(\omega_d t + \theta\right)$$

where $A$ is the amplitude of the vibration, $t$ is time, and $\theta$ is the phase. The $\omega_d$ is the damped angular frequency defined by the equation

$$\omega_d = \sqrt{\frac{k}{m} - \frac{c^2}{4m^2}}$$

which clearly shows that damping decreases the angular frequency; derivation of Eq. 4.29 can be found in Appendix B. While damping affects the frequency, adding mass affects the damping. Angular frequency is related to cyclic frequency by the following equality:

$$f = \frac{\omega}{2\pi}$$

Inserting Eq. 4.29 into Eq. 4.30 and simplifying, a relationship for detecting frequency shifts, similar to Eq. 4.19, but include damping can be showed to be

(derivation found in Appendix B)

$$f_2 = \sqrt{f_1^2 \frac{4(m + \delta m)mk - mc^2}{4k(m + \delta m)^2}}$$

where $f_1$ is the initial frequency and other parameters are as previously defined. Using Eq. 4.31, the frequency shift in the presence of damping was calculated analytically.
4.2.9. Changing stiffness in a free vibration system

Sections 4.2.6 and 4.2.8 described effects that a changing stiffness and damping, respectively, have on the frequency shift calculations. To further improve the analytical model, both parameters will be considered together in the same equation. Starting with Eq. 4.29, the equation takes the form of

\[
\delta = \sqrt{f_1^2 \frac{4(m + \delta m)mk - mc^2}{4(k + \delta k)(m + \delta m)^2}},
\]

which is very similar to Eq. 4.31. Equation 4.32 was used to determine the frequency shift that occurs when both the stiffness and damping changes are considered simultaneously.

4.2.10. Harmonically excited system

To model the cantilever system completely, it will be required to take into account, in addition to the parameters mentioned in Section 4.2.9, the excitation force needed to get it into its resonance. Using the general equation for a body in motion, Eq. 4.15, it is possible to calculate the maximum amplitude. The steady state solution for the second-order nonhomogeneous differential equation is the particular solution, or (Young and Freedman, 2000)

\[
y(t) = A \cos(\omega t - \theta),
\]

(4.33)
where $\omega$ is the angular frequency of excitation, $A$ is the vibration amplitude and has the solution of (Young and Freedman, 2000)

$$A = \frac{F_{\text{max}}}{k \sqrt{(1 - r^2)^2 + (2\zeta r)^2}} \quad (4.34)$$

with $F_{\text{max}}$ being the maximum force applied to the vibrating body, and $\zeta$ being the damping ratio. The parameter $r$ is defined as the frequency ratio

$$r = \left( \frac{\omega}{\omega_n} \right), \quad (4.35)$$

where $\omega_n$ is the natural frequency of the body and the solution for the phase, $\theta$, in Eq. 4.33 is (Young and Freedman, 2000)

$$\theta = \tan^{-1} \left( \frac{2\zeta r}{1-r^2} \right). \quad (4.36)$$

Looking at the parameters of Eq. 4.35 we see that the driving force will vibrate at the natural frequency and thus the entire body should be vibrating at this frequency.

When this frequency is the same as the resonance, or natural, frequency, the frequency ratio will be equal to one and the amplitude will be at its maximum, Fig. 4.8, which is exactly what is desired when attempting to detect frequencies. The amplitude ratio shown in Fig. 4.8 is equal to $Ak/F_{\text{max}}$ so that the displacement is unitless. The damping ratio,

$$\zeta = \frac{c}{c_c} = \frac{c}{2m\omega_n}, \quad (4.37)$$

is the relationship between the damping, $c$, and the critical damping, $c_c$. The critical damping coefficient is the magnitude of damping required to make vibrations decrease
the quickest, or in other words, reduce the amount of energy in the system and also prevent any subsequent amplitudes.

The equipment (vibrometer and interferometric methods) used in detecting the frequency shift, however, will be vibrating the cantilevers over a range of frequencies in order to see the resonant frequency curve peak. Because the frequency ratio will always be equal to one (once the resonance frequency is reached), the system can be modeled with the equation for frequency shift of a free vibration system.

![Graph showing vibration amplitude as a function of frequency ratio for different values of damping ratio.](image)

Fig. 4.8. Vibration amplitude as a function of frequency ratio for different values of damping ratio.
4.2.11. Uncertainty analysis

For each case considered in this Thesis, there was an associated overall uncertainty determined. These uncertainties indicate how “good” the results are and what contribution each parameter has to the specific overall uncertainty. The derivation for each case is located in Appendix B, but for illustration purposes, only one case shall be looked at in this section.

For the uncertainty analysis conducted in this Thesis, the RSS (root-sum-squares) method shall be used (Pryputniewicz, 1993). The first part of the RSS method is to write the equation that is going to be analyzed in its phenomenological form, or in an equation that lists all independent parameters of Eq. 4.23 as

\[ f_i = (h, L, E, \rho) \]  \hspace{1cm} (4.38)

where it can be seen that the independent parameters of the equation for frequency are thickness, \( h \), length, \( L \), modulus of elasticity, \( E \), and density, \( \rho \). Based on Eq. 4.38, the overall uncertainty in frequency, \( \delta f_1 \), is

\[ \delta f_1 = \left( \frac{\partial f_i}{\partial h} \delta h \right)^2 + \left( \frac{\partial f_i}{\partial L} \delta L \right)^2 + \left( \frac{\partial f_i}{\partial E} \delta E \right)^2 + \left( \frac{\partial f_i}{\partial \rho} \delta \rho \right)^2 \right)^{\frac{1}{2}} \]  \hspace{1cm} (4.39)

where \( \delta h \), \( \delta L \), \( \delta E \), and \( \delta \rho \) are the uncertainties in the specified parameters. Using Eqs 4.38 and 4.39 it is possible to calculate the percentage overall uncertainty in the resonance frequency, \( \% \delta f_i \), as

\[ \% \delta f_i = \left( \frac{\delta f_i}{f_i} \right) \times 100 \]  \hspace{1cm} (4.40)
It is also possible to calculate the percent contributions of the uncertainties in the independent parameters to the overall uncertainty by using the following form:

\[
\%\delta f_i, \delta h = \frac{\left( \frac{\partial f_i}{\partial h} \delta h \right)^2}{\delta f_i^2} \cdot 100 ,
\]

(4.41)

where \(\%\delta f_i, \delta h\) is the percent contribution of the uncertainty in thickness to the overall uncertainty in the frequency. Equation 4.41 can be applied to each parameter to determine the contributions of each of them to the overall uncertainty. This is important in order to better understand how reliable the frequency data are and to determine where any sources of errors come from. Results of uncertainty analysis for each case presented in Sections 4.2.5 through 4.2.10 are summarized in Appendix C.

4.3. Computational analysis

The ACES methodology requires thorough work with computational analysis. The computational analysis helped visualize the effects of vibration on the cantilever. Using finite element method (FEM) software, a model of the cantilever was developed. For this Thesis, Pro/Engineer was used to model the cantilevers using data gathered from measurements of the cantilever (PTC, 2003a). The software Pro/Mechanica, a FEM package, was used for the modal analysis (PTC, 2003b). Using Pro/Mechanica, the resonance frequencies of a cantilever were determined based on the model developed in Pro/Engineer. For the computational solutions, two cases were considered. The first
utilized ideal dimensional values, such as those specified by the manufacturer, and the second used the averaged values based on measurements of the cantilever. Once the initial results from Pro/Mechanica were obtained, they were checked to assure their validity, subject to the input information. This check looks at the convergence of the solution. The solution should converge to within at least of 1% to be acceptable. The convergence percent is the amount of difference between two most recent solution points. When the difference between the two calculated values is 1% or less, the solution is said to have converged.

4.4. Experimental solutions

ACES methodology requires gathering experiment data. This step was conducted with the cantilevers that were procured from MikroMasch USA as described in Chapter 3. For the analytical calculations, 6 chips (each with 3 cantilevers) were fully measured using SEM, vibrometer, AFM, and OELIM systems. Increasing the number of methods used decreases errors in results. For this Thesis, 6 chips were taken as the sample set. The experimental results are compared in Section 5.6.
4.4.1. Instrument calibration

To properly conduct experiments, it is essential that all of the testing equipment was functioning and calibrated correctly. All areas of sources of errors must be reduced to a minimum to ensure quality data. Calibration of instruments is crucial to collecting valid data. While seeming redundant, it is also important to make sure that each piece of equipment is working properly.

4.4.2. Geometrical characterization of the cantilevers

To be able to characterize dynamics of the cantilevers used in this Thesis, it was important to quantitatively determine their dimensions (Pryputniewicz, 1993; Yang et al., 2000; Pryputniewicz et al., 2002b). Using an optical microscope, geometry of the cantilevers was measured. This verified quality of fabrication and aided in the analytical calculations and the computational modeling.

Measurements of dimensions of the cantilevers were made using a measurescope equipped microscope capable of providing dimensions with the least count of 0.5 µm (Pryputniewicz, 1993). Each cantilever was measured and all the results were correlated. Since the free ends of the cantilevers were not square, it was necessary to calculate an equivalent length that compensated for the irregularly shaped tip based on the measurements that were taken. With the equivalent length for each cantilever the analytical calculations were performed.
4.4.3. SEM – scanning electron microscope

To inspect and verify the thickness of the cantilevers a scanning electron microscope (SEM) was used, Fig. 4.9. An optical microscope can easily view in the $x$-$y$ plane, but because of the geometric configuration of the chips used the thickness or $z$-axis of the cantilevers was not easily measurable and thus had to be determined using the SEM.

Fig. 4.9. SEM used for measuring thickness of the cantilevers. The samples were inserted into the chamber on the left (bottom of the black tube) and the microscope was controlled with the console on the right.
4.4.4. Determination of quality factor and damping coefficient

The quality factor (Q-value, or Q) is an important parameter of a vibrating body. It describes the “quality” or the width of the resonance frequency peak. The narrower the resonance frequency peak, the easier and more distinct the peak is to detect. The quality factor is dependent on the damping and, since the damping plays an important role in the calculations, it is necessary to measure it. In the opinion of this author, it is appropriate to discuss a procedure for the determination of Q, at this point in the chapter addressing methodology, because Q is a function of thickness, a method for determination of which was outlined in Section 4.4.3. The general relationship for the quality factor can be written as

\[ Q = \frac{m \omega_n}{c} \frac{\omega_n}{\text{bandwidth}}, \] \hspace{1cm} (4.42)

where \( \omega_n \) is the angular frequency, \( m \) is the dynamic mass of body, and \( c \) is the damping coefficient. The \( \text{bandwidth} \), appearing in Eq. 4.42, is the width of the frequency curve, Fig. 4.10, at half power point. The half power point is defined to be

\[ \frac{A}{\sqrt{2}} \] \hspace{1cm} (4.43)

of the peak value of the resonance frequency curve, where \( A \) is the maximum amplitude of the vibration at a specific frequency (Rao, 1995). Once the bandwidth is known, it is possible to calculate what the damping coefficient is using the identity

\[ \text{bandwidth} = \frac{c}{m}. \] \hspace{1cm} (4.44)
The result can then be compared to the analytically determined damping coefficient in Eq. 4.25.

![Figure 4.10](image)

Fig. 4.10. A comparison of how different resonant frequency response curves affect the width of the bandwidth, which in turn will affect Eq. 4.42.

The method described above also allows for determination of the $H$ value, or the nominal thickness of the fluid film that the object moves through, as used in Eq. 4.25. The value of $H$ is basically the maximum displacement of the cantilever at resonant frequency. For detecting the resonant frequency curve a laser vibrometer was used, as discussed in Section 4.4.7.

### 4.4.5. Optoelectronic methodology

As mentioned in the beginning of Section 4.4, an interferometric setup was used for full-field of view identification of the resonant frequencies of the cantilever samples.
Specifically, an optoelectronic laser interferometric microscope (OELIM) was used. The OELIM measured frequency values were then compared to the analytically and computationally calculated values to determine the degree of correlation between them.

Optoelectronic methodology, as presented in this paper, is based on the principles of optoelectronic holography (OEH) (Brown, 1999; Furlong, 1999; Furlong and Pryputniewicz, 2002; Pryputniewicz et al., 2000). Basic configuration of the OEH system is shown in Fig. 4.11. In this configuration, laser light is launched into a single mode optical fiber by means of a microscope objective (MO). Then, the single mode fiber is coupled into two fibers by means of a fiber optic directional coupler (DC). One of the optical fibers comprising the DC is used to illuminate the object, while the output from the other fiber provides reference against which the signals from the object are recorded. Both, the object and reference beams are combined by the interferometer (IT) and recorded by the system camera (CCD).

Images recorded by the CCD are processed by the image-processing computer (IP) to determine the fringe-locus function, $\Omega$, constant values of which define fringe loci on the surface of object under investigation. The values of $\Omega$ relate to the system geometry and the unknown vector $L$, defining deformations, via the relationship (Pryputniewicz, 1995a)

$$\Omega = (K_2 - K_1) \cdot L = K \cdot L,$$  \hspace{1cm} (4.45)

where $K$ is the sensitivity vector defined in terms of vectors $K_1$ and $K_2$ identifying directions of illumination and observation, respectively, in the OEH system, Fig. 4.11.
Quantitative determination of structural deformations due to the applied loads can be obtained, by solving a system of equations similar to Eq. 4.45, to yield

\[ L = \left( \tilde{K}^T \tilde{K} \right)^{-1} \left( \tilde{K}^T \Omega \right), \quad (4.46) \]

where \( \tilde{K}^T \) represents the transpose of the matrix of the sensitivity vectors \( K \).

Equation 4.45 indicates that deformations determined from interferograms are functions of \( K \) and \( \Omega \), which have spatial, i.e., \((x,y,z)\), distributions over the field of interest on the object being investigated. Equation 4.45 can be represented by a phenomenological equation (Pryputniewicz, 1993)
\[
\mathbf{L} = \mathbf{L}(\mathbf{K}, \Omega),
\]

based on which the RSS-type (where RSS represents the square root of the sum of the squares) overall uncertainty in \( \mathbf{L} \), i.e., \( \delta\mathbf{L} \), can be determined to be

\[
\delta\mathbf{L} = \left[ \left( \frac{\partial \mathbf{L}}{\partial \mathbf{K}} \delta\mathbf{K} \right)^2 + \left( \frac{\partial \mathbf{L}}{\partial \Omega} \delta\Omega \right)^2 \right]^{1/2},
\]

where \( \partial\mathbf{L}/\partial\mathbf{K} \) and \( \partial\mathbf{L}/\partial\Omega \) represent partial derivatives of \( \mathbf{L} \) with respect to \( \mathbf{K} \) and \( \Omega \), respectively, while \( \delta\mathbf{K} \) and \( \delta\Omega \) represent the uncertainties in \( \mathbf{K} \) and \( \Omega \), respectively. It should be remembered that \( \mathbf{K} \), \( \mathbf{L} \), and \( \Omega \) are functions of spatial coordinates \((x,y,z)\), i.e., \( \mathbf{K} = \mathbf{K}(x,y,z) \), \( \mathbf{L} = \mathbf{L}(x,y,z) \), and \( \Omega = \Omega(x,y,z) \), respectively, when performing partial differentiations. After evaluating, Eq. 4.48 indicates that \( \delta\mathbf{L} \) is proportional to the product of the local value of \( \mathbf{L} \) with the RSS value of the ratios of the uncertainties in \( \mathbf{K} \) and \( \Omega \) to their corresponding local values, i.e.,

\[
\delta\mathbf{L} \propto \mathbf{L} \left[ \left( \frac{\partial \mathbf{K}}{\mathbf{K}} \right)^2 + \left( \frac{\partial \Omega}{\Omega} \right)^2 \right]^{1/2}.
\]

For typical geometries of the OEH systems used in recording of interferograms, the values of \( \delta\mathbf{K}/\mathbf{K} \) are less than 0.01. However, for small deformations, the typical values of \( \delta\Omega/\Omega \) are about one order of magnitude greater than the values for \( \delta\mathbf{K}/\mathbf{K} \). Therefore, the accuracy with which the fringe orders are determined influences the accuracy in the overall determination of deformations (Pryputniewicz, 1981). To minimize this influence, a number of algorithms for determination of \( \Omega \) were developed. Some of these algorithms require multiple recordings of each of the two states, in the case
of double-exposure method, of the object being investigated with introduction of a
discrete phase step between the recordings (Furlong, 1999; Furlong and Pryputniewicz,
2000; Pryputniewicz, 1995b).

For example, the intensity patterns of the first and the second exposures, \( I_n(x,y) \)
and \( I'_n(x,y) \), respectively, in the double-exposure sequence can be represented by the
following equations:

\[
I_n(x,y) = I_o(x,y) + I_r(x,y) + 2\left\{ \left[ I_o(x,y) \right]\left[ I_r(x,y) \right]\right\}^{1/2} \cdot \cos \left\{ \phi_o(x,y) - \phi_r(x,y) + \theta_n \right\}
\]

(4.50)

\[
I'_n(x,y) = I_o(x,y) + I_r(x,y) + 2\left\{ \left[ I_o(x,y) \right]\left[ I_r(x,y) \right]\right\}^{1/2} \cdot \cos \left\{ \phi_o(x,y) - \phi_r(x,y) + \theta_n + \Omega(x,y) \right\}
\]

(4.51)

where \( I_o \) and \( I_r \) denote the object and reference beam irradiances, respectively, with \((x,y)\)
denoting spatial coordinates, \( \phi_o \) denotes random phase of the light reflected from the
object, \( \phi_r \) denotes the phase of the reference beam, \( \theta_n \) denotes the applied \( n \)-th phase step,
and \( \Omega \) is the fringe-locus function relating to the deformations the object incurred
between the first and the second exposures; \( \Omega \) is what we need to determine. When \( \Omega \) is
known, it is used in Eq. 4.46 to find \( \mathbf{L} \).

In the case of 5-phase-steps algorithm with \( \theta_n = 0, \pi/2, \pi, 3\pi/2, \) and \( 2\pi \) the
distribution of the values of \( \Omega \) can be determined using

\[
\Omega(x,y) = \tan^{-1} \left\{ \frac{2\left[ I_2(x,y) - I_4(x,y) \right]}{2I_3(x,y) - I_1(x,y) - I_5(x,y)} \right\}
\]

(4.52)
Results produced by Eq. 4.52 depend on the capabilities of the illumination, imaging, and processing subsystems of the OEH system. Developments in laser, fiber optic, CCD camera, and computer technologies have led to advances in the OEH metrology.

In response to the needs of the emerging MEMS technology, an optoelectronic laser interferometric microscope (OELIM) methodology for studies of objects with micron size features was developed (Brown, 1999; Brown and Pryputniewicz, 1998, 2000; Furlong and Pryputniewicz, 2000; Pryputniewicz, 1985b, 1989, 1991). In the OELIM system, Fig. 4.12, the light beam produced by a coherent light source is directed through a collimating optics. The resulting light field is then divided into reference and object beams by the splitter. The reference beam is directed towards a mirror and back to the beam splitter. The object beam is directed towards the PZT actuated MEMS under study by a long working distance microscope objective and is reflected back to the beam splitter. The two beams recombine at the beam splitter and are imaged onto the sensing element of the CCD camera, which records the resulting interference patterns. These patterns are transferred to the system computer for subsequent quantitative processing.

Using the systems shown in Fig. 4.12, issues relating to the sensitivity, accuracy, and precision, associated with application of the algorithm defined by Eq. 4.51, were studied while evaluating the effects that the use of high-spatial and high-digital resolution cameras would have on the results produced (Furlong et al., 2002). Mode shape characteristics of vibrating MEMS cantilevers were determined employing previously

4.4.6. Determination of resonant frequency by AFM

In addition to using the OELIM methodology, resonance frequencies of vibrating cantilevers were also determined using an atomic force microscope (AFM) in order to have two independent means of quantifying resonance characteristics of the MEMS cantilevers used in this Thesis. The AFM, shown in Fig. 4.13, is capable of automatically measuring the resonance frequencies of a cantilever by scanning a large frequency range.

Fig. 4.12. Optical configuration of the OELIM system (Furlong and Pryputniewicz, 2000).
and detecting where the largest amplitudes occur. It provides quick and accurate results. However, to facilitate determination of frequencies by AFM, it is necessary to know approximately where the frequencies of intent are to avoid detection of harmonics.

Fig. 4.13. AFM setup utilized: (a) overall view of the setup showing measurement and control subsystems, (b) close up of the measurement subsystem with protective lid open.

In an AFM system, a laser beam is focused and reflected off a cantilever and into a position sensitive diode (PSD) as illustrated in Fig. 2.14. As the cantilever vibrates, the angle of the deflection changes and position of the laser beam on the PSD moves. This motion is measured and used to determine a displacement curve. Wherever there is a peak in the curve, a resonant frequency is located there.

4.4.7. Laser vibrometry

In this Thesis, laser vibrometry was used to measure damping coefficients of the vibrating MEMS cantilevers. The vibrometer functions by way of using a laser and a
Mach-Zehnder interferometric setup built within it as well as its capability to measure Doppler frequency shifts (Polytec, 2003). It functions by examining a signal from an object on a point-by-point basis to measure velocity and displacement as a function of position on the object. Once those two parameters are measured, it is possible to calculate frequency of the vibrating object with an accuracy of 0.001 Hz. This vibrometer would be used to measure small shifts in frequency of a vibrating cantilever in the MEMS chemical sensor.

The cantilevers were placed on a custom made PZT (Pb-Zn-Ti) transducer, Fig. 4.14, which is capable of excitation frequencies in the MHz range containing the frequencies of intent in this Thesis.

![Fig. 4.14. A comparison of the PZT used with a MEMS chip attached to the top and a dime.](image)
The PZT transducer would be contained within a custom made test chamber, Fig. 4.15. The design of the chamber can be found in Appendix D. The chamber will allow the cantilevers to be in a gaseous environment that can be controlled. This chamber would have the gas sample flow into it and out via inputs and outputs. A glass window on the top lid would allow the vibrometer to make unobstructed measurements of frequencies of the cantilevers. For simplification of the setup, the gas would not flow through the chamber, but would be pumped into one atmosphere pressure and then sealed. Because of the volume within the chamber compared to the amount of palladium present, any effects of reduced partial pressure of hydrogen due to absorption into the palladium will be assumed negligible. Any changes would be recorded and then the gas would be released and the neutral carrier gas, nitrogen, would purge the chamber. To regulate concentration of gas, mass flow controllers would be used to adjust the gas mixture ratio, Fig. 4.15.

The entire chamber along with an aligning microscope would be contained within a hood of the vented space. This would ensure that any gas that escapes or is purged would be safely carried away. The supply gas tanks would not be required to be within the hood as they are sealed systems in themselves, but can be.

Because of space limitations, the entire setup would have to be as compact as possible. Figure 4.16 illustrates the setup that would allow for the recording of shifts in the frequency of vibrating cantilevers in a gaseous mixture containing H₂. The aligning microscope would be equipped with a CCD camera so that the cantilevers can be viewed...
outside of the hood. Because of the remote measurement capability of the vibrometer, it will be possible to place it outside of the hood.

Fig. 4.15. The custom made test chamber containing the PZT transducer, which is to be used for testing functional operation of the cantilever-sensing element in a gaseous environment.

Fig. 4.16. Laboratory setup for testing functional operation of MEMS chemical sensors; the microscope and test chamber will be contained within a vented hood.
4.5. Data analysis

Once all of the results of the ACES methodology were collected, they were analyzed in order to determine a set of parameters that would optimize performance characteristics of the MEMS cantilevers. In the analysis, several correlations between different types of data were made.

The first calculations were made of the analytical frequencies for each cantilever based on the measured dimensional data. These results were tabulated, averaged, and are presented in Section 5.1. The averaged data was then used to calculate the contributions that uncertainties in each independent parameter have on the overall percentage uncertainty of the dependent parameter, as discussed in Section 4.2.11.

Two sets of computational results were then compared to the analytically equivalent cases, as is discussed in Section 5.5. The percentage difference was calculated and correlation was determined.

Once all the analytical frequencies for each cantilever were calculated, it was possible to correlate these values with the experimentally determined results. Each analytically determined cantilever frequency was compared to the AFM and interferometric data individually. All the percent differences were then averaged and compared to the overall percentage uncertainty for the analytical case, as is discussed in Section 5.6.

For analytical calculations dealing with the coated cantilevers, several results were compared. Each case described in the Sections 4.2.5 through 4.2.10 discussing the different approaches to the problem was analytically calculated for the longest cantilever.
The overall percentage uncertainty was calculated for each case and compared in Table 5.10. The results were analyzed and conclusions were drawn as discussed in Sections 5.11.6 and 5.11.7.

Once all the data were analyzed and conclusions drawn, comments and recommendations were written for further investigations into cantilever sensors as discussed in Chapter 6.
5. RESULTS

All of the analytical, computation, and experimental results generated in this Thesis are presented in this chapter. The results are shown herein unless it is specified that they are located in a specific appendix.

5.1. Microscope and SEM data

In the beginning of the analysis of the cantilevers, quantitative measurements were made describing all of the geometric dimensions. The sample size was 6 chips, each with 3 cantilevers apiece. The physical dimensions of the cantilevers were measured using an optical microscope and a SEM. The microscope used was a Nikon Measurescope MM-11, Fig. 5.1, which has the least count of 0.5 µm. A Nikon CoolPix 5000 with a 3.2 mega-pixel sensor was connected to the microscope for taking pictures of each cantilever. Representative pictures of the cantilevers are shown in Fig. 3.2 and also in Figs 5.2 to 5.5, where it can be seen that the free ends are not square. It was discovered that the reason for this was due to the way the cantilevers were made. The MicroMasch cantilevers with tips were fabricated with the ends as shown to facilitate their use for the AFM applications. During the fabrication of tipless versions the same masks were used in the process, for cost reasons, so the ends are shaped.

For the purposes of this Thesis, three of the longest cantilevers, i.e., D, E, and F, per chip were measured for each of the six chips considered. All original measurements for cantilever D are listed in Table 5.1. Based on the measurements, the shaped areas of
the cantilever tips were calculated and an equivalent length was found for a corresponding “square” tip. This simplified the calculations. The average equivalent total length of the cantilever D, Fig. 5.2, including its minimum and maximum values, based on the original measurements listed in Table 5.1, are shown in Table 5.2, which also shows other pertinent dimensions for the cantilever D as well as for the cantilevers E and F.

![Fig. 5.1. The microscope setup used for determining dimensions of the cantilevers. A cantilever tip can be seen on the monitor in the middle while the monitor on the right displays the measured values. The Nikon Measurescope MM-11 is on the left.](image)

It was found that the geometric dimensions of the cantilevers were generally about 1% different (which for length amounted to about 2 to 3 µm) from the manufacturer’s specifications. Because the cantilevers were made for atomic force microscope, which is calibrated, the 1% difference does not affect the performance for
their originally intended use. However, the differences measured exceed the current industry practice of 1 µm tolerance on length. The geometric dimensions are summarized in Table 5.1 with a schematic guide shown in Fig. 5.2. The geometric parameters in Fig. 5.2 include the quantitative values measured and the equivalent calculated values for the corresponding “square” tip cantilever. A complete list of the dimensions of each cantilever can be found in Appendix E.

![Fig. 5.2. Cantilever details and labelling: a) photograph of the entire cantilever, b) close-up on a tip of a cantilever, c) guide for the labels used for each geometric parameter of the cantilever describing the data in Tables 5.1 and 5.2.](image)

It should be noted that the sample cantilevers all had a specific designation number according to the chip that they belonged too. This designation consists of a letter and two digits. The letter, from A through F, designates the cantilever used on each chip, differentiable by length with A designating the shortest and F designating the longest.
cantilever. The first digit designates the row number and the second number designated the column starting with ‘11’ at the upper left corner of the package in which the cantilevers were shipped and stored in, Fig. 5.3.

![Cantilevers packed in a Gel-Pack as obtained from the manufacturer.](image)

**Fig. 5.3.** Cantilevers packed in a Gel-Pack as obtained from the manufacturer.

In addition to the traditional optical microscope, a scanning electron microscope (SEM) was used. The SEM was specifically used to measure the thickness of each cantilever because of its ability to see an object in “three-dimensions” as in shown in Fig. 5.4. A few representative images of different samples of cantilevers are shown in Fig. 5.5. The values of the thickness from the SEM that were measured all tended to be approximately 5% off from the manufacturer’s specifications of 1 µm. This 5% was considered the uncertainty analysis.

Since all the cantilevers (D, E, and F) are each on the same chip, only the thickness of the longest cantilever was determined assuming that the thickness will be the same between them all. The thickness data collected were averaged and are displayed in Table 5.2.
Table 5.1. Measured dimensional data and equivalent lengths for all cantilever samples of the D type.

<table>
<thead>
<tr>
<th>Measured characteristics</th>
<th>D11</th>
<th>D12</th>
<th>D21</th>
<th>D22</th>
<th>D31</th>
<th>D32</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length, $L$ mm</td>
<td>296.5</td>
<td>295</td>
<td>293.5</td>
<td>296</td>
<td>295</td>
<td>295</td>
</tr>
<tr>
<td>Width, $b$ mm</td>
<td>36</td>
<td>36.5</td>
<td>36.5</td>
<td>35</td>
<td>35</td>
<td>36</td>
</tr>
<tr>
<td>Thickness, $h$ mm</td>
<td>1</td>
<td>1.007</td>
<td>1</td>
<td>0.96</td>
<td>0.989</td>
<td>0.956</td>
</tr>
<tr>
<td>End width, $L_1$ mm</td>
<td>14</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Eqv. length, $L_2$ mm</td>
<td>8.938</td>
<td>9.106</td>
<td>8.118</td>
<td>7.7</td>
<td>7.757</td>
<td>8.573</td>
</tr>
<tr>
<td>Eqv. total length, mm</td>
<td>305.44</td>
<td>304.11</td>
<td>301.62</td>
<td>303.70</td>
<td>302.76</td>
<td>303.57</td>
</tr>
</tbody>
</table>

Fig. 5.4. SEM photographs of the cantilevers, with a progressive close up on the tip: a) an overall view of three of the longer cantilevers (D-F), b) close-up of cantilever E, c) close-up of the tip of cantilever E showing the thickness and details of the tip.

Fig. 5.5. SEM photographs of E length cantilevers near the tip from different chips: a) chip E11, b) chip E22, c) chip E32.
Table 5.2. Summary of measured dimensions for the cantilevers of the D, E, and F types.

<table>
<thead>
<tr>
<th>Measured parameters</th>
<th>D cantilevers</th>
<th>E cantilevers</th>
<th>F cantilevers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Average</td>
<td>Max</td>
</tr>
<tr>
<td>Length, $L$ $\mu$m</td>
<td>293.5</td>
<td>295.17</td>
<td>296.5</td>
</tr>
<tr>
<td>Width, $b$ $\mu$m</td>
<td>35</td>
<td>35.83</td>
<td>36.5</td>
</tr>
<tr>
<td>Thickness, $h$ $\mu$m</td>
<td>0.956</td>
<td>0.985</td>
<td>1.007</td>
</tr>
<tr>
<td>End length, $L_1$ $\mu$m</td>
<td>9.00</td>
<td>10.08</td>
<td>11.00</td>
</tr>
<tr>
<td>Ave. total length, $\mu$m</td>
<td>303.5</td>
<td>305.25</td>
<td>307.5</td>
</tr>
<tr>
<td>Ave. eq. tot. length, $\mu$m</td>
<td>301.6</td>
<td>303.53</td>
<td>305.4</td>
</tr>
</tbody>
</table>

5.2. Analytical results

Using Eq. 4.23 and measured dimensions of the cantilevers, the frequency for each was calculated for the ideal case where they are uncoated, untreated, and assumed composed of isotropic single-crystal silicon. For example, taking the measurements gathered from the microscope and SEM for the cantilever D11 and values of modulus of elasticity and density from Table 5.3, we find that the analytical nominal frequency is

\[
f_i = \frac{1}{2\pi} \frac{h}{L^2} \sqrt{\frac{35E}{33\rho}}
\]

\[
= \frac{1}{2\pi} \left(\frac{1\mu m}{(305.44\mu m)^2}\right) \sqrt{\frac{35\left(190\times10^9\text{ Pa}\right)}{33\left(2.33\text{ g/cm}^3\right)}}
\]

\[
= 15,865 \text{ Hz}.
\]

Following the procedure used to evaluate Eq. 5.1 the results for the remaining cantilevers were determined and are summarized in Section 5.6. The idealized frequency range that the uncoated cantilevers operate in is shown in Fig. 5.6.
Table 5.3. Values of material properties of silicon (Madou, 2002).

<table>
<thead>
<tr>
<th>Values of material properties used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus of elasticity, $E$, GPa</td>
</tr>
<tr>
<td>Density, $\rho$, g/cm$^3$</td>
</tr>
</tbody>
</table>

To determine the uncertainty in the frequency results of the simplified case (uncoated and untreated) the RSS method was used, Eqs 4.39 and 4.40. Using the averaged equivalent values from Table 5.2 the percent overall uncertainty in resonance frequency of each of the three cantilevers of different lengths was found, subject to the uncertainty value for each parameter used is listed in Table 5.4. The percent overall uncertainty was then averaged from these three values. This percent overall uncertainty can now be compared to the computational and experimental data. The percent overall uncertainties were determined based on values shown in, Table 5.4, (Pryputniewicz, 1993).

Table 5.4. The uncertainties in each parameter considered.

<table>
<thead>
<tr>
<th>Parametric uncertainty values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta h =$0.05 $\mu$m</td>
</tr>
</tbody>
</table>

The averaged geometric data from Table 5.2 were used in determining the percent overall uncertainty in the frequency of the cantilevers utilizing Eqs 4.39 and 4.40. These results can be found in Appendix E. The percent overall uncertainty in frequency was plotted in terms of length and thickness of the cantilevers and is shown in Figs 5.7 and 5.8. To determine which parameters (height, length, modulus of elasticity, and/or
density) contributed to this uncertainty, each one was plotted as a function of cantilever length and thickness to determine their percent contribution to the percent overall uncertainty in the frequency, Figs 5.9 and 5.10 and from them; one can clearly see that in both figures, the uncertainty in the thickness has the highest contribution to the percent overall uncertainty in the frequency with 74.9% contribution in the 350 µm long cantilever as an example. This is an important statement in that the thickness is indeed the one parameter that has the highest relative uncertainty value of all of the independent parameters in the frequency equation. If the plot of the percentage overall uncertainty in frequency with respect to the uncertainty in thickness is generated, Fig. 5.11, the extent that \( \delta h = \pm 0.5 \, \mu m \) makes can be seen.

Fig. 5.6. Fundamental resonant frequency of a 1µm thick cantilever as a function of active length.
Fig. 5.7. The percentage overall uncertainty in the cantilever as a function of against the length while holding the thickness parameter at 1 µm to show the decreasing trend.

Fig. 5.8. The percentage overall uncertainty in the cantilever as a function of the thickness while holding the length parameter as 350 µm to show the decreasing trend.
Fig. 5.9. Percent contributions by uncertainty of each independent parameter to the overall uncertainty in resonance frequency of the cantilever, as a function of length.

Fig. 5.10. Percent contributions by uncertainty by each independent parameter to the overall uncertainty in resonance frequency of the cantilever, as a function of thickness.
5.3. Optoelectronic measurements

The optoelectronic methodology described in Section 4.4.5, was used to produce images of the first few bending modes of the cantilevers (up to the 5th bending was found), Fig. 5.12. The first bending mode was very important, however, for it corresponded to the natural resonant frequency that was analytically calculated. With the setup used, it was possible to determine this resonant frequency with the accuracy of 10 Hz or better than 0.1% of the experimental determined frequencies as shown in Section 5.6. To determine the resonant frequencies of each cantilever, a range of frequencies from 1 Hz to 1 MHz was scanned through and the resonances were determined. The first

Fig. 5.11. Overall uncertainty in the frequency of the cantilever as a function of the uncertainty in the thickness, for different lengths of the microcantilevers.
bending resonant frequency is shown in Fig. 5.13 for each cantilever (D, E, and F) on chip 22. The results from the OELIM measurements are summarized in Section 5.6.

Fig. 5.12. OELIM images of cantilever E32 vibrating under resonant conditions: a) the 1st bending mode (resonant frequency) of the F length cantilever where the fringes indicate the magnitude of deformation and the mode shape at 12,650 Hz, b) 2nd bending mode at 81,400 Hz, c) 3rd bending mode with torsional bending at 115,890 Hz, d) 4th bending mode at 456,150 Hz, e) 5th bending mode at 754,640 Hz.

Fig. 5.13. OELIM images of the cantilevers (D, E, and F) of chip 22 vibrating at their fundamental mode of vibration: a) the D length cantilever, resonating at 14,356 Hz, b) the E length cantilever, resonating at 10,602 Hz, c) the F length cantilever, resonating at 20,716 Hz.
5.4. AFM results

The cantilever chips were loaded on to a chip carrier and then into the AFM. Because the chips were originally designed for a use with an AFM, they were easy to set up and get results. The AFM then scanned the frequency ranges and the resonant frequency could be detected with an accuracy of 10 Hz. Figure 5.14 shows an example of the AFM frequency scan with the resonant peak clearly defined and marked for the cantilever F12. This was how the values were found for each cantilever. The results of AFM measurements are summarized in Section 5.6.

![NCM Frequency Set](image)

Fig. 5.14. A screen capture of the AFM frequency scan for the cantilever F12, where a resonant frequency peak is identified as 22,160 Hz with the accuracy of 10 Hz.
5.5. Computational results

For the computational analysis, Pro/Engineer was used to build the model and Pro/Mechanica was used for the modal analysis. The model used is shown in Fig. 5.15 where all three cantilevers were analyzed at the same time. The model shown in Fig. 5.15 faithfully represents the chip used in this Thesis.

For the software to generate accurate and valid results it is necessary for the solution to converge. Current practice is to have the convergence percentage at 0.01%, but for the software used here, the lowest value attainable was 1% (PTCb, 2003), based on “fixed solution. Pro/Mechanica uses p-type (polynomial) elements for converging on the solution quickly and more accurately than with other available methods. The p-type elements utilize higher order polynomials to obtain the solution instead of increasing the number of elements as in n-type element software packages. Thus p-type elements allows for quicker, discreet solutions that are attainable with just a few steps in the calculation.

The results of the computational simulation were compared to the analytically determined values to determine degree of correlation. Ideally, the computational results would be compared to the experimental results. However, to be more efficient, since each cantilever is of different dimensions and would require a new computational solution, the computational results were compared to the analytical results for two different conditions for correlation. This way the analytical results could be directly compared with the experimental results with confidence that the computational results would be similar to the analytical results. The first case used ideal structural dimension
values (as those specified by the manufacturer in Table 3.1) for the cantilevers while the second used the averaged values as listed in Table 5.2. For example, the percent difference between the analytical and FEM results, i.e., $\text{Resn. freq. \% diff}$, was calculated as

$$\text{Resn. freq. \% diff} = \left( \frac{\text{FEM freq.} - \text{Analytical freq.}}{\text{Analytical freq.}} \right) \cdot 100$$

$$= \left( \frac{15314 - 15326}{15326} \right) \cdot 100$$

$$= 0.078\% \ .$$

These values are displayed in Table 5.5 along with the analytically calculated values.

As can be seen in Table 5.5, the computational results correlate well with the analytically determined values. For the ideal case, using values from Table 3.1, the frequency difference is only about 0.54% and for the averaged case it is about 0.47%.

<table>
<thead>
<tr>
<th>Table 5.5. Comparison of the analytical and computational resonance frequency results.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Measured parameters</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Length, $L \ \mu m$</strong></td>
</tr>
<tr>
<td><strong>Width, $b \ \mu m$</strong></td>
</tr>
<tr>
<td><strong>Thickness, $h \ \mu m$</strong></td>
</tr>
<tr>
<td><strong>Analytical freq., Hz</strong></td>
</tr>
<tr>
<td><strong>FEM freq., Hz</strong></td>
</tr>
<tr>
<td><strong>Resn. freq. % diff.</strong></td>
</tr>
</tbody>
</table>

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Fig. 5.15. Pro/Engineer model and Pro/Mechanica results of the three cantilevers considered: a) cantilever D vibrating at its resonant frequency of 14,679 Hz, b) cantilever E vibrating at its resonant frequency of 10,819 Hz, c) cantilever F vibrating at its resonant frequency of 21,270 Hz.
5.6. Comparison of results

In this section, all the results obtained in this Thesis are compared for determining quantitative correlation. The data from the OELIM and AFM are to be correlated to the simplified analytically determined percent overall uncertainty in frequency, as discussed in Section 5.2. To do this, the difference between the determined AFM frequencies of each cantilever is compared to the analytically determined frequency. This was also done for the OELIM determined frequencies and then percent differences were calculated for both methods. This difference can be seen as the uncertainty in the OELIM and AFM data if the analytical results are considered correct. These differences were then averaged so that they could be directly compared to the analytically determined uncertainties. For example, the percent difference between the analytical and AFM results for cantilever D11, i.e., $\text{Anal./AFM freq. \% diff}$, was calculated as

$$
\text{Anal./AFM freq. \% diff} = \left( \frac{\text{AFM freq.} - \text{Analytical freq.}}{\text{Analytical freq.}} \right) \cdot 100
$$

$$
= \left( \frac{15940 - 15865}{15865} \right) \cdot 100
$$

$$
= 0.47 \% .
$$

Relationships similar to Eq. 5.3 were used to determine $\text{Anal./OELIM freq. \% diff}$ for the remaining cases and the results are summarized in Table 5.6.
Table 5.6. Data comparison of analytical, OELIM, and AFM generated frequencies for each cantilever.

As can be seen from Table 5.6, the values for the OELIM and AFM methods where compared to the analytically calculated values. The overall uncertainties, listed under ‘Uncertainty’ in the table, were calculated in Section 5.2. The optoelectronic measurements, listed as ‘OELIM’ and the AFM, listed as ‘AFM’ in the table, data results were discussed in Sections 5.3 and 5.4, respectively. One final average was calculated
for the overall average percent difference between all the cantilevers for each method.

From the collected data, it is clear that the percent differences in the experimental results (AFM=5.85% and OELIM=6.11%) were similar to the analytically calculated uncertainty (Uncertainty=6.15%) results. This correlation of the data validates the parameters contributing to the overall uncertainty as analytically calculated in Section 5.2.

5.7. Parameters of the coated cantilever

Because of the idea to coat the cantilevers with palladium for hydrogen detection at room temperature and 1 atm pressure it was necessary to prove the functionality of this theory. To accurately model this Pd/H₂ system, it was necessary to include all the parameters that define the coated cantilevers like the different moduli of elasticity and densities, which would be present. These moduli and densities are listed in Table 5.7.

Using Eqs 4.6 and 4.7 we find that the equivalent moduli of elasticity and density for a 350 µm long cantilever coated with 1000 Å of Pd and 10 Å of Ti are

\[ E_{eq} = \frac{(E_{Si} \cdot E_{Ti} \cdot E_{Pd})V_i}{E_{Si}E_{Pd}V_{Si} + E_{Si}E_{Ti}V_{Ti} + E_{Si}E_{Ti}V_{Pd}} \]

\[ = \frac{116 \cdot 121(12,250 \mu m^3) + 190 \cdot 121(25.24 \mu m^3) + 190 \cdot 116(2538.52 \mu m^3)}{190 \cdot 116 \cdot 121(14,813.76 \mu m^3)} \]

\[ = 172.9 \text{ GPa} \]

\[ \rho_{eq} = \frac{\rho_{Si}V_{Si} + \rho_{Ti}V_{Ti} + \rho_{Pd}V_{Pd}}{V_{Si} + V_{Ti} + V_{Pd}} \]

\[ = \frac{2.33(12,250 \mu m^3) + 4.507(25.24 \mu m^3) + 12.023(2538.52 \mu m^3)}{12,250 \mu m^3 + 25.24 \mu m^3 + 2538.52 \mu m^3} \]

\[ = 3.995 \text{ g/cm}^3. \]
Table 5.7. Properties of materials used.

<table>
<thead>
<tr>
<th></th>
<th>Density $\rho \pm 0.005$ g/cm$^3$</th>
<th>Modulus of elasticity $E \pm 3$ GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon, Si</td>
<td>2.330</td>
<td>190</td>
</tr>
<tr>
<td>Palladium, Pd</td>
<td>12.023</td>
<td>121</td>
</tr>
<tr>
<td>Titanium, Ti</td>
<td>4.507</td>
<td>116</td>
</tr>
<tr>
<td>Equivalent values</td>
<td>3.995</td>
<td>172.9</td>
</tr>
</tbody>
</table>

5.8. Sensitivity solutions

In order to determine the correct coverage of the cantilever with palladium the sensitivity was calculated for two cases: a completely covered cantilever and a partially covered, i.e. tip only, cantilever.

It was first necessary to determine the amount of coverage to use in a partially coated cantilever case. Using Eqs 4.2 and 4.5 it was found that the “sectional” or partial mass added to the cantilever at the tip affects the overall mass more than if it were added at the base. As the partial mass that is loaded is moved closer to the base, its effect on the resonance frequency of the cantilever is reduced. It was found that when 25% of the cantilever is covered with 0.1 µm palladium at the tip it accounts for about 72% of the effective mass of the complete cantilever. In Fig. 5.16 the distribution, or percent coverage, of the mass on the cantilever is related to how much the effective mass value is affected. As a uniform amount of mass is added to the cantilever, starting from the base and depositing towards the tip, the effective mass will increase exponentially. As a coating of mass is added in the opposite direction, starting from the tip and depositing
towards the base, the effective mass slope decreases in an opposite manner to the previous loading method.

Fig. 5.16. Effective mass versus percentage of coating coverage: the dotted line illustrates the effective mass contribution as a function of the position along the cantilever moving from the base to the tip as mass is added; the solid line illustrates the same contribution as the position moves from the tip to the base as mass is added. Both cases illustrate how the position of where the mass is added, as it gets closer to the tip of the cantilever, will affect the effective mass.

Since the greatest contribution to the effective mass due to addition of mass occurs in the end/tip 25% (75% through 100% of the cantilever position), it was decided
that this was a reasonable area to use for calculations for the amount of coverage for a partial covered cantilever.

The second method of calculating the sensitivity was assuming the entire cantilever was uniformly coated. This case will be slightly different from the partially coated case, as the differentiation of the same initial equation will produce different results due to the different formulation of the derivative (see Appendix B for the derivations).

Using Eqs 4.2 and 4.5 the sensitivity was calculated for the partially and completely covered cantilever (see Appendix B.4). Using the 350 µm long cantilever with a stiffness of 0.039 N/m, a mass of 2.854x10⁻⁸ g, Δm = 10⁻¹¹ g of mass to “add”, an effective mass constant of \( n_r = 71/420 \) for a coverage of \( r = 0.25 \), the sensitivity for a partial coated cantilever is

\[
S_c = \frac{-1}{2} \frac{1}{k} \left[ \frac{k}{m} \left( \frac{k}{m + n_r r Δm} \right) \right] \frac{kn_r r}{(m + n_r r Δm)^2}
\]

\[
= -\left( \frac{0.039 \text{ kg}}{s^2} \right) \cdot \frac{71}{420} \cdot 0.25
\]

\[
= \frac{2}{33 \cdot 2.854 \cdot 10^{-8} g} \left[ \frac{33}{140} \cdot 2.854 \cdot 10^{-8} g + \frac{71}{420} \cdot 0.25 \cdot 10^{-11} g \right] \left( 2.854 \cdot 10^{-8} g + \frac{71}{420} \cdot 0.25 \cdot 10^{-11} g \right)^2
\]

\[
= -3.141 \cdot 10^9 \frac{Hz}{Hz - kg},
\]

while the sensitivity for a completely covered cantilever is
\[ S_d = - \frac{1}{2} \frac{k}{\sqrt{\frac{33}{140} M}} \frac{k}{\sqrt{\frac{33}{140} (M + \Delta m)}} \frac{33}{140} \frac{1}{(M + \Delta m)^2} \]

\[ = - \left( \frac{0.039 \text{ kg/s}^2}{s^2} \right) \frac{2}{\sqrt{\frac{33}{140} 2.854 \times 10^{-8} g}} \sqrt{\frac{33}{140} \left( 2.854 \times 10^{-8} g + 10^{-11} g \right)} \]

\[ = -1.751 \times 10^{10} \frac{Hz}{Hz - kg} \]  

As can be seen from the results of Eqs 5.6 and 5.7 for detecting the largest overall shift in resonant frequency at a steady state condition a fully coated cantilever was preferred, Table 5.8. This coincides with the conclusions of other researchers in the area of chemical sensors (Betts et al., 2000; Lange et al., 2001).

<table>
<thead>
<tr>
<th>Sensitivity at 1% H₂</th>
<th>Distributed load</th>
<th>Tip loaded</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.751E10 Hz/Hz-kg</td>
<td>-3.141E9 Hz/Hz-kg</td>
<td></td>
</tr>
</tbody>
</table>

5.9. Absorption

The main ability in the hydrogen sensor is for palladium to absorb H₂. Because of this, the absorption reaction must be well known. This reaction can be described with
two main points: the concentration that is absorbed and the amount of time required for that absorption.

The first part, the amount absorbed, is measured by the atomic ratio, or the volumetric amount of one element compared to the other at the atomic scale. This absorption is directly affected by the pressure and temperature of the gas. As the partial pressure of hydrogen decreases the absorption decreases. This is an important characteristic because of the conditions of this Thesis to have the sensor work at 1 atm, or approximately sea level pressure, and with a concentrations equal and less than 1%, the partial pressure will only be <0.01 atm. This is different than with the temperature, which seems to show an increase in the atomic ratio as the temperature decreases. These changes can be seen in Fig. 4.3. This figure, and most data currently available, about hydrogen absorption into palladium are from experimental data collected throughout the years (Lewis, 1967). It is important to note that the experimental data available for determining the atomic ratio of the absorption of hydrogen in palladium at low concentrations are limited. For this reason, the atomic ratio absorption at lower concentrations (<1%) is approximated using a square root proportionality decrease from Sievert’s law (Lewis, 1967).

Since measuring the lower concentrations (<1%) is what is of interest, the equations used had 1% hydrogen concentration as the upper limit. In addition to assuming Sievert’s law for absorption amount, another formula (located in Appendix C.2.2 as Eq. C.80) was generated, simulating Fig. 4.6, to estimate the change in modulus of palladium with hydrogen concentration being the variable. Equation C.80 was
integrated into the equivalent modulus of elasticity relationship so that it could
compensate for the change in the modulus of elasticity of the palladium during
absorption. The final equation then that represented the equivalent amount of mass of
hydrogen accumulated on the cantilever by absorption at different concentrations was

\[ \Delta m = (\text{absorption}\_\text{multiplier})(H_2\_\text{density})(Pd\_\text{volume}) \]  \hspace{1cm} (5.8)

where \text{absorption}\_\text{multiplier} is the conversion of the atomic ratio into the equivalent
volume as described in Table 4.1, \text{H}_2\_\text{density} is determined with Eq. 4.9, and \text{Pd}\_\text{volume}
is the palladium coating layer volume, which although changes with the absorption
process it does not increase in the overall volume mass (number of palladium molecules).
It is important to note though the importance of the partial pressure of the hydrogen, as it
will affect the amount of absorption greatly and thus the results.

The other important parameter in the absorption process is the length of time
required to reach certain concentration of hydrogen within the palladium, Fig. 5.17.

Using Fick’s second law of diffusion in conjunction with Sievert’s law, it was
possible to estimate the length of time required to reach any particular percentage amount
of equilibrium concentration in the palladium, Fig. 5.17, which was prepared for a
cantilever with a 0.1 µm coating of palladium in a hydrogen concentration of 1%, using
Eq. 4.12. From Fig. 5.17, is it clear that the diffusion occurs very quickly and that within
less than a second the concentration is greater than 90% of the equilibrium. This is very
useful and enabling for a sensor as speed is important in detecting agents.
Fig. 5.17. Concentration as a function of time for a cantilever coated with 0.1 µm thick layer of palladium. The time to reach 90% of an equilibrium concentration of 1%, or 10000 ppm, is about 1 second.

5.10. Determination of the damping coefficient

Unless the cantilever is vibrating in a vacuum, there will be some sort of damping acting on the system. To accurately model the system, it was necessary to estimate the damping coefficient, which in this case would be for the damping fluid air. This was accomplished by utilizing the quality factor equations and the vibrometer. Using a microscope, the Polytec Instruments vibrometer laser beam was focused into a spot of about 20 µm in diameter. This spot was smaller than the width of the cantilevers that were examined, which was required to ensure that the vibrometer was only reading the cantilever and not the underlying substrate. Once the vibrometer was set up, a digital
signal generator (Wavetek 2MHz Variable Phase Synthesizer model 650) was used to scan a frequency range that would cover the first bending mode resonant frequency.

Using the spectrum analyzer (HP Spectrum Analyzer 3588A) a resonant frequency peak curve was produced as shown in Fig. 5.18. The maximum peak was found and then two half-power points (described in Section 4.4.4) were found at 1/\sqrt{2} (~70.8%) of the amplitude value. These two points were used for measuring the bandwidth, which is directly related to the mass and damping as was shown in Eq. 4.44. For the cantilever D22, for which Fig. 5.18 represents the data, the damping was found to be

\[
c = \text{bandwidth} \cdot m = (21.880 \text{Hz} - 21.155 \text{Hz}) \cdot 2.04 \cdot 10^{-8} g = 1.48 \cdot 10^{-8} \frac{kg}{s}.
\] (5.9)

In addition, using the result from Eq. 5.9, since the damping is defined by Eq. 4.25 and the parameters \(L\) and \(b\) are known values and \(\mu\), which is the viscosity of nitrogen at 1.77·10^{-11} kg/\mu m-s, it is possible to determine \(H\) as

\[
H = \frac{2\mu L b}{c} = \frac{2 \left(1.77 \cdot 10^{-11} \frac{kg}{\mu m - s}\right) (252.818 \mu m)(33 \mu m)}{1.48 \cdot 10^{-8} \frac{kg}{s}} = 21.8 \mu m.
\] (5.10)

Table 5.9 lists the calculated values for Eq. 4.25 and the bandwidth data measured for a sample chip (D22) and the corresponding calculated damping. It should be noted that during the frequency sweep, some harmonic resonance frequencies were found, as
can be seen in Fig. 5.18. The bandwidth was measured for these harmonics using the formulation from Eq. 5.9 and it was found that the results are similar to the resonant frequency bandwidths, Table 5.9. All the damping coefficient values are presented in Table 5.9. As can be seen from the table, the values for the damping are all of the same order of magnitude and fairly close to one another. This damping coefficient data were then used to analytically model the absorption under different cases as will be discussed in Sections 5.11.1 and 5.11.7.

![Fig. 5.18. A digitally enhanced image of a screen capture from the HP Spectrum analyzer taken while measuring the frequencies of a cantilever. The resonant frequency can be seen as the distinctive spike (with a diamond marker at the tip) at the frequency of 21,590 Hz. The other peaks are the harmonic frequencies.](image)
Table 5.9. Summary of analytically calculated and experimentally determined damping coefficients.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Measured</th>
<th>D22</th>
<th>E22</th>
<th>F22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity of nitrogen, kg/µm-s</td>
<td>1.86x10^{-11}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density, ρ g/cm³</td>
<td>2.33</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Length, L µm | 303.7 | 353.4 | 252.82 |
| Width, b µm  | 35    | 34.5  | 33    |
| Thickness, h µm | 0.96 | 0.96  | 0.96  |
| Height, H µm  | 21.8  | 21.8  | 21.8  |
| Mass, m kg   | 2.377x10^{-11} | 2.727x10^{-11} | 1.866x10^{-11} |
| Damping calculated, c kg/s | 1.725x10^{-11} | 1.979x10^{-11} | 1.354x10^{-11} |
| Bandwidth of resonance, ΔHz | 653 | 1088 | 725 |
| Damping experiment, kg/s | 1.553x10^{-11} | 2.967x10^{-11} | 1.353x10^{-11} |
| Bandwidth of harmonics, ΔHz | 724 | 507 | -- |
| Damping experiment, kg/s | 1.721x10^{-11} | 1.383x10^{-11} | -- |

5.11. Complete cantilever analysis

In order to fully investigate absorption of hydrogen into the palladium coated cantilever the system had to be analytically investigated. This investigation considered different cases of varying complexity characterized by different parameters. Four cases were considered and each one included an increase of mass by absorption of hydrogen. They are: a simple case with only mass changing, a case with mass and stiffness changing, a case with changing mass and damping present, and a case with changing mass and stiffness in the presence of damping. For calculations, the 350 µm long E cantilever with ideal dimensions and coated with 1000Å of palladium on top of 10Å of titanium was used as the sensing element. All four cases and results obtained are
presented in Sections 5.11.1 through 5.11.7 and the derivations for each equation within these sections are located in Appendices B and C.

5.11.1. Case 1: changing mass

The simplest of the cases considers the situation where there is no damping and the stiffness does not change. This situation is an idealized case. Using the equivalent density and modulus of elasticity listed in Table 5.7, the equation used can be rewritten from Eq. 4.19 into the following form:

\[
f_2 = \frac{1}{2\pi L^2} \sqrt[3]{\frac{35 E_{eq}}{33 \rho_{eq}}} \frac{h}{\frac{\Delta m}{m} + 1},
\]

(5.11)

where the change in mass due to hydrogen absorption is \( \Delta m \) and other parameters are as previously defined. It was calculated, Section C.2.1, that the percent overall uncertainty in the frequency shift is 6.926% when the concentration of hydrogen is at 1%. These results are listed in Table 5.8 where it can be seen that for case 1, at 1% concentration of hydrogen, the frequency will shift by \(-1019.801\) Hz, where the negative sign indicates that the frequency will decrease. With an uncertainty of \(539.106\) Hz in the shifted frequency of \(7783.268\) Hz, it is clear that the uncertainty is just about half of the value of the frequency shift making the accuracy of determining the shift challenging. All of the results in this section are derived in Section C.2.1.
5.11.2. Case 2: changing mass and stiffness

The next case is more complicated in that it will look at both a change in the mass as well as a change in the stiffness. Because of the experimental results of the palladium hydrogen system conducted in the past (Lewis, 1967; Alefeld and Völkl, 1978a, 1978b), there is a known contribution to the change in the stiffness from the modulus of elasticity and the volume as both can alter during absorption, Figs 4.5 and 4.6. Because of the limited data for absorption of hydrogen at small concentrations (<1000ppm) the change in the modulus of elasticity and volume due to hydrogen absorption was assumed correct without uncertainty. Equation 4.22 used for this determination is repeated here for continuity, i.e.,

\[ f_2 = \left( \frac{1}{2\pi} \frac{h}{L^2} \sqrt{\frac{35}{33}} \frac{E_{eq}}{\rho_{eq}} \right)^2 \left( 1 + \frac{\Delta k}{k} \right) \left( 1 + \frac{\Delta m}{m} \right), \]  

(5.12)

where the subscript \( l \) indicates the initial frequency. It was then calculated from Eq. 5.12 that the shift in frequency at 1% concentration is –908.546 Hz for a shifted frequency of 7894.523 Hz with a percent overall uncertainty in this shift of 6.917% equaling 546.06 Hz. As it can be seen from the values of the percent overall uncertainty of this and the previous case (Section 5.11.1) that the change is minimal due to the addition of a changing spring constant. This alludes to the conclusion that a changing stiffness will not play a major role in determining the uncertainty. The derivations of the results in this section are located in Section C.2.2.
### 5.11.3. Case 3: changing mass with damping

The third case investigates the frequency shift that occurs due to a change in mass with damping present, which for this case was calculated for the cantilever in air. The damping values used in this case were experimentally verified in Section 5.10. The results from this investigation are similar to those without any damping even though there is a significant change in the formulation. Using Eq. 4.31,

\[
f_2 = \sqrt{\frac{1}{2\pi L^2} \left( \frac{35}{33} \frac{E_{eq}}{\rho_{eq}} \right) \left[ m \left( 4k(m + \Delta m) - c^2 \right) \right]^{2} \left[ \frac{4k(m + \Delta m)}{4k(m + \Delta m)} \right]^{2}},
\]

the contribution that damping has is accounted by the parameter \( c \). When the appropriate values are substituted into Eq. 5.13 at a hydrogen concentration of 1% the percent overall uncertainty in the frequency 6.927% with an uncertainty of 539.113 Hz. The results are very similar to case 1, which had no damping, suggesting that the damping coefficient of air plays a small to indifferent role in improving the frequency data quality. The data are presented in Table 5.10.

### 5.11.4. Case 4: changing mass and stiffness with damping

The final scenario looked at incorporates all the variables: mass, damping, and stiffness. This case represents the results the most accurately. The formula modeling this system is Eq. 4.32, repeated here for continuity, i.e.,

\[
f_2 = \sqrt{\frac{1}{2\pi L^2} \left( \frac{35}{33} \frac{E_{eq}}{\rho_{eq}} \right) \left[ m \left( 4k(m + \Delta m) - c^2 \right) \right]^{2} \left[ 4(k + \Delta k)(m + \Delta m) \right]^{2}},
\]
which is very similar to the damped case described in Eq. 5.13. It has been calculated that the change in the frequency due to the changing stiffness and damping is 532.137 Hz while the final percent overall uncertainty in frequency is 6.696%. The results are similar to those of the case 3 with the changing mass and stiffness.

5.11.5. Design equation selection

In designing cantilever sensors, it is necessary to determine the level of accuracy in modeling needed in order to maximize data quality. Using the results of Sections 5.11.1 through 5.11.4, it is possible to argue what are necessary variables and considerations in designing cantilever sensors. From the data collected from each of the four cases described it was possible to determine which parameter (stiffness and damping), and in turn equation, were the most and least necessary for accurate results. All the data are compiled in the Table 5.10.

It can be seen from the analytical results in Table 5.10 that by being more accurate and including such parameters as damping and a changing stiffness the overall uncertainty in the frequency does not alter much. This means that it is not really necessary to include these other parameters to get accurate results under the conditions used in this Thesis. In other words, to model a vibration system that is damped by air, it is only necessary to account for changes in mass, as changes in any other parameter will not lead to significantly improved results. This simplifies the equations and parameters needed and also the experimental setups as less factors need to be taken into account.
This also increases the usability of the sensor in a wider variety of environments, as effects produced by these environments will not affect the results and reliability of it.

Table 5.10. The results of the four different cases investigated are compared at 1% hydrogen concentration.

<table>
<thead>
<tr>
<th>Frequency data at 1% H₂</th>
<th>Case 1: (m)</th>
<th>Case 2: (m,k)</th>
<th>Case 3: (m,c)</th>
<th>Case 4: (m,k,c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shifted freq.</td>
<td>7783.268</td>
<td>7894.523</td>
<td>7783.313</td>
<td>7673.619</td>
</tr>
<tr>
<td>Freq. shift, Hz</td>
<td>-1019.801</td>
<td>-908.546</td>
<td>-1019.756</td>
<td>-1129.450</td>
</tr>
<tr>
<td>Overall freq. uncert., Hz</td>
<td>539.106</td>
<td>546.06</td>
<td>539.113</td>
<td>532.137</td>
</tr>
<tr>
<td>Overall % freq. uncert.</td>
<td>6.926%</td>
<td>6.917%</td>
<td>6.927%</td>
<td>6.696%</td>
</tr>
</tbody>
</table>

5.11.6. Lower limit frequency shift

As determined in Section 5.11.5, it is not necessary to include variables such as damping and a changing stiffness as the quality of the results will not improve by much. With this knowledge, it was possible to estimate the frequency shift amount that would occur at lower concentrations of hydrogen, such as 1 ppm, absorbing into palladium. Of course, as mentioned in Section 4.2.4, the exact amount of absorption at such low levels is not very well known, but can be approximated using diffusion laws. With these approximations in Eq. 5.11 the frequency shift at 1 ppm was calculated using the same process as described in Section C.2.1, at room temperature and at 1 atm, as
where the mass added is very low (10^{-22} order of magnitude) and therefore the shift at this low concentration level is very small (<0.001 Hz). Figure 5.19 illustrates how the frequency shift increases as the concentration of hydrogen is increased.

It is shown that at around 10 ppm the frequency shift is almost unnoticeable and would be very difficult to detect. There are a few possible reasons for this. The first is that the data of absorption of hydrogen required to accurately graph the curve of Fig. 4.3 is not readily available at small concentrations, which can allow for misrepresentation of the behavior of the cantilever. If the palladium does in fact absorb more hydrogen than what is being used in the equations, then the shift will increase. The second reason is that the partial pressure of the hydrogen is too small to activate absorption into the palladium. Since the hydrogen will be mixed down with nitrogen, the partial pressure will be low. And the other reason is that the mass (quantity) being attempted to detect is too small in comparison to the mass of the cantilever used, which will lead to very small frequency shifts and will require highly sensitive frequency shift detecting methods and equipment.
5.11.7. Optimization of the cantilever response

In order for the cantilever to detect a shift in the frequency that is greater than $10^{-9}$ Hz, there are several factors that must be considered. Addressing the issues brought up in Section 5.11.6, parameters of the frequency equation will be altered and will be documented on their effect on the results. First, the overall length of the cantilevers was reduced by two orders of magnitude (for example: $L=3.5 \, \mu m$). Next the partial pressure, and thus in turn the overall pressure of the gas, was increased by two orders in magnitude. The frequency shift was increased by a total of 4 orders in magnitude with these modifications. Upon close inspection it was found that for each order of magnitude
increase in the partial pressure, the frequency shift increased by one order of magnitude. For the geometric dimensions, the results of decreasing the length and increasing the thickness by orders of magnitude increased the resonant frequency of the cantilever that directly affected the frequency shift. This indicates that higher frequency cantilevers are favorable for sensors as they are more sensitive to frequency shifts. To attain these cantilevers with higher resonant frequencies the overall dimensions such as length and thickness must be reduced.

This has some serious effects on the sensors capabilities due to the uncertainty in the thickness discovered. For example, if the thickness is desired to be 0.1 µm (or less) for the sensor, the current uncertainties will basically prohibit the fabrication of these cantilevers at these scales, as the uncertainties will be extremely high. If a cantilever is fabricated 5% (or greater) off from the planned structural dimensions the high uncertainty will undermine sensitivity and function of the sensors. At such small concentrations, 1 ppm or less, slight differences in the geometry will change the sensitivity and thus, regardless of calibration, the sensor will be out of specifications. For this reason, having a low uncertainty in the thickness parameter is important for the future development of cantilever sensors.
6. CONCLUSIONS

In this Thesis, MEMS cantilever-type chemical sensors were investigated. This investigation involved, several chips. Each chip had 6 cantilevers of different lengths and for this Thesis the three longest cantilevers, i.e., 250 µm, 300 µm, 350 µm, were used.

Analysis and preliminary characterization of vibrations of these cantilevers were investigated, in this Thesis, using analytical, computational, and experimental solutions (ACES) methodology.

To characterize the cantilevers, analytical calculations were performed. The primary investigated aspect involved determination of a nominal frequency and overall uncertainty in the frequency of the cantilevers. Typical values for the resonance frequency and the percent overall uncertainty were found to be around 16 kHz and 6.15%, respectively. It was also found that out of all independent parameters defining resonance frequency, uncertainty in thickness had the greatest contribution to the overall uncertainty in the frequency. More specifically, $\delta h = 0.05 \mu m$ contributed 74.9 % to the overall uncertainty in the resonance frequency of the 350 µm long cantilever. The resonant frequency for each cantilever was determined for comparison with experimental results.

Vibrometer, OELIM, and AFM methodologies were used in gathering experimental results. An AFM was used to determine the frequency response curves based on which the resonant frequencies of cantilevers were calculated. The OELIM method was particularly capable of determining mode shapes associated with specific
resonance frequencies for a number of vibration modes for each cantilever sample. The laser vibrometer was used to determine the damping coefficients.

It was found that the analytically calculated percent overall uncertainty was similar to the percent difference between the analytically calculated frequency and the frequencies measured by the AFM and the OELIM methodologies. The difference, on the order of about 0.3%, indicated that the analytically calculated uncertainty was accurate. The percent overall uncertainty contribution calculations indicated that the thickness was the greatest source of uncertainty and that the analytical and computational results correlated well with the experimental results.

Investigations into the cantilever as a chemical sensor for detecting hydrogen with the palladium/hydrogen system were also conducted. Using equations that included such variables as damping and a changing spring constant several cases were considered. It was found from the analytical results of this Thesis that, although damping due to the nitrogen environment and a changing stiffness do alter the frequency, the percent overall uncertainty in the frequency, or the quality of the results, did not change much, ~0.3% change.

Since the damping and a changing stiffness do not affect the frequency significantly, the sensitivity of the cantilever to the palladium/hydrogen system was determined without considering these parameters. The sensitivity was calculated to determine how a sensor would function the best under the conditions of room temperature (20°C) and atmosphere pressure (1 atm). It was concluded that increasing the resonant frequency is the most direct way of improving the sensitivity of the sensor.
This can be readily accomplished by changing the overall dimensions of the cantilever, i.e., decreasing length and increasing the thickness. However, if the length of the cantilevers is decreased and the thickness is increased, the overall percent uncertainty in the frequency will increase due to the uncertainty in the thickness. This will cause problems with sensors designed for detecting 1 ppm, or less, regardless of calibration because this uncertainty will produce variation in the sensitivity and may put them out of the specifications.

This Thesis investigated a MEMS cantilever-type chemical sensor and its design. It was found that to improve the sensitivity of these sensors, it will be necessary to improve the uncertainty in the thickness. More specifically, the fabrication processes that make these cantilevers would have to be improved to provide an order of magnitude decrease in the uncertainty in thickness. As fabrication processes improve, the ability to make smaller devices more accurately will facilitate development of the cantilever-type MEMS chemical sensors.
7. REFERENCES


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J. Han, D. P. Neikirk, M. Clevenger, and J. T. McDevitt, 1996, "Fabrication and characterization of a Fabry-Perot based chemical sensor," *Proc. Conf. on Microelectronic Structures and MEMS for Optical Processing II*, M. E. Motamedi and W. Bailey, editors, Austin, TX, SPIE-2881:171-178.


R. J. Pryputniewicz, 2002b, MEMS and nanotechnology, Worcester Polytechnic Institute, Worcester, MA.


APPENDIX A. PROPERTIES OF MATERIALS USED

For the materials used in this Thesis, the properties of each are tabulated below, Table A.1. The values listed in the table are the ones used in this Thesis unless otherwise specified in the text. In addition, pictures of what the materials look like are shown in Figures A.1 to A.3. These pictures are of small (no scale) samples from *The Red Blue & Green Company* (EC, 2003) for the purpose of a visual association to each element.

Table A.1. Physical properties of the materials used.

<table>
<thead>
<tr>
<th>Material name</th>
<th>Palladium</th>
<th>Hydrogen</th>
<th>Titanium</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>46</td>
<td>1</td>
<td>22</td>
<td>14</td>
</tr>
<tr>
<td>Atomic weight, g</td>
<td>106.42</td>
<td>1.00794</td>
<td>47.867</td>
<td>28.0855</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>fccp</td>
<td>hcp</td>
<td>hcp</td>
<td>diamond</td>
</tr>
<tr>
<td>Density, kg/m³</td>
<td>12023</td>
<td>no data</td>
<td>4507</td>
<td>2330</td>
</tr>
<tr>
<td>Melting point, °K</td>
<td>1828.05</td>
<td>14.01</td>
<td>1941</td>
<td>1687</td>
</tr>
<tr>
<td>Boiling point, °K</td>
<td>3236</td>
<td>20.28</td>
<td>3560</td>
<td>3173</td>
</tr>
<tr>
<td>Modulus of elasticity, GPa</td>
<td>121</td>
<td>no data</td>
<td>116</td>
<td>190</td>
</tr>
<tr>
<td>Poisson's ratio</td>
<td>0.39</td>
<td>no data</td>
<td>0.32</td>
<td>0.22</td>
</tr>
<tr>
<td>Reflectivity</td>
<td>72%</td>
<td>no data</td>
<td>no data</td>
<td>28%</td>
</tr>
</tbody>
</table>

Fig. A.1. A photograph of palladium samples (EC, 2003).
Fig. A.2. A sample of titanium, a popular material due to its corrosion resistance (EC, 2003).

Fig. A.3. A sample of untreated, unprocessed, uncut silicon (EC, 2003).
APPENDIX B. ANALYTICAL CALCULATIONS

In this Appendix, almost every equation used in the main text, Chapters 4 and 5, is derived step-by-step (Kelly, 1996). This is for validation of work and completeness.

B.1. Fundamental resonance frequency

In determining the fundamental resonance frequency of a cantilever we start with the general equation for a body in motion, Fig. 4.2,

\[ m \frac{d^2x}{dt^2} + c \frac{dx}{dt} + kx = F(x,t) \]  \hspace{1cm} (B.1)

where \( m \) is the dynamic mass of the cantilever, \( c \) is the damping coefficient, \( k \) is the spring constant, and \( F(x,t) \) is the time dependent forcing function acting on it. If we assume that there is no damping and no force acting on the cantilever, Eq. B.1 simplifies to

\[ m \frac{d^2x}{dt^2} + kx = 0 \]  \hspace{1cm} (B.2)

which is a simple homogeneous equation. The general solution for Eq. B.2 is

\[ X(t) = C_1 \cos(\omega t) + C_2 \sin(\omega t) \]  \hspace{1cm} (B.3)

\[ \frac{d^2}{dt^2} X(t) = -\omega^2 [C_1 \cos(\omega t) + C_2 \sin(\omega t)] \]  \hspace{1cm} (B.4)

where \( C_{1,2} \) are arbitrary constants. Substituting Eqs B.3 and B.4 into Eq. B.2, it is obtained
\[
\left[ m\left(-\omega^2\right) + k \right]\left( C_1 \cos(\omega t) + C_2 \sin(\omega t) \right) = 0 \quad (B.5)
\]
which produces two results. One is trivial and the other is equal to
\[
\omega = \sqrt{\frac{k}{m}}, \quad (B.6)
\]
which can be simplified into the following form
\[
f = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (B.7)
\]
by using the equality of
\[
f = \frac{\omega}{2\pi}, \quad (B.8)
\]
where \( f \) is the frequency of the body in motion and \( \omega \) is the angular frequency. Equation B.8 can be further simplified by substituting Eqs B.24 and B.33 to obtain
\[
f = \frac{1}{2\pi} \sqrt{\frac{Ebh^3}{4L^3}} \sqrt{\frac{33}{140}} \rho bhL \quad (B.9)
\]
which becomes
\[
f = \frac{1}{2\pi} \frac{h}{L^2} \sqrt{\frac{35E}{33\rho}} \quad (B.10)
\]

B.2. **Spring constant**

The general equation for the cyclic frequency of a vibrating body, given by Eq. B.7, is
\[ f = \frac{1}{2\pi} \sqrt{\frac{k}{m}}, \]  
(B.11)

where \( m \) is the dynamic mass of the structure and \( k \), the spring constant, is

\[ k = \frac{F}{y}, \]  
(B.12)

in which \( F \) is the force applied to the structure. If we assume a simple cantilever-type structure, Fig. B.1, with an applied force, the general equation of the elastic curve is

\[ \frac{d^2 y}{dx^2} = \frac{M_x}{EI}, \]  
(B.13)

where \( M_x \) is the moment acting along the cantilever, \( E \) is the modulus of the elasticity, and \( I \) is the moment of inertia.

\[ M_x = F(L-x) \]  
(B.14)

Fig. B.1. Geometric parameters of a cantilever.
Inserting Eq. B.14 into Eq. B.13 and then integrating we get

\[ \frac{dy}{dx} = \frac{F}{EI} \left( Lx - \frac{x^2}{2} \right) + C_1 \]  

(B.15)

and by integrating Eq. B.15 we obtain

\[ y = \frac{F}{EI} \left( Lx^2 - \frac{x^3}{6} \right) + C_1 x + C_2 \]  

(B.16)

In Eq. B.16, we have two unknowns. We can determine them by utilizing boundary conditions for a cantilever. The boundary conditions are

\[ \frac{dy}{dx} = 0 \quad \text{at} \quad x = 0 \]
\[ y = 0 \quad \text{at} \quad x = 0 \]  

(B.17)

Solving Eqs B.16 and B.15 with the boundary conditions of Eq. B.17 we find that

\[ C_1 = 0 \quad \text{and} \quad C_2 = 0 \]  

(B.18)

Substituting Eq. B.18 into Eq. B.15 we find that

\[ \frac{dy}{dx} = \frac{F}{2EI} \left( 2Lx - x^2 \right) \]  

(B.19)

Similarly, Eq. B.16 becomes

\[ y = \frac{F}{6EI} \left( 3Lx^2 - x^3 \right) \]  

(B.20)

If we now take Eq. B.20 and solve it at \( x=L \), we get the following equation that represents the maximum displacement

\[ y = y_{\text{max}} = \frac{F}{6EI} \left( 3L^3 \right) - \frac{F}{3EI} \]  

(B.21)

Inserting the result of Eq. B.21 into Eq. B.12 we get
\[ k = \frac{F}{y_{\text{max}}} = \frac{3EI}{L^3} , \quad (B.22) \]

where \( I \) is the moment of inertia for the cantilever, i.e.,

\[ I = \frac{bh^3}{12} . \quad (B.23) \]

When Eq. B.23 is inserted into Eq. B.22 we finally get

\[ k = \frac{Eb h^3}{4L^3} , \quad (B.24) \]

which is the stiffness for a cantilever shown in Fig. B.1.

**B.3. Dynamic mass**

To determine the dynamic mass of a vibrating cantilever we must consider the kinetic energies involved. A vibrating mass will affect these energies depending on the boundary conditions. With this in mind we start with the basic equation for a kinetic energy

\[ KE = \int dKE , \quad (B.25) \]

where the kinetic energy differential \( dKE \) can be substituted by

\[ dKE = \frac{\dot{y}^2}{2} \, dm = \frac{\dot{y}^2}{2} \rho bh \, dx , \quad (B.26) \]

where \((\dot{y})^2\) is the velocity of the vibrating body with displacement \( y_{\text{max}} \) based on the boundary conditions. Equation B.26 is assuming that the beam has a constant cross section in that the variables \( b \) and \( h \) are not changing as a function of position along the
cantilever. Assuming proportionality, we start by dividing Eq. B.21 into Eq. B.20 and getting the following form

\[ \frac{y}{y_{\text{max}}} = \frac{3Lx^2 - x^3}{2L^3}, \]  \hspace{1cm} (B.27)

which translates into

\[ y = y_{\text{max}} \left( \frac{3Lx^2 - x^3}{2L^3} \right). \]  \hspace{1cm} (B.28)

After taking the first derivative with respect to time, Eq. B.28 becomes

\[ \dot{y} = \dot{y}_{\text{max}} \left( \frac{3Lx^2 - x^3}{2L^3} \right). \]  \hspace{1cm} (B.29)

Using Eqs B.25, B.26, and B.29 and applying limits of integration we get

\[ KE = \int_{0}^{L} \frac{y_{\text{max}}^2}{2} \left( \frac{3Lx^2 - x^3}{2L^3} \right)^2 \rho bh dx. \]  \hspace{1cm} (B.30)

Solving Eq. B.30 we get

\[ KE = \left( \frac{33}{140} \rho bhL \right) \frac{y_{\text{max}}^2}{2}. \]  \hspace{1cm} (B.31)

Since the general equation for kinetic energy is

\[ KE = \frac{1}{2} mv^2 \]  \hspace{1cm} (B.32)

we find that the quantity in parenthesis in Eq. B.31 is equivalent to

\[ \frac{33}{140} \rho bhL = \frac{33}{140} M = m \]  \hspace{1cm} (B.33)

where \( M \) is the total, i.e., static mass of the beam and \( m \) is the dynamic mass of the cantilever.
B.3.1. Dynamic mass constant

If we look at the result of Eq. B.33 we see that the mass has a constant of $33/140$ in front of it. This constant describes the effect that mass will have on the cantilever. To determine the effect, or the constant, at an arbitrary point along the cantilever we start with Eq. B.30, but modify it slightly to

$$KE = \int_0^r \frac{y_{\text{max}}^2}{2} \left( \frac{3Lx^2 - x^3}{2L^3} \right)^2 \rho bhdx,$$  \hspace{1cm} (B.34)

where the upper limit of integration will be replaced with the parameter $r$ to signify the location along the cantilever that we are interested in. If we now solve Eq. B.34, it becomes

$$KE = \frac{y_{\text{max}}^2}{2} \left( \rho bh \right) \cdot \left[ \frac{1}{140} \frac{r^5}{L^5} \left( 5r^2 - 35Lr + 63L^2 \right) \right],$$  \hspace{1cm} (B.35)

and we can equate

$$\left( \rho bh \right) = C_1$$

$$\left[ \frac{1}{140} \frac{r^5}{L^5} \left( 5r^2 - 35Lr + 63L^2 \right) \right] = n(r),$$  \hspace{1cm} (B.36)

where $C_1$ is just a constant of structural properties and $n(x)$ is a function that will produce a the effective, or dynamic, mass constant along the length of the cantilever. We can then rewrite Eq. B.35 as

$$KE = \frac{y_{\text{max}}^2}{2} C_1 n(x).$$  \hspace{1cm} (B.37)
B.4. Sensitivity calculations of the cantilever

In this section, the equations for the sensitivity of the cantilever will be derived for two cases: a cantilever partially and a completely covered with palladium. The explicit quantitative solutions are in Section 5.8.

B.4.1. Sensitivity of an end-loaded cantilever

In determining sensitivity of a frequency-based sensor we can use Eq. 4.1, repeated here for continuity, i.e.,

\[ S_m = \lim_{\Delta m \to 0} \frac{1}{f_i} \frac{\Delta f}{\Delta m} = \frac{1}{f_i} \frac{\partial f}{\partial m} , \]

(B.38)

where sensitivity is a measure of normalized frequency over mass with \( f_i \) equaling the initial resonant frequency. In order to solve Eq. B.38 for an end-loaded case to determine \( S_e \), there are a few substitutions that must be made. First, we make the appropriate substitutions for frequency, mass, and change in mass into the equation so that it becomes

\[ S_e = \frac{1}{2\pi} \frac{df}{k \Delta m} \left( \frac{k}{2\pi} \sqrt{\frac{k}{\left(m + n, r \Delta m\right)}} \right) , \]

(B.39)

where \( m \) is the dynamic mass of the cantilever defined in Eq. B.33, and \( \Delta m \) is the added mass. The parameter \( r \) is the percentage coverage of the cantilever with palladium so that it can be directly compared with a fully coated cantilever later and the parameter \( n \) is the effective mass constant, or boundary condition mass factor for a cantilever, (i.e., \( n=33/140 \) for \( r = 100\% \)) of the added mass that is dependent on the value of \( r \). By
assigning the variable $r$ a value of 0.25, equaling 25% coverage of the cantilever, and using Fig. 5.13 to determine the effective mass at this value we find the effective mass equal to $n_r = 71/420$ ($\sim 0.169$). Equation B.39 can then be solved, i.e. derivative taken and solution simplified, and the final equation takes the form of

$$S_e = 2 \sqrt{\frac{k}{\frac{33}{140} M}} \left[ \frac{k}{\frac{33}{140} M + n_r \delta m} \right]^{1/2} = \frac{k n_r}{\left( \frac{33}{140} M + n_r \delta m \right)^{1/2}} . \tag{B.40}$$

If we assign nominal values to the variables in Eq. B.40, we can solve for a sample case and determine the sensitivity for it in order to compare the sensitivity of the partially and completely covered cantilever. Using the values in Table B.1, we can solve for the sensitivity of a 350 µm long cantilever.

### Table B.1. Material properties and geometric dimensions used in a sample case to determine sensitivity of the cantilever as a chemical sensor.

<table>
<thead>
<tr>
<th>Parametric values used</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus of elasticity, $E$, GPa</td>
<td>190</td>
</tr>
<tr>
<td>Density, $\rho$, g/cm$^3$</td>
<td>2.33</td>
</tr>
<tr>
<td>Thickness, $h$, µm</td>
<td>1</td>
</tr>
<tr>
<td>Length, $L$, µm</td>
<td>350</td>
</tr>
<tr>
<td>Width, $b$, µm</td>
<td>35</td>
</tr>
</tbody>
</table>

Using the values from Table B.1 we find

$$M = \rho bhL$$

$$= \left( \frac{2.33 g}{cm^3} \right) 35\mu m \cdot 1\mu m \cdot 350\mu m$$

$$= 2.854 \cdot 10^{-8} \ g \ , \tag{B.41}$$
which is the mass of the cantilever. To set a value for the change in mass, i.e., added
mass, an arbitrary number shall be picked. The $\Delta m$, or change in mass, will be assumed
to be 3 orders of magnitude less than the cantilever mass itself or

$$\Delta m = 1 \cdot 10^{-11} \, g \quad ,$$  \hspace{1cm} (B.42)

which will be held as a constant, or in other words the addition of mass will be equal to
this value and will not change. For the value of the spring constant, $k$, Eq. B.24 yields

$$k = \frac{Ebh^3}{4L^3}$$
$$= \frac{190 \text{GPa} \cdot 35 \mu m \cdot (1 \mu m)^3}{4(350 \mu m)^3}$$  \hspace{1cm} (B.43)

$$= 0.039 \frac{N}{m} \quad .$$

Then using the values of $n_r = 71/420$ and $r = 0.25$ we can determine the sensitivity, as
was solved in Section 5.8, of an end loaded cantilever with Eq. B.40 to be

$$S_e = -3.141 \cdot 10^9 \frac{\text{Hz}}{\text{Hz} - \text{kg}} \quad ,$$  \hspace{1cm} (B.44)

which is in units of changing frequency per unit frequency – mass.

**B.4.2. Sensitivity of a completely coated cantilever**

In determining the sensitivity of a uniformly distributed polymer over a cantilever
we start with Eq. B.38. The equation for a uniformly distributed load, with the same
substitutions for frequency, mass, and changing mass as done in Eq. B.39, will take the form of

$$S_d = \frac{1}{2\pi} \frac{df}{d\Delta m} \left( \frac{1}{\sqrt{\frac{33}{140} m}} \right) \left( \frac{k}{\sqrt{\frac{33}{140} (m + \Delta m)}} \right), \tag{B.45}$$

which contains parameters that were all defined previously. If Eq. B.45 is solved, i.e., the derivative and resultant equation are simplified to take the final form

$$S_d = \frac{-1}{2} \frac{k}{\sqrt{\frac{33}{140} m}} \frac{k}{\sqrt{\frac{33}{140} (m + \Delta m)}} \frac{33}{140} (m + \Delta m)^2, \tag{B.46}$$

which is similar in formulation to Eq. B.40.

Using the values of Table B.1 and from Eqs B.41 through B.43, Eq. B.46, yields

$$S_d = -1.751 \cdot 10^{10} \frac{Hz}{Hz - kg}, \tag{B.47}$$

which is in units of changing frequency per unit frequency – mass. As can be seen, the sensitivity of the distributed load is about one order of magnitude greater than for an end, or tip, loaded cantilever.

B.5. Frequency shift for a free, undamped vibration

To determine the frequency shift for an ideal, i.e. free and undamped, system the following identity is used
\[
\frac{f_1^2 - f_2^2}{f_2^2} = \frac{f_1^2 - f_2^2}{f_2^2},
\]
(B.48)

which can be rewritten, by substituting Eq. B.7 and realizing that frequency relation incorporates a change in mass as,

\[
\frac{f_1^2 - f_2^2}{f_2^2} = \left(\frac{1}{2\pi \sqrt{m}}\right)^2 - \left(\frac{1}{2\pi \sqrt{m + \Delta m}}\right)^2.
\]
(B.49)

Equation B.49 can then be simplified into

\[
\frac{f_1^2 - f_2^2}{f_2^2} = \frac{k}{m} - \frac{k}{m + \Delta m} = \frac{m + \Delta m - m}{m(m + \Delta m)} = \frac{\Delta m}{m}.
\]
(B.50)

and further to

\[
\frac{f_1}{f_2} = \sqrt{\frac{\delta m + f_1^2}{m + f_2^2}}.
\]
(B.51)

and finally reformulated, by substituting Eq. B.10 in for \(f_i\), as

\[
f_2 = \frac{1}{2\pi \sqrt{\frac{\delta m}{m} + 1}} \sqrt{\frac{35 E_{eq}}{33 \rho_{eq}}}.
\]
(B.52)

Equation B.52 can be used to determine the frequency shift due to the absorption of hydrogen.
B.6. Frequency shift for a free, undamped vibration with a changing stiffness

To determine the frequency shift for a free, undamped system that has a spring constant that changes with absorption, a different formulation will have to be used than the one used in Section B.5. For this case, Eq. B.48, can be written, with the appropriate frequency substitutions that include both a changing mass and stiffness, as

\[
\frac{f_1^2 - f_2^2}{f_2^2} = \left( \frac{1}{2\pi \sqrt{m}} \right)^2 - \left( \frac{1}{2\pi \sqrt{(m + \delta m)}} \right)^2 - \left( \frac{1}{2\pi \sqrt{(k + \delta k)}} \right)^2
\]

which can then be simplified into

\[
\frac{f_1^2 - f_2^2}{f_2^2} = \frac{k}{m} \left( \frac{(m + \Delta m)}{(k + \Delta k)} \right) = \frac{k\Delta m - m\Delta k}{m(k + \Delta k)} = \frac{m\Delta m - m\Delta k}{m(k + \Delta k)} \quad \text{(B.54)}
\]

and further to

\[
f_2^2 = \frac{f_1^2}{k\Delta m - m\Delta k} + \frac{m\Delta m - m\Delta k}{m(k + \Delta k)} = \frac{f_1^2 mk + m\Delta k}{k\Delta m + mk} \quad \text{(B.55)}
\]

and reformulated, by substituting Eq. B.10 in for \( f_i \), as

\[
f_2 = \sqrt{\frac{1}{2\pi \left( \frac{h}{L^2} \sqrt{\frac{35}{33} \rho_{eq}} \right)} \left( \frac{1}{1 + \frac{\delta k}{k}} \right) \left( \frac{1}{1 + \frac{\delta m}{m}} \right)} \quad \text{(B.56)}
\]
Equation B.56 can be used to determine the frequency shift due to the absorption of hydrogen.

**B.7. Free vibration with viscous damping**

In determining the resonance frequency of a cantilever with damping present we start with the general equation for a body in motion, i.e.,

\[
mx'' + c \frac{dx}{dt} + kx = F(x,t) .
\]  

(B.57)

If we assume that there is damping and no force acting on the cantilever, Eq. B.57 simplifies to

\[
mx'' + c \frac{dx}{dt} + kx = 0 .
\]  

(B.58)

The general solution for Eq. B.58 is assumed as

\[
X(t) = Ae^{st} .
\]  

(B.59)

If we substitute Eq. B.59 into Eq. B.58 we get

\[
ms^2 + cs + k = 0 .
\]  

(B.60)

Solving Eq. B.60 for its roots produces a quadratic solution, which when simplified takes the form of

\[
s_{1,2} = -\frac{c}{2m} \pm \sqrt{\left(\frac{c}{2m}\right)^2 - \frac{k}{m}} ,
\]  

(B.61)

which can then be substituted back into Eq. B.57 giving a solution with two parts
\[ X(t) = A_1 e^{\xi t} + A_2 e^{\xi t} \]  \hspace{1cm} (B.62)

In this Thesis, the cantilever system will be operating in air and thus it will be assumed that it resembles an under damped system (Rao, 1995). For an under damped system, the radical of Eq. B.61 is

\[
\left( \frac{c}{2m} \right)^2 - \frac{k}{m} < 1
\]

and thus the radical will be negative. Solving Eq. B.62 for the condition given by Eq. B.63 we simplify the equation with trigonometric identities to

\[ X(t) = A e^{-(c/2m)t} \cos \left( \omega_d t + \theta \right) \]  \hspace{1cm} (B.64)

where \( A \) is the amplitude, \( t \) is time, \( \theta \) is the phase shift, and \( \omega_d \) is the damped angular frequency

\[ \omega_d = \sqrt{\frac{k - c^2}{m}} \]  \hspace{1cm} (B.65)

which indicates that damping alters the resonant frequency by changing the damped angular frequency.

**B.7.1. Frequency shift for a free, damped vibration**

To determine the frequency shift for a free, damped system the same form as Eq. B.48 is used. The difference is that in substituting in the functions, Eq. B.65 will be used in the shifted frequency so that the formulation becomes
\[
\frac{f_1^2 - f_2^2}{f_2^2} = \left(\frac{1}{2\pi \sqrt{\frac{k}{m}}}\right)^2 - \left(\frac{1}{2\pi \sqrt{\left(m + \delta m\right) - \frac{c^2}{4(m + \delta m)^2}}}\right)^2.
\] (B.66)

Equation B.66 does not simplify as cleanly as Eq. 56, but after some operation, it can be put into the following form:

\[
\frac{f_1^2 - f_2^2}{f_2^2} = \frac{k}{m(m + \Delta m)} - \frac{k}{c^2} - \frac{4(m + \Delta m)^2}{4(m + \Delta m)^2} = \frac{4k(m + \Delta m)\Delta m - mc^2}{m \cdot 4k(m + \Delta m) - c^2}
\] (B.67)

and further to

\[
f_2^2 = \frac{f_1^2}{\frac{4k(m + \Delta m)\Delta m - mc^2}{4mk(m + \Delta m) - c^2} + 1} = f_1^2 \frac{m\left[4k(m + \delta m) - c^2\right]}{4k(m + \delta m)^2}
\] (B.68)

and finally reformulated, by substituting Eq. B.10 in for \(f_1\), as

\[
f_2 = \sqrt{\frac{1}{2\pi L^2} \left(\frac{35 E_{eq}}{33 \rho_{eq}}\right)^2 m\left[4k(m + \delta m) - c^2\right]} \frac{4k(m + \delta m)^2}{4k(m + \delta m)}
\] (B.69)

Equation B.69 can be used to determine the frequency shift due to the absorption of hydrogen.
B.7.2. Frequency shift for a free, damped vibration with a changing stiffness

To determine the frequency shift for a free vibration system that has damping and a changing spring constant the same form as Eq. B.48 is used. The difference is that there will also be the altering stiffness so the equation, incorporating a rewritten Eq. B.65, becomes

\[
\frac{f_1^2 - f_2^2}{f_2^2} = \left( \frac{1}{2\pi} \sqrt{\frac{k}{m}} \right)^2 - \left( \frac{1}{2\pi} \sqrt{\frac{(k + \Delta k)}{(m + \Delta m)} - \frac{c^2}{4(m + \Delta m)^2}} \right)^2.
\] (B.70)

This equation simplifies much like Eq. 69, so it can be put into the following form:

\[
\frac{f_1^2 - f_2^2}{f_2^2} = \frac{k}{m} \frac{(k + \delta k)}{(m + \delta m)} - \frac{c^2}{4(m + \delta m)^2} = \frac{4(k\Delta m - m\Delta k)(m + \Delta m) - mc^2}{m[4(k + \Delta k)(m + \Delta m) - c^2]}.
\] (B.71)

and further to

\[
f_2^2 = \frac{f_1^2}{4(k\Delta m - m\Delta k)(m + \Delta m) - mc^2} = \frac{f_1^2 m[4k(m + \delta m) - c^2]}{4(k + \delta k)(m + \delta m)^2} + 1
\] (B.72)

and finally reformulated, by substituting Eq. B.10 in for \(f_1\), as

\[
f_2 = \sqrt{\left( \frac{1}{2\pi} \frac{h}{L^2} \sqrt{\frac{35}{33} \frac{E_{eq}}{\rho_{eq}}} \right)^2 m[4k(m + \delta m) - c^2]} / 4(k + \delta k)(m + \delta m)^2}
\] . (B.73)

Equation B.73 can be used to determine the frequency shift due to the absorption of hydrogen, as discussed in Section 3.2.
B.8. Harmonically excited system with viscous damping

In determining the resonance frequency of a cantilever under harmonic excitation we start with the general equation for a body in motion

\[ m \frac{d^2x}{dt^2} + c \frac{dx}{dt} + kx = F \cos(\omega t) \]  \hspace{1cm} (B.74)

If we look at the particular solution for this case, we can assume a solution of the form

\[ X(t) = A\cos(\omega t - \theta) \]  \hspace{1cm} (B.75)

The homogeneous solution to Eq. B.75 will not play a part, as it will be zero under equilibrium conditions. By substituting Eq. B.75 into Eq. B.74 we get

\[ X\left[(k - m\omega^2)\cos(\omega t - \theta) - c\omega \sin(\omega t - \theta)\right] = F \cos(\omega t) \]  \hspace{1cm} (B.76)

Using trigonometric relations

\[ \cos(\omega t - \theta) = \cos(\omega t)\cos(\theta) + \sin(\omega t)\sin(\theta) \]
\[ \sin(\omega t - \theta) = \sin(\omega t)\cos(\theta) - \cos(\omega t)\sin(\theta) \]  \hspace{1cm} (B.77)

we can simplify Eq. B.76 into two forms

\[ X\left[(k - m\omega^2)\cos(\theta) + c\omega \sin(\theta)\right] = F \]
\[ X\left[(k - m\omega^2)\sin(\theta) - c\omega \cos(\theta)\right] = 0 \]  \hspace{1cm} (B.78)

By solving Eq. B.78 simultaneously, it is obtained (Hsu, 2002)

\[ X = \frac{F}{k \sqrt{(k - m\omega^2)^2 + c^2\omega^2}} \]  \hspace{1cm} (B.79)

where the solution for the phase is

\[ \theta = \tan^{-1}\left(\frac{c\omega}{k - m\omega^2}\right) \]  \hspace{1cm} (B.80)
If the following equations:

$$\omega_n = \sqrt{\frac{k}{m}}, \quad \zeta = \frac{c}{2m\omega_n}, \quad \text{and} \quad r = \frac{\omega}{\omega_n}$$

(B.81)

are substituted into Eqs B.79 and B.80, they can be rewritten as

$$X = \frac{F_{\text{max}}}{k \sqrt{(1-r^2)^2 + (2\zeta r)^2}}$$

(B.82)

where $X$ is the amplitude and the phase is

$$\theta = \tan^{-1} \left( \frac{2\zeta r}{1-r^2} \right),$$

(B.83)

which allows Eqs B.82 and B.83 to be functions of the frequency ratio $r$. 
APPENDIX C. UNCERTAINTY ANALYSIS

In this Appendix the uncertainty calculations used in this Thesis are performed.

C.1. Uncertainty in fundamental resonant frequency

In this Section the calculations of the uncertainty in frequency for the ideal, uncoated cantilever are shown.

C.1.1. Uncertainty calculations for the 350 µm long cantilever

To determine the overall percentage uncertainty in the resonant frequency for the averaged, uncoated case, we start with the general relationship for fundamental frequency, based on Eq. 4.23, i.e.,

\[ f = \frac{1}{2\pi} \frac{h}{L^2} \sqrt{\frac{35E}{33\rho}}, \]  

(C.1)

where \( h \) is the thickness of the cantilever, \( L \) is the length, \( E \) is the modulus of elasticity, and \( \rho \) is the density. The values used for this calculation are listed in Table C.1 and include the averaged geometric dimensions measured for these cantilevers.
If the values listed in Table C.1 are inserted into Eq. C.1 we get
\[ f = \frac{1}{2\pi} \frac{h}{L} \sqrt{\frac{35E}{33\rho}} \]
\[ = \frac{1}{2\pi} \frac{0.985\mu m}{(353.2\mu m)^2} \sqrt{\frac{35(190GPa)}{33(2.33 \frac{g}{cm^3})}} \]
\[ = 11690.232 \text{ Hz} \] .

To determine the overall percentage uncertainty in the resonant frequency, the RSS (root-sum-squares) method is used. The phenomenological equation, corresponding to Eq. C.1, is
\[ f = (h, L, E, \rho) \] . (C.3)

Using Eq. C.3 we write the equation for the overall percentage uncertainty as
\[ \delta f = \left[ \left( \frac{df}{dh} \delta h \right)^2 + \left( \frac{df}{dL} \delta L \right)^2 + \left( \frac{df}{dE} \delta E \right)^2 + \left( \frac{df}{d\rho} \delta \rho \right)^2 \right]^{1/2} \] . (C.4)

where \( \delta h, \delta L, \delta E, \) and \( \delta \rho \) are the uncertainties in each independent parameter defining the resonance frequency of the cantilever. The values used for each of these parameters are listed in Table 5.4, and are also repeated in Table C.2, for completeness of this Section.

<table>
<thead>
<tr>
<th>Parametric values used</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus of elasticity, ( E ), GPa</td>
<td>190</td>
</tr>
<tr>
<td>Density, ( \rho ), g/cm(^3)</td>
<td>2.33</td>
</tr>
<tr>
<td>Thickness, ( h ) ( \mu m )</td>
<td>0.9853</td>
</tr>
<tr>
<td>Length, ( L ) ( \mu m )</td>
<td>353.2</td>
</tr>
</tbody>
</table>
Table C.2. The uncertainties in each parameter considered.

<table>
<thead>
<tr>
<th>Uncertainty in parameters defining $f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta h = 0.05 \ \mu m$</td>
</tr>
</tbody>
</table>

Contributions by the uncertainties of each independent parameter to the overall uncertainty in $f$ are

$$
\left( \frac{df}{dh} \right) = \left( \frac{df}{dh} \right) = \left[ \frac{1}{2\pi L^2} \sqrt{\frac{35E}{33\rho}} \right] \delta h
$$

$$
= \left( \frac{1}{2\pi L^2} \sqrt{\frac{35E}{33\rho}} \right) \delta h
$$

$$
= \frac{1}{2\pi (353.2\mu m)^2} \sqrt{\frac{35E}{33\rho} \left( 0.05 \mu m \right)}
$$

$$
= 593.232
$$

$$
\left( \frac{df}{dL} \right) = 330.981
$$

$$
\left( \frac{df}{dE} \right) = 92.291
$$

$$
\left( \frac{df}{d\rho} \right) = 12.543
$$

Substituting Eqs C.5 to C.8 into Eq. C.4, the overall uncertainty in $f$ is calculated to be

185
\[
\delta f = \left[ \left( \frac{df}{dh} \delta h \right)^2 + \left( \frac{df}{dL} \delta L \right)^2 + \left( \frac{df}{dE} \delta E \right)^2 + \left( \frac{df}{d\rho} \delta \rho \right)^2 \right]^{1/2}
\]
\[
= \left[ (593.232)^2 + (330.981)^2 + (92.291)^2 + (12.543)^2 \right]^{1/2}
= 685.673 \text{ Hz} .
\]

Once the overall uncertainty in the frequency is found, it is possible to determine the percentage uncertainty in \( f \) as

\[
\% \delta f = \frac{\delta f}{f} \cdot 100
= \frac{685.673}{11690.232} \cdot 100
= 5.865\% ,
\]

which is fairly high.

To discover the source of the uncertainty in Eq. C.10, it is possible to calculate the percent contribution by each parameter listed in Eq. C.3, as

\[
% \delta f \delta h = \frac{\left( \frac{df}{dh} \delta h \right)^2}{\left( \delta f \right)^2} \cdot 100
= \frac{(593.232)^2}{(685.673)^2} \cdot 100
= 74.854\% 
\]

\[
% \delta f \delta L = 23.301\% ,
\]

\[
% \delta f \delta E = 1.812\% ,
\]

\[
% \delta f \delta \rho = 0.033\% .
\]
where it can be seen that the thickness, \( h \), contributes the most with 74.8% to the overall percentage uncertainty in the frequency. It should be noted that all the percent contributions, Eqs C.11 thru C.14, add up to 100%, as they should. Therefore, the most effective way to reduce the overall uncertainty in \( f \) is to improve fabrication processes and decrease the \( \delta h \).

### C.1.2. Uncertainty calculations for the 300 µm long cantilever

The determination method of the overall percent uncertainty in the resonance frequency for this shorter cantilever is the same as with the 350 µm long one. Thus, the values from Tables C.1 and C.2 are used with the exception of the length value, which is now shorter at \( L=303.53 \) µm long and the explicit solutions are the same as those in Section C.1.1. Using Eq. C.4, the contributions due to uncertainties of each individual parameter to the overall uncertainty in \( f \) are

\[
\left( \frac{df}{dh} \delta h \right) = 803.272 \quad \text{(C.15)}
\]

\[
\left( \frac{df}{dL} \delta L \right) = 521.506 \quad \text{(C.16)}
\]

\[
\left( \frac{df}{dE} \delta E \right) = 124.968 \quad \text{(C.17)}
\]

\[
\left( \frac{df}{d\rho} \delta \rho \right) = 16.984 \quad \text{(C.18)}
\]
Substituting Eqs C.15 to C.18 into Eq. C.4, the overall uncertainty in $f$ is calculated, following the same formulation as C.9, to be

$$\delta f = 965.982 \text{ Hz}$$ \hspace{1cm} (C.19)

which is a higher value than that of the 350 µm long cantilever. Once the overall uncertainty in the frequency is found to 965.982 Hz, the percent overall uncertainty in $f$ is determined to be

$$\% \delta f = 6.102\% ,$$ \hspace{1cm} (C.20)

which is higher than with the 350 µm long cantilever.

To discover the source of the uncertainty in Eq. C.20, it is possible to calculate the percent contribution of each parameter listed in Eq. C.3 following the same formulation as Eq. C.11, as

$$\% \delta f \delta h = 69.149\%$$ \hspace{1cm} (C.21)

$$\% \delta f \delta L = 29.146\%$$ \hspace{1cm} (C.22)

$$\% \delta f \delta E = 1.674\%$$ \hspace{1cm} (C.23)

$$\% \delta f \delta \rho = 0.031\% ,$$ \hspace{1cm} (C.24)

where it can be seen that the thickness, $h$, once again contributes the most with 69.1%, although less than for the 350 µm long cantilever, to the overall percentage uncertainty in the frequency. The total sum of the percentages adds up to 100%, as they should.
C.1.3. Uncertainty calculations for the 250 µm long cantilever

The final determination of the overall percent uncertainty in the resonance frequency for the 250 µm long cantilever will be the same as in Sections C.1.1 and C.1.2. Thus, the values from Tables C.1 and C.2 are used with the exception of the length value, which is now even shorter at L=252.99 µm long and the explicit solutions are the same as those in Section C.1.1. Using Eq. C.4, the contributions due to uncertainties of each individual parameter to the overall uncertainty in $f$ are

$$\left( \frac{df}{dh} \right)_h = 1156.27$$  \hspace{1cm} (C.25)

$$\left( \frac{df}{dL} \right)_L = 900.647$$  \hspace{1cm} (C.26)

$$\left( \frac{df}{dE} \right)_E = 179.885$$  \hspace{1cm} (C.27)

$$\left( \frac{df}{d\rho} \right)_\rho = 24.448$$  \hspace{1cm} (C.28)

Substituting Eqs C.25 to C.28 into Eq. C.4, the overall uncertainty in $f$ is calculated, following the same formulation as C.9, to be

$$\delta f = 1476.848 \text{ Hz}$$  \hspace{1cm} (C.29)

which is higher than that of both the 300 and 350 µm long cantilevers. This is because of the shorter length of cantilever D and higher effect the uncertainty in length has. Once the overall uncertainty in the frequency is found to be 1474.848 Hz, the percent overall uncertainty in $f$ is determined to be

$$\% \delta f = 6.482\%$$  \hspace{1cm} (C.30)
which is higher than both the 300 and 350 µm long cantilever.

To discover the source of the uncertainty in Eq. C.10, it is possible to calculate the percent contribution of each parameter listed in Eq. C.3 following the same formulation as Eq. C.11, as

\[
\% \delta f \delta h = 61.298\% \quad (C.31)
\]

\[
\% \delta f \delta L = 37.191\% \quad (C.32)
\]

\[
\% \delta f \delta E = 1.484\% \quad (C.33)
\]

\[
\% \delta f \delta \rho = 0.027\% \quad , \quad (C.34)
\]

where it can be seen that the thickness, \( h \), for a third time contributes the most with 61% to the overall percentage uncertainty in the frequency. The total sum of the percentages adds up to 100%, as they should.

### C.1.4. Average overall percentage uncertainty in frequency

Once all the overall percentage uncertainties were found for each cantilever of different length, they were averaged for an overall percentage. Taking the results of Eqs C.10, C.20, and C.30 we obtain

\[
\left( \frac{5.865 + 6.102 + 6.482}{3} \right) = 6.15\% \quad (C.35)
\]

and thus the overall percentage uncertainty in the resonant frequency for these cantilevers is 6.15%.
C.2. Frequency uncertainty in a palladium coated cantilever

Sections C.2.1 through C.2.4 discuss the uncertainty in the frequency for several different cases for a palladium-coated cantilever absorbing a 1% hydrogen concentration at 20°C and 1 atm pressure. The concentration will not be considered for anything above 1%. For each case as described in Sections 5.11.1 through 5.11.4 the overall uncertainty, percent uncertainty, and contributing variables uncertainties will be calculated for an ideal cantilever of $L=350$ µm long, $h=1$ µm thick, and $b=35$ µm wide. Table C.3 presents the values used for this analysis.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density $r$ (g/cm$^3$)</th>
<th>Modulus of elasticity $E$ (GPa)</th>
<th>Thickness $h$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon, Si</td>
<td>2.330</td>
<td>190</td>
<td>1</td>
</tr>
<tr>
<td>Palladium, Pd</td>
<td>12.023</td>
<td>121</td>
<td>0.1</td>
</tr>
<tr>
<td>Titanium, Ti</td>
<td>4.507</td>
<td>116</td>
<td>0.001</td>
</tr>
<tr>
<td>Equivalent values</td>
<td>3.995</td>
<td>172.9</td>
<td>1.101</td>
</tr>
</tbody>
</table>

C.2.1. Uncertainty in frequency for a free vibrations system

The uncertainty in frequency for a free, undamped vibrating system will be determined in the equation for the frequency shift. Equation 5.11, which relates to the frequency shift due to hydrogen absorption, is
\[
\frac{1}{2\pi L^2} \sqrt{\frac{35E_{eq}}{33\rho_{eq}}} \sqrt{\frac{\Delta m}{m} + 1}
\]

where \(\Delta m\) is the increase in mass, \(m\) is the initial dynamic mass, \(E_{eq}\) is the equivalent modulus as defined in Eq. 4.6, and \(\rho_{eq}\) is the equivalent density as defined in Eq. 4.7. The values for the equivalent modulus and density can be found in Table C.3. The increase in mass, \(\Delta m\), can be written as

\[
\Delta m = \left(\text{absorption multiplier}\right) \left(H_2\text{-density}\right) \left(V_{\text{atm}}\right)
\]

where it is desirable to write each component in terms of the concentration in units of ppm. Thus, based on Table 4.1,

\[
\text{absorption multiplier} = 1.25 \cdot 10^3 \left(\frac{\text{ppm}}{10000}\right)^2 0.621
\]

\[
\text{absorption multiplier} = 1.25 \cdot 10^3 \left(\frac{10000}{10000}\right)^2 0.621
\]

\[
\text{absorption multiplier} = 776.25
\]

converts the atomic ratio into the equivalent multiplier factor of the volume of hydrogen in the palladium in terms of the concentration. Using Eq. 4.9, density of hydrogen at 1% concentration, 20°C, and 1 atm (0.01 atm partial pressure) is written as
\[ H_{2\_density} = \left( \frac{ppm\cdot molecular\_weight\cdot 273\cdot p}{0.0224 \, m^3\cdot T\cdot 1\text{atm}} \right) \]

\[ H_{2\_density} = \left( \frac{10000\, ppm\cdot 2\cdot 1.00794 \, g}{mol} \cdot (273\, K) \cdot (0.01\text{atm})}{0.0224 \, m^3\cdot (293\, K)\cdot 1\text{atm}} \right) \tag{C.39} \]

\[ H_{2\_density} = 8.385 \, \frac{kg}{m^3}, \]

where \( ppm \) is the gas concentration, \( molecular\_weight \) is the molecular weight of the diatomic hydrogen, and \( p \) and \( T \) are the partial pressure (in atm) and temperature (in °K) of the gas, respectively. Since the concentration is directly related to the partial pressure, \( p \), it can be written in terms of concentration as

\[ p = \frac{ppm}{10^6} \cdot 1\text{atm}, \tag{C.40} \]

when the total pressure of the gas mixture, in this case \( H_2 \) and \( N_2 \), is equal to 1 atm. The last part of Eq. C.37, \( V_{Pd} \), is the volume of palladium deposited on the cantilever and it can be written as a function of just the cantilever dimensions and the layer thickness of \( Pd \) and \( Ti \) as

\[ V = bhL \]
\[ = 35\, \mu m \cdot 1\, \mu m \cdot 350\, \mu m \]
\[ = 12,250 \, \mu m^3, \tag{C.41} \]

\[ V_{Ti} = \left[ \left( b+2h \right) \left( h+2h \right) \left( L+h \right) \right] - V \]
\[ = \left[ \left( 35+2\cdot 0.001 \right) \mu m \cdot \left( 1+2\cdot 0.001 \right) \mu m \cdot \left( 350+2\cdot 0.001 \right) \mu m \right] - 12,250\mu m^3 \tag{C.42} \]
\[ = 25.236 \, \mu m^3, \]
\[ V_i = \left( b + 2(h_{Ti} + h_{Pd}) \right) \left( h + 2(h_{Ti} + h_{Pd}) \right) \left( L + h_{Ti} + h_{Pd} \right) \]
\[ = \left( 35 + 2(0.001 + 0.1) \right) \mu m \cdot \left( 1 + 2(0.001 + 0.1) \right) \mu m \]
\[ = 14,813.755 \mu m , \]

and
\[ V_{Pd} = V_i - \left( V_{Ti} + V \right) \]
\[ = 14,813.755 \mu m^3 - \left( 25.236 \mu m^3 + 12,250 \mu m^3 \right) \]
\[ = 2538.519 \mu m^3 , \]

with \( h_{Ti} \) and \( h_{Pd} \) being the thickness of the titanium and palladium layer, respectively. As can be seen the increase in mass, \( \Delta m \), will be comprised of Eqs C.38, C.39, and C.44 and will have five uncertainty contributing variables aside from being in terms of ppm. Thus we will write \( \Delta m \) as
\[ \Delta m = \Delta m \left( b, h, L, h_{Ti}, h_{Pd} \right) \]  
(C.45)
to show which parameters \( \Delta m \) depends on. Using the values listed in Table C.3, a concentration of 1% hydrogen can be found to be equal to
\[ \Delta m = \left( \text{absorption multiplier} \right) \left( H_2 \text{-density} \right) \left( V_{Pd} \right) , \]
\[ = (776.25) \left( 8.385 \frac{kg}{m^3} \right) (2538.519 \mu m^3) , \]
\[ = 1.652 \cdot 10^{-11} \text{kg} , \]
which is quite large compared to
\[ m = \rho V + \rho_{pd} V_{pd} + \rho_{Ti} V_{Ti} \]
\[ = \frac{2.33 \, g}{cm^3} \cdot 12,250 \mu m^3 + 4.507 \frac{g}{cm^3} \cdot 25.236 \mu m^3 + \]
\[ 12.023 \frac{g}{cm^3} \cdot 2538.519 \mu m^3 \]
\[ = 5.918 \times 10^{-11} \text{ kg} \]

which is the mass for the entire cantilever.

The uncertainty analysis of Eq. C.36 will be very similar to that of Section C.1 except Eq. C.36 will contain many more parameters. The mass and equivalent modulus and density are functions of other variables themselves. They can be written as

\[ m = m\left(b, h, L, h_{Ti}, h_{pd}\right) \]
\[ \left(\text{C.48}\right) \]

\[ E_{eq} = E_{eq}\left(b, h, L, h_{Ti}, h_{pd}, E_{Si}, E_{Ti}, E_{pd}\right) \]
\[ \left(\text{C.49}\right) \]

and

\[ \rho_{eq} = \rho_{eq}\left(b, h, L, h_{Ti}, h_{pd}, \rho_{Si}, \rho_{Ti}, \rho_{pd}\right) \]
\[ \left(\text{C.50}\right) \]

Thus, based on Eqs C.48 to C.50, Eq. C.36 can be written in terms of all the variables that comprise it as

\[ f_2 = \frac{1}{2\pi L^2} \sqrt{\frac{35E_{eq}\left(b, h, L, h_{Ti}, h_{pd}, E_{Ti}, E_{pd}\right)}{33\rho_{eq}\left(b, h, L, h_{Ti}, h_{pd}, \rho_{Si}, \rho_{Ti}, \rho_{pd}\right)}} \]
\[ \frac{\Delta m\left(b, h, L, h_{Ti}, h_{pd}\right)}{m\left(b, h, L, h_{Ti}, h_{pd}\right) + 1} \]
\[ \left(\text{C.51}\right) \]

based on which the frequency shift equation in its phenomenological form is
\[ f_2 = f_2 \left( b, h, L, h_{Ti}, h_{Pd}, E_{Si}, E_{Ti}, E_{Pd}, \rho_{Si}, \rho_{Ti}, \rho_{Pd} \right) \]  \quad \text{(C.52)}

If the values listed in Table C.3 are inserted into Eq. C.51 we get a resonant frequency of

\[
f_2 = \frac{1}{2\pi L} \sqrt{\frac{35 \rho_{eq}}{33 \rho_{eq}}} \cdot \frac{1}{m^{+1}} (\Delta m)
\]

\[
f_2 = \frac{1}{2\pi (350 \mu m)^2} \sqrt{\frac{35 (172.9 \text{GPa})}{33 (3.995 \text{g cm}^{-3})}} \cdot \frac{1}{\sqrt{1.652 \cdot 10^{-11} \text{kg}^2 + 1}} \cdot \frac{1.652 \cdot 10^{-11} \text{kg}}{5.918 \cdot 10^{-11} \text{kg}} \quad \text{(C.53)}
\]

\[ f_2 = 7783.268 \text{ Hz} \]

for this case. Using Eq. C.51, it is now possible to write the overall uncertainty equation

\[
\delta f_2 = \left[ \left( \frac{df_2}{db} \delta b \right)^2 + \left( \frac{df_2}{dh} \delta h \right)^2 + \left( \frac{df_2}{dL} \delta L \right)^2 + \left( \frac{df_2}{dh_{Ti}} \delta h_{Ti} \right)^2 + \left( \frac{df_2}{dh_{Pd}} \delta h_{Pd} \right)^2 + \right]
\]

\[
\left( \frac{df_2}{dE_{Si}} \delta E_{Si} \right)^2 + \left( \frac{df_2}{dE_{Ti}} \delta E_{Ti} \right)^2 + \left( \frac{df_2}{dE_{Pd}} \delta E_{Pd} \right)^2 + \left( \frac{df_2}{d\rho_{Si}} \delta \rho_{Si} \right)^2 + \left( \frac{df_2}{d\rho_{Ti}} \delta \rho_{Ti} \right)^2 + \left( \frac{df_2}{d\rho_{Pd}} \delta \rho_{Pd} \right)^2 \right], \quad \text{(C.54)}
\]

where each parameter will individually be taken into account to determine its contribution to the overall uncertainty. The values used for each of the parameters appearing in Eq. C.54 are listed in Table C.4.
Table C.4. The uncertainty values used based on current industry practice.

<table>
<thead>
<tr>
<th>Uncertainty in parameters defining $f$</th>
<th>$\delta h =0.05 \ \mu m$</th>
<th>$\delta L =5 \ \mu m$</th>
<th>$\delta E_{Si} =3 \ \text{GPa}$</th>
<th>$\delta \rho_{Si} =0.005 \ \text{g/cm}^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta h_{Ti} =0.0005 \ \mu m$</td>
<td>$\delta b =3 \ \mu m$</td>
<td>$\delta E_{Ti} =3 \ \text{GPa}$</td>
<td>$\delta \rho_{Ti} =0.005 \ \text{g/cm}^3$</td>
<td></td>
</tr>
<tr>
<td>$\delta h_{Pd} =0.0005 \ \mu m$</td>
<td>--</td>
<td>$\delta E_{Pd} =3 \ \text{GPa}$</td>
<td>$\delta \rho_{Pd} =0.005 \ \text{g/cm}^3$</td>
<td></td>
</tr>
</tbody>
</table>

Contributions due to uncertainties of each individual parameter to the overall uncertainty in $f$, using the values in Table C.4 and the steps shown in Eq. C.5, are

\[
\frac{df}{db} \delta b = 5.806 \quad (C.55)
\]

\[
\frac{df}{dh} \delta h = 488.218 \quad (C.56)
\]

\[
\frac{df}{dL} \delta L = 222.33 \quad (C.57)
\]

\[
\frac{df}{dh_{Ti}} \delta h_{Ti} = 1.353 \quad (C.58)
\]

\[
\frac{df}{dh_{Pd}} \delta h_{Pd} = 10.248 \quad (C.59)
\]

\[
\frac{df}{dE_{Si}} \delta E_{Si} = 46.243 \quad (C.60)
\]

\[
\frac{df}{dE_{Ti}} \delta E_{Ti} = 0.256 \quad (C.61)
\]
\[
\frac{df}{dE_{pd}} \delta E_{pd} = 23.628 \quad (C.62)
\]

\[
\frac{df}{d\rho_{Si}} \delta \rho_{Si} = 3.149 \quad (C.63)
\]

\[
\frac{df}{d\rho_{Ti}} \delta \rho_{Ti} = 0.006 \quad (C.64)
\]

\[
\frac{df}{d\rho_{pd}} \delta \rho_{pd} = 0.653 \quad . \quad (C.65)
\]

Substituting Eqs C.55 to C.65 into Eq. C.54, the overall uncertainty in \( f \) is calculated, following similar steps as in Eq. C.9, as

\[
\delta f_2 = 539.106 \text{ Hz} \quad , \quad (C.66)
\]

which is the deviation possible in the resonance frequency for a system absorbing hydrogen, based on the values of the parameters used in the uncertainty analysis. Thus the overall percentage uncertainty in the frequency, following similar steps as in Eq. C.10, for this case is

\[
\% \delta f_2 = 6.926\% \quad , \quad (C.67)
\]

which is similar to the simplified case in Section C.1.

To discover the contributing factors to this percent uncertainty, each variable listed in Eq. C.54 is evaluated and the percent contributions are determined. The percent contribution by uncertainties of each independent parameter, following similar steps as Eq. C.11, is
where it can be seen that the thickness, $h$, contributes the most with 82% to the overall percentage uncertainty in the frequency. The total sum of the percentages adds up to 100%, as they should.

### C.2.2. Uncertainty in frequency for a free vibrations system with changing stiffness

For a free, undamped vibrating system that has a spring constant that changes the equation for the frequency shift will be slightly different that that one of Eq. C.36.

Equation 5.12 relates the frequency shift due to hydrogen absorption as
\[ f_2 = \sqrt{\frac{1}{2\pi L^2}} \left( \frac{35 E_{eq}}{33 \rho_{eq}} \right)^2 \left( 1 + \frac{\Delta k}{k} \right) \left( 1 + \frac{\Delta m}{m} \right) \]  

(C.79)

where \( \Delta k \) is the change in the damping coefficient. The change in the stiffness will come from the ability for the modulus of elasticity of palladium to change as it absorbs hydrogen. Using Fig. 4.6, a function was created to fit along the curve. This function takes a complex form and for a concentration of 1% becomes

\[ \Delta E_{incr} = 1 + \frac{5}{100} \cos \left( \left( \frac{ppm}{10000} \right)^2 \cdot 0.621 - 0.05 \left( \frac{\pi}{0.621} \right), \right) - \frac{5}{100} \cos \left( 0.05 \left( \frac{\pi}{0.621} \right), \right) \]

\[ = 1 + \frac{5}{100} \cos \left( \left( \frac{ppm}{10000} \right)^2 \cdot 0.621 - 0.05 \left( \frac{\pi}{0.621} \right), \right) - 0.049 \]

\[ = 0.915 \]

and fits into the equivalent modulus equation, Eq. 4.6. If Eq. C.80 is substituted into Eq. 5.4 and solved for the case of 1%, or 10000 ppm, hydrogen it becomes

\[ E_{eq} = \frac{(E_{Si} \cdot E_{Ti} \cdot \Delta E_{incr} E_{Pd} \cdot V_t)}{E_{Ti} \Delta E_{incr} E_{Pd} V_{Si} + E_{Si} \Delta E_{incr} E_{Pd} V_{Ti} + E_{Si} E_{Ti} V_{Pd}} \]

\[ = \frac{(190 \cdot 116 \cdot 0.915 \cdot 121)(14,813.76)}{116 \cdot 0.915 \cdot 121(12,250) + 190 \cdot 0.915 \cdot 121(25.24) + 190 \cdot 116(2538.52)} \]

(C.81)

\[ = 167.3 \text{ GPa} \]

where the influence of the change in the modulus is put into concentration terms, ppm.

To determine the stiffness for this case, Eq. B.43 is modified so that
where \( b_t, h_t, \) and \( L_t \) are the total width, thickness, and length, respectively, following Fig. 4.7. To determine the change in the stiffness, \( \Delta k \), it will be necessary to include the changing volume, limited only to the thickness, as a function of concentration

\[
h_A = 1 + \left( \frac{ppm}{10000} \right)^2 \frac{0.621}{5} = 1 + \left( \frac{10000}{10000} \right)^2 \frac{0.621}{5} = 1.124 ,
\]

where the increase in thickness due to 1% hydrogen is accounted for. It is then possible to calculate the shifted modulus of elasticity with a modified Eq. C.82 as

\[
k_A = \frac{E_{\text{eq}} b_t h_t^3}{4L_t^3} = \frac{E_{\text{eq}} (b + 2h_{T_t} + 2h_{Pd})(h + 2h_{T_t} + 2h_{Pd})^3}{4(L + h_{T_t} + h_{Pd})^3} = 167.3 GPa \left[ (35 + 2 \cdot 0.001 + 2 \cdot 0.1) \mu m \right] \left[ (1 + 2 \cdot 0.001 + 1.124 \cdot 2 \cdot 0.1) \mu m \right] \frac{N}{m} ,
\]

(0.063)
To determine the change in stiffness the difference between Eqs C.84 and 82 is calculated as

\[ \Delta k = k_\Delta - k \]

\[ = 0.063 \frac{N}{m} - 0.062 \frac{N}{m} \]

\[ = 0.001 \frac{N}{m} . \]  (C.85)

If we use the same values listed in Table C.3 and including Eqs C.82 and C.85 we find that the frequency for Eq. C.79 is equal to

\[ f_2 = \sqrt{\frac{1}{2\pi L^2} \left[ \frac{35 E_{eq}}{33 \rho_{eq}} \right]^2 \left( 1 + \frac{\Delta k}{k} \right)} + \left( 1 + \frac{\Delta m}{m} \right) \]

\[ f_2 = \left\{ \frac{1}{2\pi} \frac{1\mu m}{(350\mu m)^2} \sqrt{\frac{35(172.9 GPa)}{33 \left( \frac{3.995 \text{ g}}{\text{cm}^3} \right)}} \right\}^2 \left( 1 + \frac{0.001 \frac{N}{m}}{0.062 \frac{N}{m}} \right) + \left( \frac{1.652 \cdot 10^{-11} \text{ kg}}{5.918 \cdot 10^{-11} \text{ kg}} \right) \]  (C.86)

\[ f_2 = 7894.523 \text{ Hz} . \]

The phenomenological relation for Eq. C.86 is the same as in Section C.2.1, i.e.,

\[ f_2 = f_2 \left( b, h, L, h_e, h_f, E_{eq}, E_{eq}, E_{eq}, \rho_{eq}, \rho_{eq}, \rho_{eq} \right) \]  (C.87)

where the change in the stiffness does not add any additional variables. Thus, we can use the same overall uncertainty given by Eq. C.54 and determine the contributions due to uncertainties of each individual parameter to the overall uncertainty in \( f \), using the values in Table C.4 and the steps as in Eq. C.5, as
\[
\left( \frac{df}{db} \right) = 6.172
\]
(C.88)

\[
\left( \frac{df}{dh} \right) = 492.682
\]
(C.89)

\[
\left( \frac{df}{dL} \right) = 229.036
\]
(C.90)

\[
\left( \frac{df}{dh} \right) = 1.556
\]
(C.91)

\[
\left( \frac{df}{dh} \right) = 9.54
\]
(C.92)

\[
\left( \frac{df}{dE} \right) = 46.584
\]
(C.93)

\[
\left( \frac{df}{dE} \right) = 0.257
\]
(C.94)

\[
\left( \frac{df}{dE} \right) = 26.002
\]
(C.95)

\[
\left( \frac{df}{d\rho} \right) = 3.244
\]
(C.96)

\[
\left( \frac{df}{d\rho} \right) = 0.007
\]
(C.97)
\[ \left( \frac{df}{d \rho_{pd}} \delta \rho \right)_{\rho_{pd}} = 0.672 \]  \hspace{1cm} (C.98)

Substituting Eqs C.88 to C.98 into Eq. C.54, the overall uncertainty in \( f \) is calculated as

\[ \delta f_2 = 546.06 \text{ Hz} \]  \hspace{1cm} (C.99)

which is the deviation possible in the resonance frequency for a system absorbing hydrogen. Thus the overall percentage uncertainty in the frequency for this case is

\[ \% \delta f_2 = 6.917\% \]  \hspace{1cm} (C.100)

which is very similar to the result of Eq. C.67.

To discover the contributing factors of the percent uncertainty given by Eq. C.100, each variable listed in Eq. C.54 is evaluated and the percent contribution is determined. The percent contribution of each parameter is

\[ \% \delta f \delta b = 0.013\% \]  \hspace{1cm} (C.101)

\[ \% \delta f \delta h = 81.405\% \]  \hspace{1cm} (C.102)

\[ \% \delta f \delta L = 17.593\% \]  \hspace{1cm} (C.103)

\[ \% \delta f \delta h_{ti} = 8.116 \cdot 10^{-4} \% \]  \hspace{1cm} (C.104)

\[ \% \delta f \delta h_{pd} = 0.91\% \]  \hspace{1cm} (C.105)

\[ \% \delta f \delta E_{Si} = 0.728\% \]  \hspace{1cm} (C.106)

\[ \% \delta f \delta E_{ti} = 2.223 \cdot 10^{-5} \% \]  \hspace{1cm} (C.107)

\[ \% \delta f \delta E_{pd} = 0.227\% \]  \hspace{1cm} (C.108)

\[ \% \delta f \delta \rho_{St} = 0.004\% \]  \hspace{1cm} (C.109)
\[
\% \delta f \delta \rho_{Ti} = 1.498 \cdot 10^{-8}\% \tag{C.110}
\]

\[
\% \delta f \delta \rho_{pd} = 1.515 \cdot 10^{-4}\% , \tag{C.111}
\]

where it can be seen that the thickness, \( h \), contributes the most with 81.4\% to the overall percentage uncertainty in the frequency. The total sum of the percentages adds up to 100\%, as they should.

### C.2.3. Uncertainty in frequency for a free vibrations system with damping

For a free, damped vibrating system the equation for the frequency shift will be different as the angular frequency is now different, see Eq. B.69. The new equation that relates the frequency shift due to hydrogen absorption, is

\[
f_2 = \sqrt{\left( \frac{1}{2\pi L^2} \frac{35 E_{eq}}{33 \rho_{eq}} \right) - \left( \frac{4k (m + \Delta m) - c^2}{4k (m + \Delta m)^2} \right)^2} \tag{C.112}
\]

where \( c \) is the damping coefficient. The damping coefficient, Eq. 4.25, is equal to

\[
c = \frac{2\mu L b}{H} = 2 \left( 1.77 \cdot 10^{-11} \frac{kg}{\mu m \cdot s} \right) \left( 350 \mu m \right) \left( 35 \mu m \right) \frac{21.8 \mu m}{350 \mu m \cdot 35 \mu m} \tag{C.113}
\]

\[
= 1.988 \cdot 10^{-8} \frac{N \cdot s}{m}
\]

which shows that it is a function of the variables \( \mu, L, b, \) and \( H \) and we can write it in its phenomenological form as
\[ c = c(\mu, L, b, H) \]  
(C.114)

for simplification. This indicates that there are now two additional variables to the frequency and thus the phenomenological relation based on Eq. C.112 becomes

\[
f_2 = f_2 \left( b, h, L, h, E_{\text{Si}}, E_{\text{Pd}}, \rho_{\text{Si}}, \rho_{\text{Pd}}, \mu, H \right),
\]
(C.115)

where the viscosity, \( \mu \), and the damping fluid thickness, \( H \), are listed. If we use the values listed in Table C.3 and additionally in Table C.5 we find that the frequency for Eq. C.112 is equal to

\[
f_2 = \left[ \frac{1}{2\pi} \frac{h}{L^2} \sqrt{\frac{35}{33} \frac{E_{\text{eq}}}{\rho_{\text{eq}}}} \right]^2 \left( \frac{m}{m + \Delta m} \right) - \frac{mc^2}{4k (m + \Delta m)^2} \\
= \left[ \frac{1}{2\pi} \frac{1\mu m}{(350\mu m)^2} \sqrt{\frac{35(172.9\text{GPa})}{33(3.995\text{g/cm}^3)}} \right]^2 \cdot \left\{ \frac{(5.918 \cdot 10^{-11} \text{kg})}{(5.918 \cdot 10^{-11} \text{kg} + 1.652 \cdot 10^{-11} \text{kg})} - \frac{(5.918 \cdot 10^{-11} \text{kg})(1.988 \cdot 10^{-8} N \cdot s/m)}{4 \left( 0.062 \frac{N}{m} \right) (5.918 \cdot 10^{-11} \text{kg} + 1.652 \cdot 10^{-11} \text{kg})^2} \right\}^{1/2} \\
= 7783.313\text{Hz}.
\]

Because of the two additional variables, the overall uncertainty equation is going to change to take them into account and thus the equation takes the form of
\[ \delta f_2 = \left[ \left( \frac{df}{db} \right)^2 \delta b \right]^2 + \left( \frac{df}{dh} \delta h \right)^2 + \left( \frac{df}{dL} \delta L \right)^2 + \left( \frac{df}{dh_{ri}} \delta h_{ri} \right)^2 + \]

\[ + \left( \frac{df}{dh_{pd}} \delta h_{pd} \right)^2 + \left( \frac{df}{dE_{si}} \delta E_{si} \right)^2 + \left( \frac{df}{dE_{ri}} \delta E_{ri} \right)^2 + \]

\[ + \left( \frac{df}{d\rho_{si}} \delta \rho_{si} \right)^2 + \left( \frac{df}{d\rho_{ri}} \delta \rho_{ri} \right)^2 + \]

\[ + \left( \frac{df}{d\mu} \delta \mu \right)^2 + \left( \frac{df}{dH} \delta H \right)^2 \] \hspace{1cm} (C.117)

where each variable will individually be taken into account as before with the viscosity and damping fluid thickness included.

**Table C.5. Values of the two additional independent parameters in the damped case.**

<table>
<thead>
<tr>
<th>Parameter values</th>
<th>( \mu ) kg/( \mu )m-s</th>
<th>( \delta \mu =5 \times 10^{-14} )</th>
<th>( \delta m = 1.769 \times 10^{-11} )</th>
<th>( \delta H = 0.05 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity of nitrogen, ( \mu ) kg/( \mu )m-s</td>
<td>1.769 \times 10^{-11}</td>
<td>( \delta \mu = 5 \times 10^{-14} )</td>
<td>( \delta m = 1.769 \times 10^{-11} )</td>
<td>( \delta H = 0.05 )</td>
</tr>
<tr>
<td>Damping fluid thickness, ( H ) ( \mu )m</td>
<td>21.8</td>
<td>( \delta H = 0.05 )</td>
<td>( \delta H = 0.05 )</td>
<td>( \delta H = 0.05 )</td>
</tr>
</tbody>
</table>

Contributions due to uncertainties of each individual parameter to the overall uncertainty in \( f \), using the values in Table C.4 and the steps as in Eq. C.5, are

\[ \left( \frac{df}{db} \right)^2 \delta b = 5.806 \] \hspace{1cm} (C.118)

\[ \left( \frac{df}{dh} \right)^2 \delta h = 488.225 \] \hspace{1cm} (C.119)

\[ \left( \frac{df}{dL} \right)^2 \delta L = 222.333 \] \hspace{1cm} (C.120)
\[
\frac{df}{dh_{Ti}} \delta h_{Ti} = 1.353 \quad \text{(C.121)}
\]
\[
\frac{df}{dh_{Pd}} \delta h_{Pd} = 10.247 \quad \text{(C.122)}
\]
\[
\frac{df}{dE_{Si}} \delta E_{Si} = 46.244 \quad \text{(C.123)}
\]
\[
\frac{df}{dE_{Ti}} \delta E_{Ti} = 0.256 \quad \text{(C.124)}
\]
\[
\frac{df}{dE_{Pd}} \delta E_{Pd} = 23.628 \quad \text{(C.125)}
\]
\[
\frac{df}{d\rho_{Si}} \delta \rho_{Si} = 3.149 \quad \text{(C.126)}
\]
\[
\frac{df}{d\rho_{Ti}} \delta \rho_{Ti} = 6.487 \cdot 10^{-3} \quad \text{(C.127)}
\]
\[
\frac{df}{d\rho_{Pd}} \delta \rho_{Pd} = 0.652 \quad \text{(C.128)}
\]
\[
\frac{df}{d\mu} \delta \mu = 4.664 \cdot 10^{-4} \quad \text{(C.129)}
\]
\[
\frac{df}{dH} \delta H = 3.785 \cdot 10^{-4} \quad \text{(C.130)}
\]
Substituting Eqs C.118 to C.130 into Eq. C.117, the overall uncertainty in $f$ is calculated, following similar steps as in Eq. C.9, as

$$\delta f_z = 539.113 \text{ Hz}, \quad (C.131)$$

which is the deviation possible in the resonance frequency for a system absorbing hydrogen. Thus the overall percentage uncertainty in the frequency for this case is

$$\% \delta f_z = 6.927\% \quad (C.132)$$

which is very similar to the result of Eq. C.100.

To discover the contributing factors of this percent uncertainty, each variable listed in Eq. C.54 is evaluated and the percent contribution is determined. The percent contribution of each parameter is

$$\% \delta f \delta b = 0.012\% \quad (C.133)$$

$$\% \delta f \delta h = 82.012\% \quad (C.134)$$

$$\% \delta f \delta L = 17.008\% \quad (C.135)$$

$$\% \delta f \delta h_{Ti} = 0.001\% \quad (C.136)$$

$$\% \delta f \delta h_{pd} = 1.05\% \quad (C.137)$$

$$\% \delta f \delta E_{Si} = 0.736\% \quad (C.138)$$

$$\% \delta f \delta E_{Ti} = 2.248 \cdot 10^{-5}\% \quad (C.139)$$

$$\% \delta f \delta E_{pd} = 0.192\% \quad (C.140)$$

$$\% \delta f \delta \rho_{Si} = 0.003\% \quad (C.141)$$

$$\% \delta f \delta \rho_{Ti} = 1.448 \cdot 10^{-8}\% \quad (C.142)$$
\[ \%\delta f \delta \rho_p = 1.465 \cdot 10^{-4}\% \quad (C.143) \]

\[ \%\delta f \delta \mu = 7.484 \cdot 10^{-11}\% \quad (C.144) \]

\[ \%\delta f \delta H = 4.93 \cdot 10^{-11}\% \quad , \quad (C.145) \]

where it can be seen that the thickness, \( h \), contributes the most with 82\% to the overall percentage uncertainty in the frequency. The total sum of the percentages adds up to 100\%, as they should.

**C.2.4. Uncertainty in frequency for a damped, changing stiffness vibrations system**

For a free, damped vibrating system that has a spring constant that changes the equation for the frequency shift will be slightly different than that one of Eq. C.112. The final modified equation that relates the frequency shift due to hydrogen absorption, is

\[
 f_2 = \sqrt{ \frac{1}{2\pi L^2} \left[ \frac{35 E_{eq}}{33 \rho_{eq}} \right]^2 m \left[ \frac{4k (m + \Delta m) - c^2}{4(k + \Delta k) (m + \Delta m)^2} \right] } \quad (C.146)
\]

where \( \Delta k, \Delta m, \) and \( c \) are all included. If we use the same values listed in Tables C.3 and C.5 we find that the frequency for Eq. C.146 is equal to
\[ f_2 = \sqrt{\frac{1}{2\pi L} \left( \frac{35 E_{eq}}{33 \rho_{eq}} \right)} \cdot \frac{m}{4(k + \Delta k) (m + \Delta m)} \]

\[ = \left[ \frac{1}{2\pi} \frac{1_\mu m}{(350 \mu m)^2} \sqrt{\frac{35(172.9 \text{ GPa})}{33 \left(3.995 \frac{\text{g}}{\text{cm}^3}\right)}} \right]^2 \]

\[ \frac{\left(5.918 \cdot 10^{-11} \text{ kg}\right) \left[4 \left(0.062 \frac{N}{m}\right) \left(5.918 \cdot 10^{-11} \text{ kg} + 1.652 \cdot 10^{-11} \text{ kg}\right)\right]}{4 \left(0.062 \frac{N}{m} + 0.001 \frac{N}{m}\right) \left(5.918 \cdot 10^{-11} \text{ kg} + 1.652 \cdot 10^{-11} \text{ kg}\right)} - \frac{\left(5.918 \cdot 10^{-11} \text{ kg}\right) \left(1.988 \cdot 10^{-8} \frac{N - s}{m}\right)}{4 \left(0.062 \frac{N}{m} + 0.001 \frac{N}{m}\right) \left(5.918 \cdot 10^{-11} \text{ kg} + 1.652 \cdot 10^{-11} \text{ kg}\right)} \right]^{1/2} \]

\[ = 7673.619 \text{ Hz} \]  

The phenomenological form for Eq. C.147 is the same as the damped case, expressed by Eq. C.112, so the phenomenological relationship takes the form of

\[ f_2 = f_2 \left(b, h, L, h, h, \rho_{si}, \rho_{si}, \rho_{pd}, \rho_{pd}, \mu, H\right) \]  

where all the variables are included. Thus, we can use the same overall uncertainty as Eq. C.117 and determine the contributions due to uncertainties of each individual parameter to the overall uncertainty in \( f \), using the values in Table C.4 and the steps as in Eq. C.5, are

\[ \left(\frac{df}{db}\right)^2 \delta b = 5.457 \]  

(C.149)
\[
\left( \frac{df}{dh} \delta h \right) = 483.599 
\]
\[
\left( \frac{df}{dL} \delta L \right) = 215.823 
\]
\[
\left( \frac{df}{dh} \delta h \right)_T = 1.162 
\]
\[
\left( \frac{df}{dh} \delta h \right)_P = 10.905 
\]
\[
\left( \frac{df}{dE} \delta E \right)_S = 45.883 
\]
\[
\left( \frac{df}{dE} \delta E \right)_T = 0.254 
\]
\[
\left( \frac{df}{dE} \delta E \right)_P = 21.372 
\]
\[
\left( \frac{df}{d\rho} \delta \rho \right)_S = 3.056 
\]
\[
\left( \frac{df}{d\rho} \delta \rho \right)_T = 0.006 
\]
\[
\left( \frac{df}{d\rho} \delta \rho \right)_P = 0.633 
\]
\[
\left( \frac{df}{d\mu} \delta\mu \right) = 4.527 \cdot 10^{-4} \quad (C.160)
\]

\[
\left( \frac{df}{dH} \delta H \right) = 3.674 \cdot 10^{-4} . \quad (C.161)
\]

Substituting Eqs C.149 to C.161 into Eq. C.117, the overall uncertainty in \( f \) is calculated, following similar steps as in Eq. C.9, as

\[
\delta f_2 = 532.137 \text{ Hz} , \quad (C.162)
\]

which is the deviation possible in the resonance frequency for a system absorbing hydrogen. Thus the overall percentage uncertainty in the frequency for this case is

\[
%\delta f_2 = 6.696% , \quad (C.163)
\]

which is very similar to the result of Eq. C.100.

To discover the contributing factors of this percent uncertainty, each variable listed in Eq. C.54 is evaluated and the percent contribution is determined. The percent contribution of each parameter is

\[
%\delta f \delta b = 0.011% \quad (C.164)
\]

\[
%\delta f \delta h = 82.589% \quad (C.165)
\]

\[
%\delta f \delta L = 16.449% \quad (C.166)
\]

\[
%\delta f \delta h_{ri} = 4.764 \cdot 10^{-4}% \quad (C.167)
\]

\[
%\delta f \delta h_{pd} = 1.189% \quad (C.168)
\]

\[
%\delta f \delta E_{St} = 0.743% \quad (C.169)
\]

\[
%\delta f \delta E_{Ti} = 2.271 \cdot 10^{-5}% \quad (C.170)
\]
\[
\% \delta f \delta E_{pd} = 0.161\% \\
\% \delta f \delta \rho_{Si} = 0.003\% \\
\% \delta f \delta \rho_{Ti} = 1.4 \cdot 10^{-8}\% \\
\% \delta f \delta \rho_{pd} = 1.417 \cdot 10^{-4}\% \\
\% \delta f \delta \mu = 7.238 \cdot 10^{-11}\% \\
% \delta f \delta H = 4.768 \cdot 10^{-11}\% ,
\]

where it can be seen that the thickness, \( h \), contributes the most with 82.3% to the overall percentage uncertainty in the frequency. The total sum of the percentages adds up to 100%, as they should.
APPENDIX D.  TEST CHAMBER

In this Appendix the blueprints for the test chamber are shown along with some pictures of the finished component.

Fig. D.1. Specifications of the main body of the test chamber.
Fig. D.2. Specifications of the lid for the main body of the test chamber.

Fig. D.3. Fully disassembled view of the chamber showing all parts.
Fig. D.4. Fully assembled view of chamber with PZT inside.

Fig. D.5. Isometric view of the assembled chamber.
APPENDIX E. ANALYTICAL FREQUENCY DATA

Using measured dimensions of the cantilevers, it was possible to calculate the theoretical resonant frequency for each cantilever based on Eq. 4.23. Figure E.1 illustrates the guide for the measurements taken and labels used while Table E.1 has the values for the modulus of elasticity and the density used. The parameters $L_1, L_3, b_1,$ and $b_2$ are used to determine the area, $A=L_2 \times b$, represent by the shaded part in Fig. E.1.

Table E.1. Material properties of silicon used for the analytical calculations.

<table>
<thead>
<tr>
<th>Parameter values used</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus of elasticity, $E$, GPa</td>
<td>190</td>
</tr>
<tr>
<td>Density, $\rho$, g/cm$^3$</td>
<td>2.33</td>
</tr>
</tbody>
</table>

Fig. E.1. Schematic of the cantilever and the dimensions used for the data analysis.
Taking cantilever D12 as an example, the resonance frequency is

\[
f_i = \frac{1}{2\pi L^2} \sqrt{\frac{35 E}{33 \rho}}
\]

\[
f_i = \frac{1}{2\pi} \frac{1.007 \mu m}{(304.106 \mu m)^2} \sqrt{\frac{35 \times (190 GPa)}{33 \times \left(2.33 \frac{g}{cm^3}\right)}}
\]

\[
f_i = 16,116.660 \text{ Hz}
\]

where the values for each parameter and result for each cantilever are listed in Table E.2.

Table E.2. Geometrical and resonant frequency data of the cantilever utilized.

<table>
<thead>
<tr>
<th>Measured characteristics</th>
<th>D12</th>
<th>E11</th>
<th>F11</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Typical</td>
<td>Typical</td>
<td>Typical</td>
</tr>
<tr>
<td>Length, ( L ) mm</td>
<td>295</td>
<td>345</td>
<td>244</td>
</tr>
<tr>
<td>Width, ( b ) mm</td>
<td>36</td>
<td>35.5</td>
<td>36.5</td>
</tr>
<tr>
<td>Thickness, ( h ) mm</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>End width, ( L_1 ) mm</td>
<td>14</td>
<td>13</td>
<td>14.5</td>
</tr>
<tr>
<td>End length, ( b_1 ) mm</td>
<td>11</td>
<td>11.5</td>
<td>10.5</td>
</tr>
<tr>
<td>Offset, ( b_2 ) mm</td>
<td>2</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Point width, ( L_3 ) mm</td>
<td>4.5</td>
<td>2</td>
<td>4.5</td>
</tr>
<tr>
<td>Added area, ( A ) mm²</td>
<td>321.75</td>
<td>318.875</td>
<td>308.25</td>
</tr>
<tr>
<td>Eqv. length, ( L_2 ) mm</td>
<td>8.938</td>
<td>8.982</td>
<td>8.445</td>
</tr>
<tr>
<td>Resonance freq., ( f ) Hz</td>
<td>16116.660</td>
<td>11801.434</td>
<td>23175.895</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Measured characteristics</th>
<th>D12</th>
<th>E12</th>
<th>F12</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Typical</td>
<td>Typical</td>
<td>Typical</td>
</tr>
<tr>
<td>Length, ( L ) mm</td>
<td>295</td>
<td>345.5</td>
<td>244</td>
</tr>
<tr>
<td>Width, ( b ) mm</td>
<td>36.5</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td>Thickness, ( h ) mm</td>
<td>1.007</td>
<td>1.007</td>
<td>1.007</td>
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<tr>
<td>End width, ( L_1 ) mm</td>
<td>15</td>
<td>18</td>
<td>15</td>
</tr>
<tr>
<td>End length, ( b_1 ) mm</td>
<td>11</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>Offset, ( b_2 ) mm</td>
<td>3</td>
<td>3.5</td>
<td>4</td>
</tr>
<tr>
<td>Point width, ( L_3 ) mm</td>
<td>3</td>
<td>4.5</td>
<td>4</td>
</tr>
<tr>
<td>Added area, ( A ) mm²</td>
<td>332.375</td>
<td>355.75</td>
<td>345.5</td>
</tr>
<tr>
<td>Eqv. length, ( L_2 ) mm</td>
<td>9.106</td>
<td>9.882</td>
<td>9.597</td>
</tr>
<tr>
<td>Resonance freq., ( f ) Hz</td>
<td>16116.660</td>
<td>11801.434</td>
<td>23175.895</td>
</tr>
</tbody>
</table>

219
<table>
<thead>
<tr>
<th>Measured characteristics</th>
<th>D21</th>
<th>E21</th>
<th>F21</th>
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<tbody>
<tr>
<td></td>
<td>Typical</td>
<td>Typical</td>
<td>Typical</td>
</tr>
<tr>
<td>Length, $L$ mm</td>
<td>293.5</td>
<td>342.5</td>
<td>239.5</td>
</tr>
<tr>
<td>Width, $b$ mm</td>
<td>36.5</td>
<td>34</td>
<td>34</td>
</tr>
<tr>
<td>Thickness, $h$ mm</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>End width, $L1$ mm</td>
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