A theoretical and experimental study of piezoelectric microdiaphragm platforms for physical and biological sensing

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A Theoretical and Experimental Study of Piezoelectric Microdiaphragm Platforms for Physical and Biological Sensing

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Doctor of Philosophy

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Abstract

In recent years, development of new types of sensors based on microelectromechanical systems (MEMS) technology has found great popularity among researchers. These sensors have found extensive functionality in broad aspects of sensing; including thermal, tactile, chemical, and biological. Microcantilevers as the icon of MEMS sensors with advantages such as high sensitivity, label-free detection, robust structure and high reproducibility have benefited diverse fields of research since their inception. Recently, piezoelectric based microdiaphragms have been proposed with high sensitivity, low power consumption, and compact size in response of some drawbacks of microcantilevers, including their fragile structure, and their low quality factor in liquid.

This thesis reports theoretical and experimental study of piezoelectric microdiaphragm platform for physical and biological sensing. The microdiaphragms were first designed and then fabricated by MEMS fabrication processes. Their different characteristics such as frequency behavior, mode shapes, coupling factor, quality factor (Q -factor), nonlinear vibrations, mass sensitivity, and pressure sensitivity were studied theoretically and experimentally. Finally, they have been applied for two different schemes of sensing; mass sensing and pressure sensing. These experimental results demonstrate promising perspective of piezoelectric microdiaphragms as physical and chemical sensors.

Significant amount of residual stresses, which were generated in the microdiaphragm during the fabrication process, were characterized first. It was concluded that both flexural rigidity and tension contribute to the resonant frequency of the microdiaphragm. When the tension parameter k is less than 2, the resonant frequency almost remain constant with respect to k . However, when

k is larger than 20, the resonant frequency increases rapidly. So the transition between plate behavior to membrane behavior can be seen in the region $2 \leq k \leq 20$. Different vibration modes of the microdiaphragm were measured and visualized by laser Doppler vibrometer and reflection digital holography microscope, respectively. It was founded that in higher frequency modes, influences of stiffness on the frequency increases. For instance, in a diaphragm with $a\sqrt{T/D} = 10$, corresponding to $a = 0.4 \text{ mm}$, $D = 4.57 \times 10^{-7} \text{ N.m}$, and $T = 285 \text{ N/m}$, the contribution of the diaphragm stiffness in the first resonant frequency is just about 6%, however this contribution is around 46% in the mode (0,3).

Electromechanical coupling factor of the piezoelectric microdiaphragm was theoretically and experimentally studied. The stored mechanical and supplied electrical energy of the piezoelectric microdiaphragm were first calculated. The coupling factor of the device is the ratio of the stored mechanical energy over the supplied electrical energy. It was concluded that initial stress in the microdiaphragms decreases the coupling coefficient. This reduction correlated to lesser amplitude of vibration due to the initial stress inside the microdiaphragm. The experimental values of electromechanical coupling factor of the fabricated piezoelectric microdiaphragms are around 1%. Theoretically calculated electromechanical factors are around 2%.

In higher excitation voltages, piezoelectric microdiaphragms demonstrate nonlinear vibration behavior. Observation of these nonlinearities was correlated to higher displacement values of the diaphragm in higher voltages by help of Duffing's equation. To better understand this behavior, the microdiaphragms were tested in vacuum. The measurement results indicate the same nonlinear behavior, which confirmed that the nonlinearity was aroused in the system due to

higher displacement amplitudes in vacuum. These nonlinearities induce spring hardening effect, which results in the increase of the resonant frequency of the microdiaphragm.

Medium damping influences on the resonant frequency and quality factor (Q -factor) of the piezoelectric microdiaphragm sensors were also investigated theoretically and experimentally. The acoustic radiation and viscosity damping as the two main sources of energy dissipation in medium were theoretically measured and their influences on the frequency and Q -factor were studied. The piezoelectric microdiaphragms were tested in vacuum, air, and in ethanol. The Q -factor of the device was 292.8 at 0.05 atm, 111.195 in air, and this amount reduces to 23.908 in ethanol. Measured results are then compared with theoretical results, where fairly good correlation was observed.

Mass sensing capability of piezoelectric microdiaphragms was investigated by gold deposition and bioentities immobilization. Both of these tests clearly demonstrate the capability of piezoelectric diaphragm as a physical or biological sensor. Comparing the frequency shift of different peaks shows that the mass sensitivity of the device increases in higher vibration modes. For example, the frequency shift of the sensor after deposition of 150 nm gold for the first mode is 4.852 kHz, while this frequency for the ninth mode is 13.386 kHz. The observation is in accordance with the conducted finite element simulations.

Finally, pressure sensitivity and its influences on the vibration characteristics of piezoelectric microdiaphragm based sensors were investigated theoretically and experimentally. A high value of pressure sensitivity, as high as 280 Hz/mbar, has been achieved; this value is 2.43 times higher than the currently reported sensitivity (i.e., 115 Hz/mbar) in the literature. Overall, the achieved theoretical and experimental results clearly demonstrate that piezoelectric

microdiaphragms with high sensitivity, high quality factor, rapid response, and very compact size have great potential to be implemented as a physical or biological sensor.

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Table of Symbols

f	<i>Resonant frequency</i>
T	<i>Tension</i>
ρ	<i>Density</i>
h	<i>Thickness</i>
D	<i>Flexural rigidity</i>
E	<i>Young's modulus</i>
ν	<i>Poisson's ratio</i>
z	<i>Height</i>
w	<i>Deflection profile</i>
∇^2	<i>Laplacian</i>
γ	<i>Eigen value</i>
a	<i>Radius</i>
m	<i>Mass</i>
I	<i>Modified Bessel functions of first kind</i>
J	<i>Bessel functions of first kind</i>
K	<i>Modified Bessel functions of second kind</i>
Y	<i>Bessel functions of second kind</i>
ω	<i>Natural frequency</i>
k	<i>Tension parameter</i>
d_{ij}	<i>Piezoelectric coefficient</i>
e_{ij}	<i>Piezoelectric coefficient</i>

k^2	<i>Electromechanical coupling factor</i>
U_D	<i>Elastic energy of diaphragm</i>
U_S	<i>Stretching energy of diaphragm</i>
U_P	<i>Coupling energy of diaphragm</i>
U_{ele}	<i>Electrical energy of diaphragm</i>
z_s	<i>Height of neutral plane</i>
Π	<i>Electric field</i>
ε	<i>Strain</i>
$\varepsilon\varepsilon$	<i>Permittivity</i>
α	<i>Nonlinearity</i>
Q	<i>Quality factor</i>
Q_{ar}	<i>Acoustic radiation Q-factor</i>
Q_{vis}	<i>Viscous Q-factor</i>
T_p	<i>Kinetic energy of diaphragm</i>
T_f	<i>Kinetic energy of surrounding fluid</i>
c_p	<i>Velocity of sound in diaphragm</i>
β	<i>Added virtual mass</i>
ψ	<i>Stream function</i>
Ω	<i>Vorticity</i>
v	<i>velocity</i>
S_m	<i>Mass sensitivity</i>
P	<i>Pressure</i>

S_p	<i>Pressure sensitivity</i>
η_{mn}	<i>Generalized coordinate</i>
N_{mn}	<i>Generalized force</i>

List of Publications

Journal papers

1. **M. Olfatnia**, Z. Shen, J.M. Miao, L.S. Ong, T. Xu, M. Ebrahimi, "Medium damping influences on the resonant frequency and quality factor of piezoelectric circular microdiaphragm sensors" *Journal of micromechanics and microengineering*, vol. 21, p 045002, 2011.
2. **M. Olfatnia**, V. R. Singh, T. Xu, J. M. Miao, L. S. Ong, "Analysis of vibration modes of piezoelectric circular microdiaphragms" *Journal of micromechanics and microengineering*, vol. 20, p. 085013, 2010.
3. **M. Olfatnia**, T. Xu, J.M. Miao, L.S. Ong, X.M. Jing, L. Norford "Piezoelectric Circular Microdiaphragm based Pressure Sensors" *Sensor and Actuators A: Physical*, vol. 163, p32-36, 2010.
4. **M. Olfatnia**, T. Xu, L S Ong, J. M. Miao, Z. H. Wang, "Investigation of residual stress and its effects on the vibrational characteristics of piezoelectric-based multilayered microdiaphragms" *Journal of micromechanics and microengineering*, vol. 20, p. 5007, 2010.
5. X.M. Jing, J.M. Miao, T. Xu, **M. Olfatnia**, L. Norford "Vibration characteristics of micromachined piezoelectric diaphragms with a standing beam subjected to airflow" *Sensor and Actuators A: Physical*, vol. 164, p. 22-27, 2010.
6. **M. Olfatnia**, T. Xu, J. M. Miao, L. S. Ong, "Effect of Non-Uniform Adsorption of Proteins on the Response of Microdiaphragm Based Biosensors" *Sensor Letters*, vol. 8, p. 258-261, 2010.
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8. G. P. Kottapalli, C. W. Tan, **M. Olfatnia**, J. M. Miao, G. Barbastathis, and M. Triantafyllou, "A liquid crystal polymer membrane MEMS sensor for flow rate and flow direction sensing applications," *Journal of micromechanics and microengineering*, vol. 21, Aug 2011.
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10. **M. Olfatnia**, T. Xu, J.M. Miao, L.S. Ong, "Excitation voltage and added mass effect influences on the onset of nonlinear vibration of piezoelectric circular microdiaphragms" *Submitted to Sensor and Actuators A: Physical*.

Conference papers

11. **M. Olfatnia**, T. Xu, J.M. Miao, L.S. Ong, “Analysis of acoustic radiation and viscous damping on the vibration of piezoelectric circular microdiaphragms” IEEE Transducers, Beijing, China, 2011.
12. **M. Olfatnia**, V. R. Singh, T. Xu, J. M. Miao, L. S. Ong, “Response of Piezoelectric Circular Microdiaphragm Sensors in Higher Frequency Mode” IEEE Sensors, USA, November 3- 8, 2010.
13. **M. Olfatnia**, T. Xu, J.M. Miao, L.S. Ong, “Microdiaphragm Resonating Biosensors in Higher Frequency Modes” IEEE International NanoElectronics Conference (INEC) City University of Hong Kong, January 3- 8, 2010.

Chapter 1: Introduction

This chapter presents the background and current status of electromechanical based sensors. Two main platforms including Quartz crystal microbalance (QCM), and MEMS based sensors (microcantilevers and microdiaphragms) are discussed and the need for further study of piezoelectric microdiaphragm based sensors is explained. Finally, the motivation and the objectives of this research study are briefly explained and the organization of this Ph.D. thesis is presented.

1.1 Background

Built on the 50 years success of microelectronics industry, microelectromechanical systems (MEMS) has shown significant opportunities for miniaturized electromechanical devices based on silicon technology. Miniaturization leads to three main improvements in electromechanical systems. First and foremost it increases the precision and sensitivity of the devices. For instance, the improvements in micropositioning systems in scanning probe microscopy, or increases in the sensitivity of microcantilever based sensors. MEMS can also increase the functionality of the devices by incorporating many small elements in a very little space. The last main advantage of

microelectromechanical systems is high cost saving by batch processing and low power consumption.

In start of MEMS technology, materials which were used in fabrication processes were restricted to the ones used in microelectronics in order to profit from materials and processes that are readily available. However, for exploiting all the capability of MEMS technology in sensing and actuating, gradually different functional materials and polymers were added to the existing base materials [1].

An important group of functional materials is piezoelectric materials. In this group of materials, charge can be accumulated in the matter in response to applied mechanical strain. The first demonstration of piezoelectric effect was conducted by Pierre and Jacques Curie in 1880. Since then, the piezoelectric materials have been applied in many diverse devices. Among piezoelectric materials, the ferroelectric materials based on PZT $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x}\text{O}_3)$ are known to be the leading piezoelectric bulk materials for actuator and ultrasonic applications. The first attempts to integrate piezoelectric materials with MEMS technology was conducted by other thin film materials such as the (non-ferroelectric) ZnO and AlN, due to their better compatibility with standard silicon processing and their easier deposition methods. However, an optimal PZT film of equal thickness develops 10 times larger forces, and produces a 100 times larger acoustic power density. Therefore, there was a period of time where numerous research groups works on the methods of optimized integration of PZT thin films with MEMS standard fabrication processes [2, 3]. Once the problematic issues of integration of PZT thin films on the standard MEMS processes were solved, numerous applications such as micropumps [4, 5], micromotors [6, 7], microphones [8], droplet ejectors [9], filters [10], sonar transducers [11], energy harvesters [12, 13], actuators [14], switches [15], and sensors [16-18] were introduced.

The main challenge on growth of PZT based piezoelectric film is generation of high residual stress during the fabrication process. Piezoelectric films based on PZT are generally deposited by pulsed laser deposition, sputtering, or chemical solution deposition (sol-gel technique) [19]. In these fabrication methods, stress is generated either by accumulation of impurities into the film during the deposition process (Intrinsic stress), or due to the differences between the thermal expansion coefficients of different layers during the cooling from deposition or annealing temperature to room temperature (Thermal stresses). The generated stress in the device bend the membrane downward or upward, influences mechanical and electrical property of the films, and finally changes device's resonant frequency and sensitivity.

Several researchers investigated the effects of initial tension on the diaphragm's resonant frequency, either theoretically or by the finite element analysis [20, 21]. They concluded that initial tension stiffens the diaphragm and increases its resonant frequency. In fact the vibrational behavior of the diaphragm changes from that of a plate with negligible tension to one that is governed by membrane with negligible stiffness, due to development of residual stresses in the diaphragm. This behavior is firstly investigated by Sheplak et al. [22] in static case and then followed by Yu et al. [23] for a sound-pressure measuring sensor in dynamic mode. For a piezoelectric mass sensing biosensor, the sensitivity is the rate of change of the resonant frequency in response to the change of the uniformly distributed mass loading per unit area [24]; therefore a well-defined relation between residual stress and resonant frequency is needed for an accurate mass sensing.

Quartz crystal microbalance (QCM), as the first piezoelectric mass sensor, has been extensively employed since 1959 after the Sauerbrey's discovery that there is linear relationship between their frequency response and the deposited mass on them [25]. A typical mass

sensitivity of a 5 MHz QCM is around $0.057 \text{ Hzcm}^2\text{ng}^{-1}$ [26]. This high sensitivity gained its importance as a device for monitoring thicknesses in vacuum and air since 1960; however, their application in liquid medium was postponed till the design of suitable oscillator circuit by Nomura in 1982 [27]. Currently, quartz crystal microbalances play an important role as a physical, chemical, or biological sensor in diverse fields of research by transforming the mass or thickness of a measurand analyte to an electrical signal.

In pursuit of higher sensitive devices, microcantilever based sensors were introduced. Microcantilevers are generally operated in either the static mode, where binding surface stress results a measurable deflection in cantilever, or the dynamic mode, with the same working principle as quartz crystal microbalances. These sensors have implemented different scheme of actuation or sensing, including electrostatic, electromagnetic, and piezoelectric in order to detect biological and chemical entities [28]. Although their high sensitivity, microcantilevers mainly suffer from low Q -factor in liquid medium and their fragility. These drawbacks provoke scientists to design new type of sensors, including piezoelectric microdiaphragm based sensors.

Piezoelectric microdiaphragm based sensors were introduced as a mass sensitive biosensor by Nicu et al. [16]. They designed and fabricated a micromachined resonating piezoelectric membrane based biosensor, which was easy to characterize, and simultaneously addressed problems such as the fragility of the microcantilevers, their low Q -factors, and also the lack of integration potential in the QCM biosensors. Although, the sensitivity of these sensors is smaller than the microcantilevers; however, their higher reliable structure and higher quality factor in aqueous medium [17] makes them a successful choice for physical or chemical sensing.

1.2 Motivations

Piezoelectric microdiaphragms resonating in their flexural vibration modes have been previously reported as physical pressure sensor [29], rheology sensor [30], and biological sensor [16, 18]. In all abovementioned works, the main effort of authors is to first fabricate the device and then experimentally testify the capability of piezoelectric microdiaphragm as a sensing element. They mainly deposited PZT layer by RF sputtering method, and achieved high sensitivities as high as 115 Hz/mbar for pressure sensor and around 10 Hz/ng for mass sensor. However, piezoelectric microdiaphragms have other important physical behaviors, such as their frequency response and electromechanical coupling factor under initial stresses, their different vibration modes and nonlinear vibration behavior, and their frequency response in different mediums, which have great influences on their sensing capability, and needs further investigations.

The main motivation of this work is to study piezoelectric microdiaphragms theoretically and experimentally as a platform for physical and biological sensing. The microdiaphragms were first designed and then fabricated by MEMS fabrication process methods. Their different characteristics such as frequency behavior, mode shapes, non-degenerated modes, coupling factor, quality factor (Q -factor), nonlinear vibrations, mass sensitivity, and pressure sensitivity were studied theoretically and experimentally. Finally, piezoelectric microdiaphragm was applied for two different schemes of sensing, mass sensing and pressure sensing.

1.3 Objectives and scope of the thesis

This research is focused on the study of piezoelectric microdiaphragm platform for physical and biological sensing. This broad main topic could not be thoroughly covered, unless by discussing the main challenges ahead of piezoelectric microdiaphragm as a sensing element in detail. These challenges are on the fabrication, theoretical understanding of the device and its interaction with the surrounding medium, and finally the practical methods of employing piezoelectric microdiaphragm as sensors. These main challenges as the main objectives of this thesis are listed below. Overall, this research attempts to shed a light on different aspects of piezoelectric microdiaphragms as physical and biological sensors, and demonstrates their great potential as a new generation of commercial sensors.

- To fabricate piezoelectric microdiaphragm based sensors in different configurations by MEMS fabrication technology and characterize the stress generated in the device during the fabrication process
- To theoretically analyze vibration behavior of microdiaphragms and establish the governing equation for its resonant frequency in a mixed mode of tension and flexural rigidity
- To theoretically and experimentally calculate the electromechanical coupling factor of piezoelectric microdiaphragm
- To measure and visualize different vibration modes of piezoelectric microdiaphragms, and investigate their different mass sensing capability

- To investigate influences of higher excitation voltages on the vibration of piezoelectric microdiaphragms, and justify the nonlinear vibration behavior of the device theoretically and experimentally
- To investigate influences of medium damping including acoustic radiation and viscous damping on the resonant frequency and Q -factor of the piezoelectric microdiaphragms theoretically and experimentally
- To analyze the mass sensitivity of piezoelectric microdiaphragms and the influential parameters on it, and experimentally characterize the mass sensing capability of piezoelectric microdiaphragm by physical and biological testing
- To theoretically calculate the pressure sensitivity and dynamic response of piezoelectric microdiaphragms under pressure, and experimentally characterize its pressure sensing capability

1.4 Organization of the report

This report is structured into nine chapters as detailed below:

Chapter 2: In this chapter, the sensor is first defined and its different classification will be reviewed. In the second part of this chapter we will discuss piezoelectric thin film and their integration in standard MEMS fabrication process.

Chapter 3: This chapter summarizes the fabrication processes and will report the preliminary electrical and mechanical characterization of piezoelectric microdiaphragms.

Chapter 4: This chapter reports the formulization of the resonant frequency and electromechanical coupling factor of piezoelectric microdiaphragms.

Chapter 5: In this chapter, different mode shapes of the fabricated microdiaphragm will be measured and visualized. Influences of higher excitation voltages on the mode shapes, and the nonlinear vibration behavior observed will be explained.

Chapter 6: Medium damping influences including acoustic radiation and viscous damping will be investigated on the resonant frequency and Q -factor of the piezoelectric microdiaphragms theoretically and experimentally in this chapter.

Chapter 7: In this chapter the piezoelectric microdiaphragms mass sensitivity will be first investigated, then its capability on mass sensing will be experimentally testified by gold deposition and bioentities immobilization.

Chapter 8: This chapter reports application of piezoelectric microdiaphragm as a pressure sensor. First, the pressure sensitivity and the diaphragm dynamic behavior under pressure will be investigated; then the diaphragm will be tested on the experimental setup as a pressure sensor.

Chapter 9: This chapter provides a brief summary of the accomplished work in the thesis, highlights the major contributions, and suggests some future work.

Chapter 2: Literature Review

This chapter presents a detailed review of the four main groups of sensors, including thermal, electrochemical, optical, and electromechanical sensors. Piezoelectric microdiaphragm based sensor was chosen among them for further study and analysis due to its great potential capabilities. The second part of this chapter will review the characteristics and challenges of the design, and fabrication of thin film piezoelectric based microsensors.

2.1 Introduction

Sensor is a device that measures a chemical, biological, or physical quantity and converts it into a signal, which can be analyzed by an instrument or by an observer [31]. Sensors are always classified based on their transduction mechanism. This classification is varied by the case of study. Here, we chose biosensors as the desired case of study. Therefore, we divide the sensor into four main groups. These groups includes [32, 33]: i) thermal (calorimetric) sensors, ii) electrochemical sensors, iii) optical sensors, and iv) electromechanical sensors. Each one of these four categories is also divided into different subgroups. Figure 2-1 shows the different transduction mechanism of sensors which we are studying throughout this chapter. Each of these

sensing mechanisms has its own particular advantages and disadvantages with respect to its sensitivity, selectivity, resolution, manufacturing cost, and robustness to disturbances. Always, the sensor with the highest sensitivity, selectivity, accuracy, and the lowest fabrication cost is the most favorable choice.

Throughout the review of different types of sensors, it was found that piezoelectric microdiaphragm based sensors as a member of electromechanical group has shown great capability as well as promises for sensing application. Therefore, the second part of this chapter will review the characteristics and challenges of the design, fabrication, and application of these sensors.

Figure 2-1: Different transduction mechanisms

2.2 Sensors

In this section, the working principles and characteristics of different types of sensors based on the classification presented in Figure 2-1 are reviewed and compared. For this aim, a subclass of sensors, biosensors are chosen, and their capability in detection of bioentities is compared. The attempt here is to present a brief and comprehensive study on the main types of transduction mechanisms.

2.2.1 Calorimetric/Thermal sensors

Thermal or calorimetric sensors use the first law of thermodynamics (“Any process in which the internal energy of the system changes is accompanied by absorption or evaluation of heat” [34]) as a base of their transduction mechanism. They determine the presence or concentration of a chemical by measuring the enthalpy changes caused by the absorption or desorption of analyte molecules in the sensitive layer. These enthalpy changes cause temperature variations, which can be transduced into an electrical signal. To achieve the best performance in calorimetric sensors, the sensing parts should be isolated from the surrounding area. Therefore this kind of sensors often placed on thermally isolated micromachined structure [35]. There are three different ways for transforming the temperature changes to electrical signal e.g. using a thermistor or a platinum resistance thermometer (pellistor) or a pyroelectric material.

2.2.1.1 *Thermal sensors with thermistors and pellistors*

Catalytic thermal sensors measure the heat produced by controlled combustion of flammable gaseous compounds on a hot catalyst (e.g., Pt or Pd) surface through resistance thermometers. By flowing electrical current through the heater, the catalyst surface is heated up to a temperature

sufficient for oxidizing the combustible gas mixture catalytically. The heat of oxidation is then measured by a resistance thermometer, thermistor or pellistor. These catalytic thermal sensors are typically used for detecting flammable gases such as methane, butane, hydrogen, carbon monoxide, propane or propylene in gaseous environments [36, 37].

A thermistor is a very sensitive device, and it usually composed of a temperature-dependent semiconductor. The temperature change due to the chemical reaction is measured by observing the variation of electrical resistance of the thermistor. Thermistors are commercially available in different sizes and shapes, and usually constructed in the form of small glass beads and so can be regarded as miniaturized systems. Their resistance usually changes for one degree rise about 4-7% [32]. There is limited reports on application of thermistors as a biosensor, however Ramanathan et al. [38] reported a sol-gel (SG) based glucose biosensor using thermometric measurement. They entrapped the enzymes (glucose oxidase, GOD and catalase, CAT) on the surface of reticulated vitreous carbon cylinder (RVC cartridge) and placed it within the column of an enzyme thermistor (ET) device. They recorded the thermometric peaks resulted from the injection of various glucose concentrations by a sensitive thermistor.

Another form of catalytic gas sensor is pellistor, which is shown in Figure 2-2. The principle is the same as above, except that here the platinum wire resistance thermometer/heating wire is embedded in a ceramic bead. The catalyst layer, usually palladium, is coated on the surface of the bead. Such a system operates at a temperature of 500° for various gases, e.g. methane [39]. In comparison with thermistors, pellistors are less thermal sensitive but they usually tolerate much more temperatures than the thermistors.

The sensors discussed in this section are usually used in the gases, since in liquid the thermal conductivity is much higher than the gases [40]. There are a few reports on application of

thermal biosensors; however, some researchers determined several important bioentities, such as ascorbic acid [41], ethanol [42], penicillin-V [42], and cholesterol [43] by help of these sensors.

Figure 2-2: Thermometric (calorimetric) sensors. left: thermistor, right: platinum resistance thermometer (pellistor) [39]

2.2.1.2 Pyroelectric Sensors

A search for probes with higher temperature sensitivity resulted in experiments with pyroelectric materials. Pyroelectricity is a material property of certain crystals; enable to generate electrical potential whenever faced with temperature changes. Sometimes pyroelectricity and piezoelectricity encountered in a material simultaneously [39]. In fact, both of terms are closely related to each other, in another way, the polarization in material can be generated by applying either strain or temperature on the crystal.

Pyroelectricity mainly used in infrared detectors for detecting the infrared radiation [44, 45], but it has capability of application in chemical and biological sensors, especially for gas sensing [46]. Pyroelectric crystals could be used as a thermal sensor, if high rate of temperature changes for the chemical reaction is expected. This work could be done, e.g. by “periodic switching

between analyte and reference gas flows or by temperature modulation [47]”. Pyroelectric-based biosensor has never been used in liquid media until now.

2.2.2 Electrochemical sensors

Electrochemical sensors are the largest and the oldest group of chemical and biological sensors. The ability of generating electrical signal immediately is one of the main advantages of this kind of sensors. Typical electrochemical sensors are composed of two electrodes, a sensing and a reference electrode, separated by a chemically sensitive layer. Electrochemical reactions or charge transfer at the electrode surface are transduced into an electrical signal, generally a current, potential or conductance change. Therefore electrochemical sensors are divided into potentiometric, measurement of voltage, conductimetric, measurement of conductivity, and amperometric, measurement of current, sensors [48].

2.2.2.1 Potentiometric sensors

Potentiometric sensors derive the analytical information by measuring the potential difference between the sensing electrode, and the so-called reference electrode. The potential difference exhibits a logarithmic relation with the analyte concentration in the sample. Today, the potentiometric sensors represent the largest and the most matured type of biosensors [49]. They have capability of working in both gases and liquids media and are the most popular biosensor. The reason of this popularity is the point that the potentiometric sensors could be miniaturized into a field effect transistor, FET, usually called chemically sensitive FET (CHEMFET), without any degradation of transduced signal. In fact, the transduced signal that carries the chemical information does not depend on the sensing area, and therefore permits any

miniaturization. Moreover, noise and signal-to-noise ratio does not degrade significantly with miniaturization.

There are three different chemical way for modulating the CHEMFET gate. This modulation give rise to three different types of CHEMFETs, including, the enzymatically selective FET (ENFET), which is equivalent to a potentiometric enzyme electrode; the ion-sensitive FET (ISFET), which is a direct equivalent of the macroscopic ion-selective electrode; and the work function FET, which has its macroscopic counterpart in the Kelvin probe [48, 50]. Moreover, CHEMFET is represented in various formats for gas and liquid sensing, and this diversity is increasing more and more by introducing new designs [51, 52]. Figure 2-3 shows two different type of them, the thin-film transistors (TFT) and insulated gate FET (IGFETs) for gas sensing. The difference of these two designs is that in a TFT the current flows through the sensing layer, while in the IGFET it flows through the silicon.

Figure 2-3: (a) IGFET with polymeric gate conductor for gas sensing. (b) Organic TFT [39]

Metal oxide semiconductor FET (MOSFET) is composed of three different parts, a gate, which is usually metal or heavily doped polysilicon, the insulator, which is silicon oxide or sometimes silicon nitride, and a channel, which is p/n-doped silicon passage between the n/p-doped zones [53]. In chemical sensing, the ISFET is fabricated by adding the ion selective layer

on the surface of the gate. A schematic view of an ISFET is shown in Figure 2-4. Any change of the surface potential from a chemically induced charge accumulation at the gate-surface interface, cause voltage difference between gate and source, here reference electrode. This voltage is like an input voltage to amplifier circuit and control the current between source and drain. The primary disadvantage of ISFETs is that a large reference electrode is unavoidable for stable operation, limiting their practical application [54].

Figure 2-4: ISFET structure [39]

Work function FETs are the second types of CHEMFETs. In this type of sensors, a chemically selective layer is used as a conductive gate instead of completely removing the metal gate. The FET with a palladium gate is a well-known microsensor of this type for the detection of gases such as hydrogen and ammonia [55-57]. When two chemically different materials are electrically connected via a dielectric layer, the equalization of the Fermi-levels leads to the formation of an electric field in the dielectric layer. This field is proportional to the difference in the work-function of the two plate materials. The work-function change of the gate conductor caused by a chemical reaction modulates the threshold voltage of the FET, and the analyte concentration can be derived. The major advantage of this type of sensor over the ISFET and

ENFET in realizing miniaturized potentiometric sensors is the absence of a large reference electrode since the fully enclosed silicon is an excellent reference [48].

The ENFET is another CHEMFET structure without a conducting gate; a chemically sensitive enzyme layer forms either a part or the entire insulation layer of the FET structure. The conversion of a sample in the immobilized enzyme membrane results in a local change in pH, which in turn modulate the gate-source voltage of FET by the surface potential change at the insulation layer. However, potentiometric enzyme sensors suffer from a nonlinear response induced by two reasons: i) the pH changes in the immobilized enzyme membrane depend on the initial pH of the solution, and ii) the enzymatic reaction of the immobilized enzyme is pH dependent. Because of this problem, ENFETs have only limited usefulness in biochemical sensing applications [48].

2.2.2.2 Amperometric sensors

Amperometric sensors measure the current, which is produced during a chemical reaction (oxidization at the anode and reduction at the cathode). In this type of sensor a constant electrical potential is applied to electrodes, which is sufficient for oxidization or reduction of interested chemical solution, then the produced current, which is the flow of ions and electrons measured. This current is proportional to the analyte concentration. Amperometric sensors are usually preferred to potentiometric sensors, because they are more sensitive, faster, and also more precise and accurate. The fabrication process of them is relatively easy and therefore they are the most commercially successful group of biosensors [48, 58].

For biological application, a biological material usually an enzyme covers the electrodes. Oxidization or reduction of analyte or enzyme's substrate results flow of current through the

electrodes, which depends on analyte concentration. The first kind of amperometric biosensors, which is based on oxygen consumption monitoring, is called the first generation. The second generation used mediator, which is a redox substrate capable of transferring electron between the enzyme and electrode. Third generation working principle is based on direct electro transfer between enzyme and electrode. Amperometric biosensors have been used for sensing many bio entities, such as glucose [59, 60], lactate [61] and cholesterol [62].

2.2.2.3 Conductometric sensors

Conductometric sensors measure variations of circuit impedance between two electrodes, where these variations could be in the bulk region or at interface. These sensors are able to detect antigen/antibody reaction, biomolecular reaction between proteins and DNA [63]. Due to their easy and inexpensive fabrication method, and simplicity of usage, conductometric sensors have found great popularities among researchers. However, the application of this kind of sensors is just limited to non-conductive media such as gases or dielectric liquids. Conductometric sensors have been used for detection of various entities such as toxins [64], agents of biothreat [65] and biochemicals [66].

2.2.3 Optical sensors

Optical detection techniques are perhaps the most common due to their prevalent use in biology and life sciences [63]. Generally, there are two kind of detection implemented in optical biosensing: fluorescence-based detection and label-free detection [67]. In fluorescence-based detection, the target entity or recognition element is labeled with fluorescent tags, such as dyes; based on the intensity of fluorescence light which is observed, the presence of the analyte or

interaction of analyte and recognition element is indicated. For label-free detection, interested molecules are not labeled or altered, and are detected in their natural forms. The main advantage of label-free detection over fluorescence-based is that the sensing signal doesn't depend on the number of target molecules in the sensing volume and therefore it is capable of detecting very small volumes, such as nanoliter or picoliter. It is also cheaper and easier than fluorescence-based detection [67, 68].

Due to the wide variety of optical ways for detection of biomolecules the precise classification of them is difficult, and different resources do the classification in different ways. Here the approach of Gorton for classification of optical biosensors [68], which classified the optical sensors into three different categories: integrated sensors using planar/channel waveguides, fiber optical (FO) sensors, and surface plasmon resonance sensors, is implemented.

2.2.3.1 Surface plasmon resonance sensors

Since the first demonstration of surface Plasmon resonance (SPR) biosensor by Leidberg et al. in 1983, it has been used numerously in detection of biochemical solutions [69, 70]. Quantization of plasma oscillations results formation of a quasi particle called plasmon. In fact, plasmons are collective oscillations of the free electron gas density, often at optical frequencies. Those plasmons, which are confined to the surfaces interacting strongly with light, are surface plasmons. At the interface of two media with dielectric constants of opposite signs, like a metal and a dielectric, a quantum optical-electrical phenomenon may be exist, which is induced by oscillations of charge-density called surface plasmon resonance (SPR) [33, 67, 70].

SPR sensors consist of optical and electrical systems. Optical system excites and interrogates surface plasmon wave (SPW) which is a transduction medium for interrelating the

optical and biochemical domains. Electronic system supports the optoelectronic components of the sensor and allows data processing. During the past years SPR has been used for detection of proteins with a detection limit from picomolar to nanomolar [71], and detection of DNA molecules [72]. It also provides sensitive and fast detection of cancer biomarkers [73, 74] and other biomarkers [75] with the detection limit at ng/mL level for medical diagnosis.

2.2.3.2 Fiber optic sensors

Optical fibers consist of a cylindrical core, usually doped by Germanium, and a surrounding cladding, both made of silica. The reason of core doping in optical fiber is increasing the refractive index of core relative to the cladding's refractive index, and therefore propagation of light with its total internal refraction (TIR).

There are two parts for light propagation through an optical fiber; guided field, which is in the core region, and the evanescent field, which is in the cladding. For a uniform-diameter optical fiber, signal loss reaches almost zero within the cladding. For using the fiber optics as a sensor, fiber should interact with its surrounding. It means that a part or some parts of cladding should be removed or reduced to allow the interaction of evanescent field with surrounding, eg. analyte. This interaction results magnitude variation of the evanescent field, which is the optical output of the fiber [76].

In the past 20 years, the design of fiber optic sensors has evolved from the use of simple de-cladded fibers to tapered geometries with surface modifications. Fiber optic sensors have been used for many biological applications such as the detection of pathogens, medical diagnosis based on protein [77-79], and real-time detection of DNA hybridization [80, 81].

2.2.3.3 *Integrated optical sensors*

Instead of using optical fibers, the optical sensors can use a planar substrate as their base. These sensors usually called integrated optical sensors. Integrated optical sensors utilize the microfabrication techniques in order to fabricate the components, which are needed for these sensors, such as gratings, dividers, and combiners [68]. Interferometric and grating coupling devices are the two main types of integrated optical biosensors and classifications of them is reviewed here.

Interferometer-based biosensor is one of the main parts of integrated optical biosensors and is classified into four main categories. i) Mach-Zehnder interferometer, ii) Young's interferometer, iii) Hartman interferometer, and iv) Backscattering interferometer. All of these four categories are based on the common principle that two waves that have the same phase will amplify each other while two waves that have opposite phases will cancel each other, if both waves have the same amplitude [67, 68].

Grating coupler based sensors are based on the coupling of light into a thin waveguide by means of a grating coupler covered with a sensing layer. By monitoring the coupling angle, the refractive index variation in the sensitive layer induced by a biochemical interaction can be accurately determined. There are two main types of grating coupler based sensors: input grating coupler and output grating coupler sensors [82, 83].

2.2.4 **Electromechanical Sensors**

Electromechanical sensors monitor the mechanical property changes of the sensor, such as its mass, elastic modulus and deflection, and they are capable of determining the analyte concentration in solution. Electromechanical sensors are classified into two main groups,

acoustic wave sensors and MEMS based sensors. The working principle of acoustic wave devices is frequency depression due to accumulation of mass on the sensing area of the device, and divided into two main groups; bulk acoustic wave (BAW) devices and surface acoustic wave (SAW) devices. MEMS based sensors are divided in three different structures; cantilevers, bridges, and diaphragms. Microcantilevers work in either static or dynamic sensing mode. In static mode the deflection due to the chemically induced surface stresses, which arise by accumulation of analyte on the sensing area is measured. Working principle of dynamic mode is similar to acoustic wave devices, but the monitoring method of frequency may be changed. Microbridges and microdiaphragms always work in dynamic mode. In the following section, we will review both acoustic wave devices and MEMS based sensors. In this review, the concentration would be on the application of these sensors as a biosensor in liquid medium.

2.2.4.1 Microcantilever based sensors

Inception of microelectromechanical systems in the early 1970s, introduced new devices like microcantilever, which has numerous application in different majors such as atomic force microscopy (AFM) or biological sensing. Fabrication of Microcantilever based sensor, like any other MEMS fabrication process typically takes advantage of one of two common MEMS fabrication processes—bulk or surface micromachining. These two processes are simplified and shown schematically in Figure 2-5. The key difference between these techniques is the sacrificial layer which, when removed, releases the devices from the substrate. In bulk micromachining, the bulk silicon wafer is used as the sacrificial layer. The device layer, such as silicon nitride, is grown directly on a wafer that has been oxidized on the bottom. This oxide is then patterned in order to mask an anisotropic silicon etch, like KOH or tetramethyl ammonium hydroxide

(TMAH), that will undercut the devices and release them from the substrate, allowing them to bend or resonate. In surface micromachining, there is no backside processing, and the silicon wafer is left intact. A sacrificial oxide layer is first grown on a silicon wafer, followed by deposition of the device layer. Standard photolithography techniques are used to mask the device. Anisotropic etching typically dry reactive ion etching is performed to pattern the device layer. Finally, hydrofluoric acid is used to etch the sacrificial oxide layer and release the structures, suspending them above the silicon substrate [28]. One of the main advantages of cantilever based biosensor is label free detection of bioenteties which means detecting ability of bimolecular compounds without the need of optically labeling them. The fabricated microcantilever can work in two different modes for biological sensing; static or dynamic.

Figure 2-5: Basic depiction of (a) bulk and (b) surface micromachining processing steps leading to suspended devices [28].

2.2.4.1.1 Static or stress sensing mode

Static-mode electromechanical sensors determine the analyte concentration by measuring the deflection of a microcantilever due to chemically induced surface stresses [33]. For use as

biological and chemical sensors, the microstructures are typically modified so that one surface is passive while the other surface exhibits a high affinity to the target analyte. While biochemical reaction is performed on the active layer, a change in surface free energy results a surface stress change, which cause a measurable deflection of cantilever. The deflection then can be measured by optical method like in AFM, which laser reflected from the cantilever surface into a quad positioning detector or by using a piezoresistor [63, 84].

There are three different mechanisms, which explain the relation between the cantilever deflection and the chemical molecular absorption/adsorption. When the sensing layer is so thin in comparison with the thickness of microstructure, spontaneous adsorption processes result in the reduction of the interfacial stress and, thus, expand the surface. Analyte induced swelling of the coating is the predominant deflection mechanism in thick sensing layer. In nanostructured coating bulk, surface and intersurface interactions results deflection of the cantilever [84].

Microcantilevers in static mode have been used for diverse biochemical sensing, especially during recent years many interesting and significant achievements obtained in biological detection by help of them. Fritz et al [85] reported the specific transduction of DNA hybridization and receptor-ligand binding by surface stress changes of a microcantilever. Hybridization of DNA and detection of single based mismatches on DNA strands has been demonstrated on cantilevers with a thin Au gold layer on one side and it is shown in Figure 2-6. Thiolated capture DNA strands are attached to the Au layer and the deflection of cantilevers can be detected when the target strands bind to the capture strands [85, 86].

Figure 2-6: Scheme illustrating the hybridization experiment. Each cantilever is functionalized on one side with a different oligonucleotide base sequence. (A) The differential signal is set to zero. (B) After injection of the first complementary oligonucleotide, hybridization occurs on the cantilever that provides the matching sequence. (C) Injection of the second complementary oligonucleotide causes the cantilever functionalized with the second oligonucleotide to bend [85].

Figure 2-7 illustrates an artificial nose which is an array of cantilevers functionalized with a variety of polymer coatings and are capable of detecting a number of alcohols, solvents, and natural flavors in the gas phase [87]. These sensors can also be used to detect proteins and cancer markers [71]. By immobilizing glucose oxidase on the surface of 320-mm long, gold coated silicon nitride cantilevers, Subramanian et al. [88] created a glucose sensor that responds to presence of glucose in the aqueous medium due to the enzyme-induced exothermic processes. Deflection-based cantilever based sensors have shown potential for widespread use as biological sensors. A summary of these sensors and their respective materials systems are shown in Table 2-1.

Figure 2-7: Array of eight cantilevers used as deflection sensors for several chemical solvent vapors. The cantilevers, measuring 500*100*1 mm (length*width* thickness), are each coated with a different polymer in order to define a particular set of responses based on how each polymer responds to a given analyte [87].

Table 2-1 Examples of deflection-based cantilever biosensor applications

<i>Microcantilever material</i>	<i>Detection mechanism</i>	<i>Detected analyte</i>	<i>Reference</i>
Silicon	Optical	Glucose	[88]
Silicon	MOSFET	Biotin	[89]
Silicon nitride	Piezoresistor	PSA	[90]
Silicon nitride	Piezoresistor	DNA	[91]

2.2.4.1.2 *Dynamic or resonant mode*

In the dynamic or resonant mode, the cantilever is excited mechanically; hence, it vibrates at its resonant frequency. The resonant frequency changes while the bioentities is captured on the sensing area. This frequency shift is measured using electrical or optical means, and represents the mass of accumulated biomolecules. In order to decrease the minimum detectable mass the mass sensitivity and quality factor of the device should be increased. The quality factor decreases drastically in liquid and therefore the stress detection mode is inherently preferred in a fluid.

In the last several years, MEMS/NEMS resonators have been increasingly studied as ultrasensitive biological detectors, and various mass measurements are reported in literatures. A summary of these achievements is given in Table 2-2. Ilic et al. fabricated cantilevers with length of hundreds of micrometers for the detection of *E. coli* bacteria; as few as 16 cells, or about 6 pg total. In their subsequent works, they used cantilevers with length of order of 10 micrometers, shown in Figure 2-8a, to measure the frequency shift due to a single cell of *E. coli* (665 fg) adsorbed at the end of the cantilever [92, 93]. Similar experimental analysis also is conducted on a thiol-based self assembled monolayer (SAM). Mass detection of 5.5 fg in air [94], and a few attograms in vacuum [95], were reported. Mass of single virus particle is also demonstrated in different literatures. It was obtained that the mass of baculu virus particles are 1.5 fg [96], and vaccinia viruses are 9.5 fg [97, 98], shown in Figure 2-8c and d. Ilic et al. [99] also detected

single dsDNA molecules (1587 bp) with a mass of 1.65 ag by using cantilevers functionalized by gold.

Table 2-2 Example of achievements are done by microcantilever in dynamic mode

<i>Microcantilever material</i>	<i>Actuation/Detection mechanism</i>	<i>Detected analyte</i>	<i>Reference</i>
PZT/Silicon nitride	Piezoelectric/ Optical	PSA	[100]
Silicon nitride	Electrostatic/ Optical	BSA	[101]
Silicon nitride	Piezoelectric/ Optical	Thiol SAMs	[95]
Silicon	Electrostatic/ Optical	IgG	[102]
PZT/Silicon	Piezoelectric/ Piezoelectric	Myoglobin	[103]
Silicon nitride	Optical/Optical	dsDNA	[99]

The best mass resolution has been achieved is $\sim 7\text{zg}$ ($1\text{zg} = 10^{-21}\text{g}$). This mass is equivalent to ~ 30 xenon atoms or the mass of an individual 4 kDa molecule. This work was conducted by Roukes et al. [104] They did this situ measurements in real time with mass noise floor $\sim 20\text{zg}$, by help of very high frequency (VHF) nanoelectromechanical systems (NEMS).

Figure 2-8: Scanning electron micrograph of bio entities loaded cantilever beam, (a) A single E. coli bound near the cantilever tip [93] (b) The nanoscale gold dot bind with thiol-based[95], (c) and (d) Single viruses are immobilized on the cantilever surface [97, 98].

2.2.4.1.3 Microfluidic Enhanced Microcantilever based biosensor

In life science application of sensors, liquid media is generally the working environment. As it is discussed earlier, the problem of fluid is reduction of quality factor of the device. The microfluidic enhanced sensors are the remedy of this problem. Microfluidic is the science and technology of systems that process or manipulate small (10^{-9} to 10^{-18} liters) amounts of fluids, using channels with dimensions of tens to hundreds of micrometres [105]. Burg et al [101] were the first group, which reports the application of microfluidic enhanced biosensor. They placed the solution inside a hollow resonator that is surrounded by vacuum and therefore solved the

problem of viscous damping which suffered the quality factor of the microcantilever [101, 102, 106, 107]. They demonstrate that suspended microchannel resonators can weigh single nanoparticles, single bacterial cells and sub-monolayers of adsorbed proteins in water with sub-femtogram resolution (1 Hz bandwidth). The combination of the low resonator mass (100 ng) and high quality factor (15,000) enables an improvement in mass resolution of six orders of magnitude over a high-end commercial quartz crystal microbalance.

Park et al [108] recently developed a method, living cantilever arrays, which is suitable for measuring the mass of single adherent live cells in fluid using silicon cantilever mass sensor. They used HeLa cells as a model cell line in the experiment. HeLa cells are immortal human cervical cancer cells, which are one of the most widely used cancer cells [109]. They injected HeLa cells into microfluidic channels with a linear array of functionalized silicon cantilevers and the cells were subsequently captured on the cantilevers with positive dielectrophoresis. The captured cells were then cultured on the cantilevers in a microfluidic environment and the resonant frequencies of the cantilevers were measured. The mass of a single HeLa cell then was extracted from the resonance frequency shift of the cantilever.

2.2.4.2 Microdiaphragm based sensors

Microdiaphragm based sensors are a new kind of sensors, which their working principle is the same as microcantilever in dynamic modes. This device simultaneously addresses problems such as the fragility of the microcantilevers, and the lack of integration potential in the QCM biosensors. The first integration of these sensors as a biosensor was reported in a work by Nicu et al. [16] in 2005. Figure 2-9 shows their fabricated sensor. Although, the sensitivity of these sensors is smaller than the microcantilevers; however, their higher reliable structure and higher

quality factor in aqueous medium [17] makes them a successful choice for physical or chemical sensing. The design principles and the detailed characteristic of this type of sensors are presented in the next chapters of this work.

Figure 2-9: Overview of a chip with 16 micromachined circular membranes. Inset shows a close-up view on four micromembranes [17].

2.2.4.3 Acoustic wave based sensors

An acoustic wave is implemented as the sensing mechanism in acoustic wave sensors. Any variation in the propagated wave on the surface or inside of the device will result in a change of the wave characteristics, which in turn shift the resonant frequency of the device. This shift in frequency of the device can be correlated to the physical, chemical, or biological variation of the measurand [110, 111].

Acoustic wave device are usually fabricated from piezoelectric materials. Quartz is the most common piezoelectric material in the world; however, till date there is no method available for deposition of quartz as a thin film. Therefore, quartz substrates are not suitable for thin film

MEMS devices. There are other examples of piezoelectric materials, which are suitable for thin film deposition such as lead zirconate titanate (PZT), zinc oxide (ZnO), and polyvinylidene fluoride (PVDF). These materials and their integration in MEMS fabrication processes are discussed in the last part of this chapter. In the next following sections, a review on different types of acoustic wave sensors is presented.

Acoustic wave sensors are classified as bulk acoustic wave (BAW) and surface acoustic wave (SAW) sensors. These names are given to the sensors based on the propagation medium of the wave on the sensor; if the wave propagates in the substrate it is called bulk acoustic wave, and if it propagates on the surface, it is surface acoustic sensors. Acoustic plate mode (APM) and thickness shear mode (TSM) resonators are the most common BAW devices. Flexural plate wave (FPW) and shear horizontal acoustic wave (SH-SAW) are the two most common surface acoustic wave (SAW) sensors. Figure 2-10 illustrates different types of acoustic wave sensors and the wave propagation direction on them [110, 112, 113].

Figure 2-10: Schematic sketches of the four common types of acoustic resonators and their wave propagation modes. The particle displacement is indicated by a black arrow and the direction of the wave propagation by an open arrow. TSM: thickness shear mode resonator also known as quartz crystal microbalance; FPW: flexural plate wave resonator; SAW: surface acoustic wave resonator and SH-APM: shear horizontal acoustic plate mode resonator [26].

2.2.4.3.1 Bulk Acoustic wave (BAW) devices

Aforementioned, BAW sensors are divided into the two main types, APM and TSM. In the following section, TSM is just reviewed due its higher application as a sensing device. For study of APM sensors, interested reviewers are referred to reference [112].

Thickness Shear mode (TSM) resonators

The most widely used and the best known bulk acoustic wave (BAW) sensors without any doubt is quartz crystal microbalance (QCM) [26]. QCM is composed of a thin disk of AT-cut quartz, which is sandwiched between two electrodes. Applying voltage between electrodes induces shear deformation of the crystal and a standing wave is created between the QCM's faces. Therefore, Quartz crystal microbalance resonates in its thickness shear mode. In this mode of oscillation, the generated bulk waves travel in perpendicular direction to the sensing surface. The highest displacement of the wave is happened at the surface of QCM, thus, QCMs are very sensitive to surface interactions. Their normal operating frequency range is between 5 MHz and 400 MHz [26, 114].

Fabrication and characterization of QCM is a well-established science. The main advantage of QCM is its high Q -factor; $Q_{water}=2000$. This high Q factor in water enable the QCM to work in liquid medium and thus grant them great functionality in biological sensing [115]. QCMs were first implemented as sensors for monitoring deposition thickness in vacuum and air in 1960s and 1970s; however, after development of proper oscillator circuits for shear wave devices in fluid environment, biological application has been started [27]. Since then, QCM has been implemented as a device to estimate the thickness of adsorbed monolayer or multilayer protein

molecules [116, 117], or as an immunosensor to quickly detect different bioentities including human serum albumin (HSA) or hepatitis B virus (HBV) [113, 114, 118-120].

2.2.4.3.2 *Surface Acoustic Wave (SAW) Devices*

Following invention of interdigital transducers (IDTs) in 1965 surface acoustic wave (SAW) devices were introduced to the field of engineering [121]. The acoustic wave is generated on the surface of piezoelectric substrate by help of these metal interdigitated electrodes. Applying an AC voltage to the IDTs produces a periodic strain field in the piezoelectric substrate, which generates a standing surface acoustic wave on it. Thus, in surface acoustic wave sensors, the sensing surface and the applied electric field are parallel, and the particle displacement as it was shown in Figure 2-10 is perpendicular to the substrate. The wavelength of the acoustic wave is much lesser than the substrate's thickness, which implies that the substrate can be imagined as a semi-infinite medium with a confined region at the surface for propagation of the wave with the approximate thickness of one acoustic wavelength. The SAW operating frequency is between 30 MHz and 300 MHz. The main disadvantage of SAW sensors is that they are not suitable for biological and chemical sensing in liquid medium because of two reasons. Firstly, their displacement direction is perpendicular to the sensing surface and induces low Q factor in liquid. Secondly, the radiation of compressional waves in the liquid medium, mainly due to their higher wave velocity than the velocity of sound in water, which causes energy dissipation of the wave in fluid [110, 112, 121].

2.2.4.3.3 Flexural Plate Wave (FPW) Devices

Flexural plate wave (FPW) devices in fact are very thin membranes clamped all around of their edges. They resonate at their flexural vibration modes, which imply normal displacement to the membrane surfaces. Since their generated wave velocity is much less than the sound velocity in most of liquids (sound velocity in most liquid is between 900 m/s and 1500 m/s), FPW sensors are able of operation in liquid as opposed to SAW devices [113]. The sensitivity of FPW is inversely depends on the mass per unit area of the device; hence, by reducing the thickness of the membrane, one can expect higher sensitivity. In fact, due to the very thin membrane thickness in FPW sensors ($\sim 1\text{-}5\mu\text{m}$), their sensitivity is higher than other types of acoustic wave sensors [110].

Another advantage of FPW sensors is their lower operating frequency in the kHz to low MHz range. This implies cheaper and simpler electronic circuits and devices for characterization and sensor signal detection for FPW based sensors. FPW devices can be fabricated by the help of well-established microelectronics fabrication process, which imply precise, fast and cheap method of fabrication. FPW have been used to detect E. coli with the detection limit of 10^3 in less than half an hour in 1990s [122]. PVDF based FPW sensor with the resonant frequency of 100 kHz has been fabricated by Walton et al. to detect IgG protein. They reported high sensitivity as high as 30 times of TSM sensor; however, very low Q -factor ($Q_{air}=8$ and $Q_{water}=3$) [123]. Table 2-3 summarizes the different acoustic wave devices discussed in the previous sections. In this table, the sensitivity is defined as the relative frequency shift due to mass loading on a unit surface area. As it was discussed earlier, flexural plate wave sensor demonstrates the highest sensitivity value at the lowest resonant frequency among different types of acoustic wave sensors.

Table 2-3. Comparison of different acoustic resonators; λ is the wavelength of the acoustic wave

<i>Resonator</i>	<i>Thickness</i>	<i>Medium</i>	<i>Resonant frequency (MHz)</i>	<i>Mass sensitivity S_m (cm²/g)</i>
TSM	$\lambda/2$	gas/liquid	4-30	14 (6 MHz)
SAW	$\gg \lambda$	gas	30-500	200 (158 MHz)
FPW	$< \lambda/2$	gas/liquid	1-7	380 (5.5 MHz)

2.3 Comparisons of sensors

As it was discussed in the previous sections, we choose the biosensors as the main subject of our review. Biosensor technology is a wide branch of science, which has versatile applications in different industries such as food, biological diagnostics and agriculture. This versatility makes comparison of biosensor subjective and difficult, because in each application area, the sensor should fulfill the requirement of that field. However, a high sensitivity and selectivity, a simple and inexpensive fabrication process, a wide sensing range, and the simplicity of the overall sensing system are common aspects, which are figures of merits for a sensor. Here, we discussed and compared the general advantages and disadvantages of each sensor type mentioned earlier regarding to the above-mentioned features. A summary of this discussion is presented in Table 2-4.

Calorimetric biochemical sensors exhibit moderate sensitivity and selectivity and a good operational stability for continuous monitoring. High selectivity in biological sensing application can be achieved by coating the sensor with specific catalysts such as enzymes and antibodies. However, thermal sensors detect enthalpy changes during analyte absorption/desorption and, thus, are sensitive to analyte concentration changes only. In contrast with the other biosensors types they found less attention because of their lower sensitivity. Moreover, in liquid, the

sensitivity is often lowered because of the high thermal conductivities of the surrounding fluid and the sensor package [124].

Electrochemical sensors are undoubtedly the most commercially successful type of chemical and biochemical sensor. This success is mainly because of their simple structure, relatively easy and inexpensive fabrication processes and number of lesser advantages such as low power consumption, and low weight. However, for continuous monitoring of analyte concentrations the long-term stability of these sensors is typically not sufficient. This effect and poor sensor's selectivity and parasitic capacitance effects between the electrodes, makes the sensor response to analyte concentration generally in a non-explicit form. Therefore, the interpretation of the sensor response is rather complicated and generally requires extensive calibration. Moreover, the sensor signal is highly dependent on the quality of the sensitive layer, e.g. its thickness and surface morphology, thus causing irreproducible sensor responses.

Optical biosensors offer many advantages, such as high selectivity and sensitivity, fast response time, low detection limit with, e.g., refractive index resolutions on the order of 10^{-5} ~ 10^{-7} and limits of detection $0.1\sim 10$ pg/mm² [83]. Moreover, multiple analyte analyses have been conducted with them. These attractive features result in commercialized optical sensors with a number of biological and chemical sensing applications. However, optical biochemical sensors also have certain disadvantages. The main one is their system complexity and the difficulty in integrating all optical components, onto a single substrate, which result in a bulky and expensive system. Other drawbacks are: interference from ambient light, narrow dynamic range, limited stability caused by photobleaching of the immobilized sensing layer, and high sensitivity to temperature changes [67].

Microcantilever based sensors in static mode have been widely investigated as a chemical sensing platform. They have exhibited high selectivity and sensitivity with detection limits in order of a few femto-grams mass loading in air. They operate in vacuum, gases and liquids, but the sensors show long response times in comparison with the other chemical sensing methods. Moreover, low signal-to-noise ratios, temperature-induced drifts, and sensitivity to external vibration are other drawbacks. The main disadvantage of these sensors is the need of an optical method for measuring the deflection of the cantilever, which is a costly method, and requires proper alignment with the cantilever that it is a time consuming work. Moreover, this measurement method needs a transparent media, and a minimum required reflecting area. In liquid, the change of the output signal by optical properties changes of the medium is another problem.

Mass-sensitive dynamic mode sensors have several attractive features including high mass sensitivity, wide dynamic range, small size with on-chip actuation and sensing elements, a relatively simple fabrication process, fast response time, and robustness to external vibrations. Microcantilever and microdiaphragm based sensors in dynamic mode have several advantages including, CMOS compatible fabrication processes, small size and low power consumption, and the feasibility of fabrication of sensor arrays. However, the sensitivity of microdiaphragm is lesser than the microcantilevers. The main advantage of microdiaphragms is their higher Q -factor in liquid than the microcantilevers. Microcantilever sensors have high Q -factor in air; however, their Q -factor degrades drastically in liquid due to the high viscous damping of liquid environment.

Among acoustic wave devices, QCM has high Q -factors both in air and in liquid and therefore good frequency stability. However, it suffers from low sensitivity. Higher aging rate,

higher background noise floor and higher power consumption of the associated digital circuitry degrade the performance of QCM due to its high resonance frequency (typically 5~300 MHz) [26]. FPW has much higher sensitivity and less resonance frequency than the QCM. However, its quality factor is less than the QCM.

Table 2-4: Summary of the properties of biochemical sensors [28, 33, 39, 40]

Transduction mechanism	Resolution	Advantages	Disadvantages
Electromechanical	Thermal Moderate	Capability of on-line monitoring of measurand.	Only can detect variations of analyte concentration. Sensitive to thermal properties of the surrounding medium.
	Static High	Operable in vacuum, air, liquid. Microscale size and therefore high sensitivity. Inexpensive fabrication.	Low signal-noise ratio. May need very equipped and expensive optical system for characterization.
	Dynamic High	Microscale size and therefore high sensitivity. Very fast response. Inexpensive fabrication.	Low quality factor in liquid medium. Sensitivity maybe depends on external parameters.
	Optical High	High sensitivity and selectivity. Multi-analyte sensing. Fast response time.	Bulky, expensive and complicated setup. Labeling of the measurand before experiment.
	Electrochemical Moderate	Inexpensive Fab and simple structure. Very well-known and stabilized method.	Dependent to the quality of sensing layer. High background noise floor.

2.4 Piezoelectric Materials

Aforementioned, piezoelectricity is the charge accumulation in certain materials, which their crystal lacks a center of inversion symmetry, in response to applied mechanical strain. The word

Piezo in Greek means, “to squeeze or press”; therefore, piezoelectricity means electricity resulting from pressure. The piezoelectric materials also demonstrate the reverse effect, which means generation of a mechanical strain resulting from an applied electrical field. Pierre and Jacques Curie were the pioneers in demonstrating the direct piezoelectric effect in 1880. Their discovery was based on their previous study on the pyroelectricity effect (generation of electric potential in a material in response to a temperature change), and their knowledge of the crystal structures that gave rise to pyroelectricity. Two brothers demonstrated the piezoelectric effect using crystals of tourmaline, quartz, cane sugar, and Rochelle salt. The converse piezoelectric effect was first mathematically derived from fundamental thermodynamic principles by Gabriel Lippmann in 1881. This was immediately followed by the experimental confirmation of Curies’ brothers on the existence of the reverse effect [125, 126].

There are 32 crystal classes, which among them 21 crystals lack a center of inversion symmetry. This means that the crystal can support an internal electric polarization in the absence of an applied external electric field. Among these 21 point groups, 20 of them demonstrate non-zero piezoelectric constants. The piezoelectric materials used in microfabrication can be classified in three different categories: piezoelectric substrates such as quartz, lithium niobate, and gallium arsenide; thin-film piezoelectrics, such as zinc oxide, aluminum nitride and lead zirconate-titanate (PZT); and polymer-film piezoelectrics, such as polyvinylidene fluoride (PVDF) [127, 128].

2.4.1 AlN and ZnO

In this review, our concern is more on thin film piezoelectric materials, therefore in this section we first study the AlN and ZnO thin film characteristics. PZT thin film will be reviewed

in next section under the name of ferroelectric materials. Both AlN and ZnO are wurtzite structured materials which show a piezoelectric response along (0001) [3]. The main method for growing these layers in MEMS applications is sputtering [129]. The deposition temperature between 100° and 900°C was reported for AlN sputtering [130]; however, ZnO sputtering exhibit conductivity problems, therefore, in order to achieve a high resistivity, ZnO layers are commonly deposited in room temperature [131].

Inherently, AlN has two major advantages over ZnO. First, AlN is well suited for MEMS technology; however, Zn is a fast diffusing ion, and therefore it is problematic in MEMS fabrication processes. Moreover, AlN is a large band gap (6 eV) material, and therefore with a high resistivity, whereas ZnO with a band gap of 3.0 eV exhibits semiconductor properties with the inherent risks that off-stoichiometry might lead to doping (as e.g. Zn interstitials [132]) and thus to an increased conductivity. In fact, deposition of ZnO layer with high resistivity is practically difficult. The main disadvantage of low resistive films is their high dielectric loss especially at low frequencies, which deteriorate the performance of sensors and actuators working at frequencies below about 10 kHz.

Although, aforementioned advantages of AlN, ZnO has found more application in the field of piezoelectric MEMS devices. The reasons of this preference is explained by the less demanding vacuum conditions for ZnO, better availability of ZnO films, and the negative stress issues with the AlN films [3]. The thin film properties of these two materials are compared in Table 2-5. Table demonstrates that AlN and ZnO show quite similar piezoelectric properties. Even though, their longitudinal effect is slightly different, their transverse coefficient is almost equal.

Table 2-5: Thin film piezoelectric properties

<i>Coefficient</i>	<i>AlN</i>	<i>ZnO</i>	<i>PZT</i>
$e_{31,f} (C/m^2)$	-1.05	-1.0	-8...-12
$d_{33,f} (pm/V^2)$	3.9	5.9	60...130
ϵ_{33}	10.5	10.9	300...1300
$c_{33} (GPa)$	395	208	98

2.4.2 Ferroelectric materials

Ten of the 20 crystals with non-zero piezoelectric constants represent the polar crystal classes. Polar materials demonstrate a spontaneous polarization without mechanical stress due to a non-vanishing electric dipole moment associated with their unit cell, and exhibit pyroelectricity. If the spontaneous polarization can be permanently reoriented between crystallographically defined states with an applied electric field, the material is said to be ferroelectric. There are literally hundreds of materials known to be ferroelectrics. However, a group of ferroelectrics known as the “Perovskites family” is perhaps the most extensively studied and technologically important. Ferroelectrics such as $Pb(Zr,Ti)O_3$, $(Ba,Sr)TiO_3$ and $LiNO_3$ belong to this family and have the general formula of ABO_3 .

In high temperatures, many ferroelectric materials do not have a spontaneous polarization since they have a higher symmetry crystal structure (The paraelectric phase). The transition point is defined as the Curie temperature, T_c . At temperatures below T_c , a phase transformation occurs when the material distorts into a lower symmetric structure resulting in a ferroelectric phase with a spontaneous polarization. Another important characteristic of ferroelectric materials is their polarization-electric field (P-E) hysteresis loop. This loop clearly clarifies that the spontaneous polarization can be reoriented along certain crystallographic orientations [3, 128]. From the P-E loop (Figure 2-11), several distinctive characteristics can be described.

- The saturation polarization (P_s), which is the maximum degree of alignment, occurs at the highest field. This can be obtained through extrapolation of the linear portion of the loop back to the polarization axis.
- The remanent polarization (P_r), which is the presence of a net polarization even after removal of the applied electric field.
- The coercive field (E_c), which is the electric field needed to achieve a total polarization of zero.

Figure 2-11: Characteristic polarization – electric field (P - E) hysteresis loop of ferroelectric materials [133]

2.4.2.1 PZT

Lead zirconate titanate (PZT) is the most widely utilized ferroelectric thin films in piezoelectric MEMS devices. It demonstrates many of the important features of the other ferroelectric compositions, and therefore is studied here. In general, the term PZT refers to a wide range of compositions with the chemical formula $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ rather than an individual compound. Most solid solutions between PbZrO_3 and PbTiO_3 in the phase diagram of PZT (shown in Figure 2-12) possess ferroelectricity and show excellent piezoelectric properties. The

change in Zr/Ti ratio will respectively change the ferroelectric and piezoelectric properties of the PZT layer. The crystal structure of PZT above the Curie temperature (T_c) is paraelectric phase ($m3m$) with a cubic perovskites structure. It should be noted that the Curie temperature varies from 230°C to 490°C depending on the Zr/Ti ratio. After cooling below the Curie temperature, PZT undergoes the phase transition from a paraelectric phase to a ferroelectric phase. In ferroelectric phase, at low Zr contents rhombohedrally distorted perovskite ($3m$) region is dominated in the PZT phase diagram, whereas, a tetragonally distorted perovskite ($4mm$) is dominated at high Ti concentrations. Compositions in excess of ~93% Zr are known to be an orthorhombic, anti-ferroelectric structure and are not piezoelectric. The tetragonal and rhombohedral structures are separated at the morphotropic phase boundary (MPB) near the Zr/Ti ratio of 52/48, with a slice of monoclinically distorted perovskite at lower temperatures near the MPB [134, 135].

Figure 2-12: Schematic representation of the temperature-composition phase diagram of PZT [125]

The presence of both of tetragonal and rhombohedral structures in MPB region gives the material an increased number of polarization directions. Thus, the highest d and e coefficients for bulk PZT ceramic are always observed at the MPB. The same behavior is often [50–54], but not universally [55, 56] reported for thin films. The piezoelectric coefficients of PZT are substantially better than those of AlN and ZnO thin films (see Table 2-5). However, the latter films are more compatible with CMOS processes and relatively easier for fabrication. The main drawback of the PZT integration in standard CMOS method is the high temperature processes such as annealing and/or deposition conditions required for growth of high quality PZT thin films.

2.5 PZT Thin Film Technology

With the drive toward miniature devices, thin film technology has exploded with the development of numerous techniques for depositing thin films. Most of these methods have been investigated for the deposition of PZT. The primary effort was conducted by means of physical techniques such as RF planar magnetron sputtering, DC magnetron sputtering, or ion beam sputtering. Pulsed-laser deposition (PLD) was also applied for growth of PZT thin films. However, the chemical methods are currently dominated. Metal-organic-chemical vapor deposition (MOCVD) as well as chemical solution deposition (CSD) with its different routes using sol-gel reactions, or metal-organic-decomposition (MOD), is now established methods for PZT deposition. Due to its superior step coverage, MOCVD is the preferred technique for IC applications. MOD because of the low need of investment has found great importance especially for sensors and actuators applications. The main advantage of sputtering method is the low deposition temperatures. All of these methods, except CSD, allow in-situ crystallization of the

film. The CSD techniques necessarily need post-annealing treatments which is usually carried out at 600°C or more [1].

Growth of high quality PZT, independent of its deposition method, could be carried out by understanding a few key features of the PbO-ZrO₂-TiO₂ system.

- Nucleation and growth of the perovskite require a rather precise stoichiometry. Otherwise competing phases with fluorite and pyrochlore structures nucleate, which are more tolerant in oxygen and lead vacancies [1, 136]. (Lead and PbO desorbs quickly from the surface at high enough temperatures, if they are not incorporated in the perovskite lattice)
- Lead ions or PbO molecules that are not incorporated into the perovskite lattice exhibit high diffusivities and volatility above 500°C [2].
- The activation energy for nucleation of the perovskite (4.4 eV/unit cell) is considerably larger than for its growth (1.1 eV) [137].

Whereas the bulk PZT ceramics typically fabricated at high sintering temperatures, the PZT thin films can be grown at much lower temperatures. The reason is much smaller diffusion distances needed with thin-film processing techniques, which provide for a homogeneous, stoichiometric mixture on the molecular level [138]. However, the growth of the perovskite structure films needs a precise control of the deposition parameters. The different phases found in PZT for various deposition methods are schematically shown in Figure 2-13 as a function of the deposition temperature.

At low temperature, the fluorite structures with the formula Pb_{2+x}Ti_{2-x}O_{7-y} may be appeared which usually result from oxygen deficiency at the initial stage of annealing [1]. The PbTi₃O₇ pyrochlore structure is formed in high temperature, which is common to all methods. The reason

for its formation is heavy lead loss. Therefore, all processes usually work with an excess of lead, in order to compensate lead loss before perovskite formation [138].

Practically all films applied in the devices are presently deposited between 525°C and 700°C. The critical temperature depends on the deposition method and amounts to 700°C for PbTiO_3 grown by MOCVD [139]; and it was found to be lower for sputter deposition (550°C to 600°C) due to plasma effects [140]. In Sol-gel method post-annealing treatments is always carried out at 600°C [6]. In case of post annealed films, rapid thermal annealing (RTA) proved to be a good technique to provide a quick formation of the perovskite, thus reducing lead loss [141]. Various efforts have been undertaken to lower the growth temperature. With some of the coating methods, lower deposition temperatures indeed seem to be possible (see Figure 2-13). For instance, good pyroelectric thin films of PbTiO_3 are reported to grow at 450°C by in-situ sputtering, albeit with some traces of PbO second phase [142]. However, it was numerously reported that the highest quality PZT films are grown by the sol-gel method [143, 144].

Figure 2-13: Schematic phase evolution as a function of PZT growth temperature for various methods. The vertical axis reflects differences in the deposition conditions and the Zr/Ti ratio (with increasing Zr content, the deposition temperature has to be increased). In case of post-annealed films (i.e., sol-gel) the temperature refers to the final annealing temperature. The schema does not apply to transient phenomena. Abbreviations: Per; perovskite; Py; pyrochlore; Flu; fluorite at lower temperatures; α ; amorphous [1].

2.5.1 Especial issues on growth of high quality piezoelectric films

The piezoelectric properties of PZT films are strongly influenced by the film orientation, composition, grain size, defect chemistry, substrate, and mechanical boundary conditions [145]. The various figures of merit of these properties, which determine the performance of the piezoelectric devices, are in many instances proportional to the polarization that can be achieved. Therefore, the polarization characteristics of a thin film can fairly reveal its piezoelectric properties. For example, it is known that the PZT films with higher remanent polarizations have higher piezoelectric coefficients [146]. It should be also noted that the value of remanent polarization in a polycrystalline material also depends on factors, such as electromechanical

boundary conditions at grain boundaries and sample surface, available domain states, and imperfections such as elastic and charged defects in the material [133].

Grain size is a parameter that has substantial influence on 90° domain in ferroelectrics materials. Theoretical models demonstrate that the density of 90° domain walls is inversely proportional to the square root of the grain size [147]. This implies that the density of 90° domain walls and in turns the contribution of these walls to the permittivity ϵ_r per volume increases with grain size decreasing. In another words, the permittivity ϵ_r increases with grain size decreasing. On the other hand, distance-dependent repulsive force between neighboring domain walls strengthens, as the density of the domain walls increases. This gives rise to a decrease of the mobility for domain walls, and makes of domain reorientation more difficult, which leads to the decrease of permittivity (ϵ_r) with the grain size decreasing. Moreover, when the grain size decreases, the repulsive force between the neighboring domain walls increases, leading to higher activation energy required for the reorientation of the domains. This in turn results reduction of P_r and enhancement of E_c [148]. Martinera et al. [149] have shown that when the grain size of bulk PZT ceramic decreases, T_c increases, the maximum of the dielectric constant decreases, and the room temperature values of the dielectric constant become lower. Hu et al. [148] also measured that the dielectric and ferroelectric properties of $\text{Pb}(\text{Zr}_{0.45}\text{Ti}_{0.55})\text{O}_3$ films of large grain sizes grown by sol-gel method present large relative dielectric permittivity and large remanent polarization.

Tuttle and co-workers [150] have shown that the grain size influences for the film under stress is more prominent. They concluded that the domain state is governed substantially by the stress experienced by the film during cooling through the phase transformation temperature. Consequently, perovskite structured thin films, when exposed to tensile stresses during the

cooling process, tend to have their polar vectors in orientations approximately parallel to the substrate; while films under compressive stresses tend to have the polarization oriented more nearly perpendicular to the substrate. Because the mobility of non-180° domain walls in ferroelectric thin films tends to be limited compared to bulk materials, once the ferroelastic domain orientation is established, it is difficult to change at room temperature [140]. Larger grained films tend to show more complicated domain structures within a single grain, and so may be less susceptible to reduction in the remanent polarization and piezoelectric response [3].

Aforementioned, the maxima of piezoelectric coefficients usually achieved near the morphotropic phase boundary for (111), (100), or randomly oriented PZT films [151, 152]. The piezoelectric responses of the (100)-oriented PZT films is substantially larger than the (111) films. For example, in $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-PbTiO}_3$ (PMN-PT) 70/30 films on Si, the ratio of the piezoelectric response for (100) oriented films, relative to (111) ranged from 1.6–1.9 [153], with a maximum $e_{31,f}$ coefficient of -5.5 C/m^2 . In both $\text{PbYb}_{1/2}\text{Nb}_{1/2}\text{O}_3\text{-PbTiO}_3$ (PYbN-PT) 50/50 and 60/40 epitaxial films on $\text{SrRuO}_3/\text{SrTiO}_3$, $e_{31,f} (100)/e_{31,f} (111)$ was ~ 3.6 [154]. Highly (100) oriented PZT 40/60 films had higher remanent polarization ($61 \mu\text{C/cm}^2$ compared to $41 \mu\text{C/cm}^2$) and lower relative dielectric constant (368 compared to 466) than PZT 40/60 films that were randomly oriented [146].

Substrate plays an important role in achieving high quality piezoelectric layer. The substrate can influence the quality of PZT film by controlling its nucleation growth, controlling the stress in the film due to thermal mismatches, and due to the importance of its mechanical properties in controlling the boundary conditions of the film. Tuttle and coworkers [146], demonstrated that two PZT 60/40 films (rhombohedral symmetry) with a similar degree of highly preferential (111) crystalline orientation deposited on platinum coated sapphire and silicon substrates, differed by a

factor of two in remanent polarization. The remanent polarization of the film deposited on sapphire was $40.6 \pm 3.8 \text{ } \mu\text{C}/\text{cm}^2$; whereas, the remanent polarization of the film on silicon was $20.2 \pm 1.9 \text{ } \mu\text{C}/\text{cm}^2$. Films grown on Si generally have low remanent polarization values, and consequently, low $e_{31,f}$ values when poled through the film thickness. This is largely because the tensile stress in the films resulting from the mismatch in thermal expansion coefficients rotates the hysteresis loop clockwise. The result is low remanent piezoelectric response. In contrast, films grown on single crystal oxide substrates such as SrTiO_3 or LaAlO_3 , show much squarer hysteresis loops, and larger piezoelectric coefficients [3]. Work by Dubois suggests that for a given film microstructure and poling state, the magnitude of the $e_{31,f}$ coefficient increases with applied static tensile strains, and decreases for applied compressive strains [155].

The textured PZT films can be grown in desired orientation in different substrates. This means that the nucleation of PZT films can be manipulated to achieve a desired orientation. For a perovskite single crystal substrate or electrode, PZT grows almost inevitably in the same orientation as the template. However, this trend is not evident for PZT layers grown on platinum electrode. Platinum films are most often deposited with a (111) texture. It is expected that PZT grows with the same orientation as platinum because their lattice constants are rather close (2–3% mismatch); however, this is not necessarily true. A mixture of all major orientations is obtained in the general case. Control of the orientation by using thin buffer layers has been reported to be successful in sputtered films on Pt-coated substrates. For example, PbTiO_3 will often adopt a (100) orientation on Pt, and serve as a template for well-oriented PZT films, while a thin TiO_2 buffer layer can yield (111) oriented perovskites [156]. During sol-gel film processing, the concentration of excess lead, the pyrolysis temperature, as well as the ramp speed used in the rapid thermal annealing all play a substantial role for orientation control [157]. The

temporary formation of a Pt_3Pb interface layer has been identified as a mechanism promoting (111) orientation [158].

2.6 Conclusion

Throughout this chapter, different types of sensors were firstly reviewed, and their characteristics were compared. Among them, microdiaphragm based sensor was chosen for further development and study. This device simultaneously addresses problems such as the fragility of microcantilevers, and their low quality factor in liquid medium. Moreover, its low cost, mass fabrications, and high integration, which are mostly accomplished by MEMS processes, are the other advantages of this type of sensors. In order to excite and characterize the microdiaphragm based sensor, we have implemented piezoelectric behavior. This behavior, together with different types of piezoelectric thin films, their fabrication processes, and issues during the fabrication processes were the subject of the second part of this chapter. It was concluded that the piezoelectric properties of PZT films are strongly influenced by the film orientation, composition, grain size, defect chemistry, substrate, mechanical boundary conditions, and the fabrication process. The result of this study was used to fabricate a high quality piezoelectric microdiaphragm based sensor (PMS) as it is reported in the next chapter.

Chapter 3: Fabrication of Piezoelectric Microdiaphragms and Preliminary Characterization

This chapter reports on the fabrication and characterization processes of the piezoelectric microdiaphragm based sensor. The devices are fabricated in two different configurations, circular and square shape. They were fabricated by combining sol-gel PZT thin film and MEMS technology. In the second part of this chapter, the electrical and mechanical properties of the fabricated diaphragms were characterized.

3.1 Introduction

The fabrication and characterization process of the piezoelectric microdiaphragm based sensor is reported in this chapter. Square and circular shaped diaphragms were fabricated by combining sol-gel PZT thin film and MEMS technology. Electrical and mechanical characterization of the fabricated diaphragms is reported in the second part of this chapter.

3.2 Piezoelectric microdiaphragm as a sensor

Piezoelectric microdiaphragms will be implemented as physical or biological mass sensors, and physical pressure sensors in this work. The physical or biological immobilization would be done in the back side chamber of the diaphragm as it is shown in Figure 3-1. Therefore, the diaphragms should be fully clamped around its edges to form a reaction chamber for immobilizing different entities. Working principle of piezoelectric microdiaphragm as a sensor is summarized in the following few sentences and also Figure 3-2. The diaphragm vibrates at its resonant frequency when it is unloaded, while the diaphragm is loaded with a physical or biological entity its frequency drops. By measuring this frequency shift the characterization of the absorbed material could be performed.

Figure 3-1: Schematic processes of immobilizing. (a) Thin gold film was deposited onto the diaphragm. (b) Different antigens were immobilized onto the diaphragm. (c) Blocking the open surface by Blocker. (d) Hybridization of antigens and antibodies .

Figure 3-2: Response of a piezoelectric microdiaphragm when it is loaded with a physical or biological entity. The diaphragm vibrates at resonant frequency A when it is unloaded, while it is loaded with a physical or biological entity its frequency drops to B. By measuring this frequency shift the characterization of the absorbed material could be performed.

Aforementioned, the diaphragms should be fully clamped around its edges to form a reaction chamber for immobilizing different entities. A schematic view of a piezoelectric microdiaphragm is demonstrated in Figure 3-3. However, clamping reduces the diaphragm piezoelectric coupling coefficients. The reason can be explained by imagining an ideally diaphragm which is just suspended from a few points of its edges. This implies that the amplitude and its first radial derivative are zero at the borders. Hence, for this diaphragm the curvature everywhere in the membrane has the same sign, while in a clamped plate, the curvature

has opposing sign at the center and the boundary. Therefore, the clamped plate has lower amplitude of displacement compared to the free plate. Since amplitude translates directly into kinetic energy -which must be equal to the potential energy in time average- it follows that the free plate offers a larger coupling.

Figure 3-3: Schematic design of a circular piezoelectric microdiaphragm

Moreover, due to charge cancellation issues, which arises by the change in the curvature of the diaphragm, smaller electrodes should be used in the clamped diaphragm. The charge in the electrodes has two different contributors. First, there is a surface charge density due to the dielectric properties of the PZT layer, associated with the capacitive behavior of the device out of resonance. Second source of the charge is due to piezoelectric properties of the PZT layer, which depends on the stress through the constitutive equations. In the case of antisymmetric modes, as the impedance change at the resonance frequency is null, maybe there is an overall cancellation of the charges of piezoelectric origin, induced on the electrodes. This is known as charge cancellation phenomenon. Due to this term, the electrodes on the clamped diaphragms always cover 0.7 of the radius. This smaller radius means that smaller power is provided in clamped

diaphragm [159]. Although these disadvantages exist in fully clamped diaphragm design, there are numerous reports on the fabrication of such devices with high piezoelectric response [1, 16, 19, 160]. The main key to the high quality device is growing a high quality piezoelectric layer.

3.3 Device Fabrication

3.3.1 Circular Shape

The piezoelectric circular-shaped microdiaphragms were fabricated using standard bulk micromachining techniques on a 4-inch silicon-on-insulator (SOI) wafer and on a 4-inch double-sided polished (100)-direction silicon wafer. The SOI wafer, which has a device layer of 2 μm and SiO_2 layer of 0.5 μm , was used to reduce the residual stress from the silicon oxidation process. For the double-sided silicon wafer, first, a thermal silicon oxide (SiO_2) layer (1.8 μm thick) was grown on the wafer. We employed wet oxidation of silicon in H_2O steam, which occurs much faster than dry oxidation. The fabrication process was followed by low pressure chemical vapor deposition (LPCVD) of Si_3N_4 layer with a thickness of 200 nm on both sides of the wafer. LPCVD has advantages such as excellent purity and uniformity, and conformable step coverage over plasma enhanced chemical vapor deposition (PECVD); however, it suffers from low deposition rate and relatively high operating temperature. The Si_3N_4 layer role was to compensate the compressive residual stress of the SiO_2 film. The overview of fabrication process for the piezoelectric microdiaphragm fabricated on SOI wafer is shown in Figure 3-4.

Figure 3-4: Schematic fabrication process for the circular piezoelectric sensor.

Aforementioned, high quality PZT films cannot be grown directly on silicon. To prevent inter diffusion and oxidation reactions, buffer layers are needed. In most applications, bottom electrode plays the role of the buffer layer. Choice of the material that forms the bottom electrode layer has a significant effect on the properties of PZT layer. The most often reported materials include platinum [161], and the metal oxides RuO_2 [162], SrRuO_3 and $(\text{La},\text{Sr})\text{CoO}_3$ (LSCO, perovskite structure) [163]. Platinum is the best material as the electrode for PZT and similar material system because of its low resistivity, good stability against oxidation and reaction with the PZT layer during deposition and subsequent high-temperature annealing [164].

However, platinum delaminates if deposited directly on silicon nitride. Therefore, the need of an intermediate layer between silicon nitride and platinum should always be considered. According to most of the research in this area, titanium is always chosen as an adhesion layer for platinum. The problematic issue regarding the Ti adhesion layer is the diffusion of Ti to the PZT side, its reaction with oxygen and formation of nucleation centers for PZT [165]. Another issue is the appearance of blisters in the Pt layer. There is evidence that oxygen migrates along the grain boundaries through the platinum film and reacts with the Ti layer [166, 167]. This results in the formation of TiO_2 pockets in between the Pt grain boundaries, highly compressive stress in the TiO_2 layer, and therefore formation of blisters in the film [1]. Both of these phenomena occur at high temperatures, which are unavoidable in the growth of PZT films due to annealing and sintering processes. To eliminate these issues, the Ti film was replaced with a well-reacted TiO_2 layer as the adhesion layer. The TiO_2 layer is reactively sputtered from a titanium target at 500W and 1.8×10^{-3} mbar with an O_2/Ar ratio of 1:9 at 400°C using RF magnetron sputtering. The Pt layer was sputtered at 200W and 1.8×10^{-3} mbar in argon at 390°C .

The bottom electrode was patterned by using photoresist as a hard mask and as following recipe. The wafer was first soaked in diluted HF solution (10:1 H_2O : HF) to remove possible organic residue or grease on the Pt surface. Due to the strong acidic nature of the solution, the wafer can only be dipped and immersed for 10s. Next, the wafer was soaked in the heated 3:1 HCL: HNO_3 solution for 3 minutes at which the temperature must be maintained at 75°C to 80°C .

After deposition and patterning of the bottom electrode, Sol Gel deposition of the PZT thin film was followed. This step is the most important part in the whole fabrication procedure, as the quality of the deposited piezoelectric material will determine the functionality of the sensor. First, PbTiO_3 (PT) solution (Mitsubishi Materials Corporation) was spin coated on the wafer and

was baked at 200°C and 400°C for 3 min. This layer provides better adhesion to the bottom electrode and controls the orientation of PZT layer to (111) direction. After the deposition of PT seed layer, 1 ml of PZT solution ($\text{Pb}(\text{Zr,Ti})\text{O}_3$) (Mitsubishi Materials Corporation) was spin coated at a speed of 500 rpm for 5 seconds and then at 2500 rpm for 30 seconds to control thickness and uniformity. After spin coating, the solvent was evaporated, and the sol becomes a gel. A single PZT layer thickness is around 75nm. After the spin coating process, the wafer was baked at 200°C and 400°C for 3 min to evaporate solvent and decompose organics. The spin coating and baking were repeated for 2 more times to deposit 3 layers of PZT thin film on the substrate. The resultant films were annealed at 600°C for 15 minutes in quartz tube furnace for crystallization of structure in PZT films. The spin coating and baking process was repeated three times before they were sent for annealing process. The entire process was repeated until the desired thickness of PZT layer was achieved. After the PZT thin film deposition, the PZT layer was patterned and etched by a solution of HCl: HF: H_2O (50:1:50) and a thick photoresist as a mask.

In the next step, to reduce the parasitic capacitance induced by electrodes, an insulating material with low dielectric permittivity such as PECVD silicon nitride, Cytop, or Polyimide was deposited and patterned on the top surface of PZT layer. The purpose of this layer is to act as an electrical insulator between the adjacent conducting layers (Pt/Ti and PZT) at different voltages. This is vital to the functioning of an integrated chip, because high voltage difference between the conducting layers would cause a current to irreversibly surge and physically disrupt the material. This disruption is known as a breakdown and the minimum voltage is termed as the breakdown voltage. Once breakdown occurs, current leakage will occur and the integrated chip will cease to function [144].

Afterwards, the Ti/Pt top electrode was patterned and deposited by lift off process. First, the photoresist mask was coated and patterned using standard photolithography procedure. Then, deposition of Pt/Ti using the DC/RF Magnetron Sputtering machine was conducted. After sputtering, the whole wafer was immersed in acetone to strip off the photoresist layer. All the areas coated with photoresist layer will collapse, and therefore leaving only the areas that has been directly deposited onto the wafer, forming the desired pattern for the top electrode.

Finally, the backside circular holes were etched by deep reactive ion etching (DRIE). Before DRIE is carried out, a layer of photoresist was coated onto the front side of wafer to protect it from being damaged. DRIE process composed of subsequent passivation steps with C_4F_8 and isotropic etching steps with SF_6 . These two processes of deposition of passivation and etching are repeated until the final etching shape achieved. Within the chamber, there is high energetic plasma to produces a collimated stream of ions that bombard the substrate at low pressure (1 to 20 mTorr). By a process of sputtering, these ions remove the passivation from the bottom of the previous etch step, but not from the sides. The etchant chemicals can then erode only the bottom of the channels. A large number of very small isotropic etch steps taking place only at the bottom of the etched pits after the process is repeated many times. This selectivity leads to the overall anisotropy of the process. To illustrate the schematic of fabrication processes and the diaphragm cross section along its different designs following figures were drawn. The complementary explanations are written under each corresponding figures.

Figure 3-5: Optical images of a fabricated sensor array. (Left) Front view. (Right) Backside view

Figure 3-6: An SEM picture of the circular piezoelectric microdiaphragm

3.3.2 Square shape

The fabrication process of piezoelectric square-shaped microdiaphragm was also similar to circular diaphragm; however, we employed wet etching for releasing the diaphragms. A 4-inch double-sided polished (100)-direction silicon wafer was chosen as the platform of the fabrication. As shown in Figure 3-8, the fabrication process was involved of 10 main steps. First, a thermal silicon oxide (SiO_2) layer (1.8 μm thick) was grown on the wafer. Then, (Si_3N_4) layer with a thickness of 200 nm and a low temperature oxide (LTO) layer with a thickness of 350 nm were deposited on the wafer by LPCVD. The Si_3N_4 layer role was to compensate the compressive residual stress of the SiO_2 film, while the LTO layer was used as the hard mask during the Si wet etching process. Moreover, LTO reduces the rates of thermally activated defects and the redistribution of impurities.

After deposition of these layers on both side of the wafer, backside of the wafer was patterned for KOH wet etching of the Si layer. First, the LTO layer was etched by buffered oxide etch (BOE). BOE or 5:1¹ buffered hydrofluoric acid (5:1 BHF) is the often best choice for controlled etching of oxides [168]. The $\text{Si}_3\text{N}_4/\text{SiO}_2$ layers were patterned by reactive ion etching (RIE) using CF_4+O_2 . After this patterning process, anisotropic or orientation dependent etching of silicon was performed by potassium hydroxide (KOH) etchant. The potassium hydroxide (KOH) is the classic anisotropic etchant of silicon. Anisotropic or orientation dependent etching of silicon is possible due to its good single crystal characteristics. Etching rate of KOH towards $\langle 111 \rangle$ crystal plane direction is much slower than that towards $\langle 100 \rangle$ crystal plane direction due to the different densities of covalent bonds. As a result, an inverted-pyramid pit will be formed

¹ 5:1 refers to five parts by weight of 40-weight-percent ammonium fluoride (the buffer) to one part by weight 49-weight-percent hydrofluoric acids, which results in a total of about 33% NH_4F and 8.3% HF by weight

and this structure is facility for the mass-immobilization as the open surface is much larger than that in the bottom. The wet etching process was performed until the remaining thickness of silicon was about 50 μm . This remaining Si film makes the substrate more solid during the subsequent process.

The fabrication process was followed by deposition and patterning of TiO_2/Pt as bottom electrode. Then, a thick PZT layer with a required thickness of around 3.5 μm was deposited by the composite thick film deposition technique [169]. To open a contact for the bottom electrode pad wet etching of the PZT in diluted $\text{HCl}:\text{HF}:\text{H}_2\text{O}$ (50:1:50) solution was done. To minimize the parasitic capacitance induced by the patterned electrode wiring a polyimide layer was spin-coated, patterned and cured as an insulation layer. Ti/Pt layers were sputtered and patterned on the front side by using lift-off to serve as the top electrode. The metal top and bottom electrodes are firstly used to polarize the piezoelectric film and electrical pads during the testing. The remaining thin Si layer on the backside was etched by KOH or DRIE till the SiO_2 layer was exposed. SEM figures of the final device are shown in Figure 3-7.

Figure 3-7: Images of the fabricated sensor array: (Left) SEM image of the back side; (Right) Cross section of the sensor and its different layers.

Figure 3-8: Schematic fabrication process for the square piezoelectric sensor.

3.4 Device Electrical Characterization

The piezoelectric diaphragm can be characterized using impedance spectrum, which is one of the advantages of the piezoelectric based sensors. This advantage makes the piezoelectric diaphragm easy to be integrated with control circuit and thus particularly useful for physical and chemical sensing. Impedance is the ratio of the applied sinusoidal voltage to the induced current. This ratio is represented by its magnitude and by its phase shift between the voltage and the current. The induced current is the rate of change of the total charge in the electrodes. As was mentioned earlier, this charge has two contributors. One is due to the dielectric properties of the PZT layer, and the other is by the piezoelectric effect. Ideally, the phase change between the voltage applied and the induced current for the former term is -90° ; however, in reality there is some deviation from this value. At the resonance frequencies of the diaphragm the charges induced on the electrodes by the piezoelectric effect will change the impedance of the device [159]. Here, we use the Agilent 4294A impedance analyzer to measure the impedance of the fabricated sensors. A probe station was used to connect the analyzer and the wiring pads of the sensors. An example of impedance and phase response of a PCMS is shown in Figure 3-9. The measured resonance frequency f_r and the anti-resonance frequency f_a from the impedance spectrum are used to determine the effective coupling coefficient of the diaphragm [11]. The coupling factor k^2 directly influences efficiency of power emission, bandwidth, and sensitivity of the sensor [170]. For piezoelectric materials, the coupling coefficient k^2 can be defined as the ratio of the stored mechanical energy in the piezoelectric material per input electrical energy supplied by an electrical source. The coupling factor can be calculated as shown in equation (3.1) based on IEEE standard on piezoelectricity [171].

$$k^2 = 1 - \left(\frac{f_r}{f_a} \right)^2 \quad (3.1)$$

The effective electromechanical coupling coefficient k^2 of the fabricated piezoelectric circular microdiaphragm sensor (PCMS) shown in Figure 3-9 was 0.93%.

Figure 3-9: Impedance spectrum of a diaphragm with diameter of 0.8 mm shows its resonant frequency is 121.8 kHz.

In the experimental part of this work, the Q value is measured by the following relation $f_0/\Delta f$, where f_0 is the frequency at which the real part of the impedance reaches its maximum, and Δf is the width of the peak at its half height. The f_0 and Δf are estimated by fitting the measured

phase peak using Lorentz function [6]. For instance, the Q value obtained in air was 197 at a quite low operating frequency of around 122 kHz. The obtained Q value of the flexural mode sensor is comparable with that of a typical FABR on silicon nitride (200-300) layer operating at around GHz [7]. This means both of them have similar resolution in detecting frequency shift.

Figure 3-10: The Q factor is as high as 197 at relatively lower operating frequency compared with FBAR.

The P-E hysteresis loop of the device was measured using precision ferroelectric analyzer (Radiant Technology Inc). Figure 3-11 shows the measured hysteresis loop. The remanent

polarization P_r and corrective electric field E_c are $21.3 \mu\text{C}/\text{cm}^2$ and 4.92 V , respectively. These values indicate high ferroelectric properties of the device.

Figure 3-11: P-E hysteresis loop of the PZT layer on a sensor with diameter of $800 \mu\text{m}$ obtained after device fabrication.

3.5 Stress measurements

Residual stresses generated during the fabrication of ferroelectric film will certainly affect its electrical properties. It was previously reported that stresses in $\text{Pb}(\text{Zr,Ti})\text{O}_3$ ceramics influence properties such as dielectric permittivity, $\tan(\delta)$, and piezoelectric coefficients. Berlincourt [172] reported that these effects are most prominent for compressive stresses applied

parallel to the polar axis. Beside of the influences on electrical properties of the film, residual stress can also affects its mechanical characteristics. For instance, excessive tensile stresses in the films may result in film cracking and edge delamination, and compressive stresses can result in buckling of the film.

In general the growth (intrinsic) and thermal stresses are the two main sources of the total stress in the fabrication process. Intrinsic stress is due to accumulation of impurities into the film during the deposition process. The magnitude of this stress is largely dependent on the thin film deposition conditions, such as deposition rate, power or pressure. On the other hand, thermally induced residual stresses are developed from the differences of thermal expansion coefficients between different layers during the cooling from deposition or annealing temperature to room temperature. In order to measure the stress during the fabrication process, we employed three different methods (Micro-Raman technique, Wafer curvature, and Suspended membrane method). The explanation of these methods and the results of these measurements are summarized in the following sections.

3.5.1 Micro-Raman technique

We used a micro-Raman system (WIN-TEC) with 532 nm line as excitation source to measure the stress of the upper silicon in SOI wafer [173]. In micro-Raman spectroscopy, a laser beam is focused on the surface of the sample by a microscope to a spot size in micrometer level. The sample is irradiated by focused laser beam, producing the Rayleigh and Raman lines. All these signals are collected by a spectrometer. The spectrometer records the intensity of the signals as a function of frequency, called Raman spectrum. The Raman spectrum of unprocessed and unstressed sample was measured and used as a reference. When a stressed sample was

measured, the Raman peak will shift some wave numbers in frequency from the reference spectrum. This frequency shift is induced by the residual stress. By assuming biaxial strain in the x-y plane of Si (001), the stress in the silicon layer can be described as following [174, 175]:

$$\sigma(MPa) = -435 \times \Delta\omega(cm^{-1}) \quad (3.2)$$

In the formula, σ is the residual stress and the $\Delta\omega$ is the Raman shift, which compared with the reference sample. This formula means that if the Raman line shift toward the left of the Raman line of unstressed Si, the stress is tensile and otherwise it is compressive.

3.5.2 Wafer curvature method

High residual stresses are developed during the fabrication process in the deposited films. These stresses were measured by measuring the radius of curvature of the wafer. A scanning laser (FLX-2908, Tencor Inc, San Jose, CA) was used to scan the surface of the wafer. The machine utilizes a line scan consisting of 100 points to determine an accurate fit for the radius of curvature of the substrate. Then with the help of Stoney's equation [176] the residual stress inside each layer is calculated.

$$\sigma = \frac{E_s}{6(1-\nu_s)} \frac{h_s^2}{h_f} \left(\frac{1}{R} - \frac{1}{R_0} \right) \quad (3.3)$$

In this equation s and f subscripts represent the substrate and film, σ is the film stress, R_0 and R are the radii of curvature before and after a particular processing step.

3.5.3 Suspended membrane method

After backside etching of silicon with deep reactive ion etching (DRIE), suspended membrane method was used to measure the residual stress of the microdiaphragm. This method involves the center deflection measurement of the diaphragm while a uniformly distributed pressure load is applied on the membrane [19, 177]. The set-up of the measurement is shown in Figure 3-12. The specimen is mounted on the vacuum chuck, which was machined from a solid aluminum block. The vacuum chuck is connected to the rotary vacuum pump by vacuum tubes. A flow rate valve and a pressure gauge control the pressure in the backside of the membrane. The center deflection of membrane is measured by an optical imaging profiler.

Figure 3-12: Suspended membrane method set-up

Assuming that the deflection is small compared to the diaphragm radius, the relation between this deflection, vacuum pressure, and residual stress can be expressed by the following equation [178]:

$$P = \frac{8h}{3a^4} \frac{E}{1-\nu} d^3 + \frac{4h\sigma}{a^2} d \quad (3.4)$$

Where P is the differential pressure, h is the diaphragm thickness, σ is the residual stress and d is the out-of plane displacement. The Poisson's ratio in equation (3.4) was calculated using a mixing rule for multilayer structures, equation (3.5) [179].

$$\nu_{eff} = \frac{1}{h_{tot}} \sum_{i=1}^n \nu_i h_i \quad (3.5)$$

Where i represents the layer number. The Poisson's ratio and thickness of different layers are listed in Table 3-1. By measuring deflections of diaphragms at the mid-point as a function of differential pressure and fitting the data to equation (3.4), the Young's modulus and residual stress were estimated using known geometric parameters.

Table 3-1. Material properties of different layers

<i>Material</i>	<i>E</i> (GPa)	ν	ρ $10^3 \text{ Kg} / \text{m}^3$	<i>Thickness</i> (μm)
SiO ₂	72.4	0.16	2.63	0.5
Si	150	0.22	2.32	2
PZT	86.2	0.28	7.62	0.75
Pt	146.9	0.39	21.45	0.2

3.5.4 Stress measurement results

In the standard silicon-on-insulator wafer since the oxide layer has a smaller thermal expansion coefficient ($0.5 \times 10^{-6} \text{ } 1/\text{K}^\circ$) than that of the Si layer ($2.6 \times 10^{-6} \text{ } 1/\text{K}^\circ$) a high compressive stress develops in the oxide layer, while the Si wafer and the upper silicon layer experience tensile stresses [178]. Camassel et al. [180] reported a stress of 2.3, -290, and 235 MPa for upper silicon (device layer), bottom oxide, and silicon substrate, respectively. The wafer curvature method of stress measurement cannot be applied to measure the stress level of the device layer of the SOI wafer. Therefore, we used a micro-Raman technique to measure the stress of the device layer. The Raman shifts of two types of SOI wafers with different oxide

thickness were measured, and the stress of the device layer was estimated. The results of these measurements are shown in Figure 3-13. The stress of the device layer of SOI wafer (Si 2 μm /SiO₂ 0.5 μm /Si 300 μm) was around 50 MPa.

Figure 3-13: Stress measurement in SOI wafer by Raman technique

Deposition of bottom electrode, which consists of a 15 nm TiO₂ adhesion-promoting layer and a 200 nm Pt film, generates a high tensile stress. This stress was measured to be around 1 GPa, using the wafer curvature method calculated by the Stoney's equation. This stress is induced by the relatively thinner thickness of the bottom electrode and larger thermal expansion difference between the substrate and the electrode film. As it was mentioned in the fabrication

section, the PZT layer was grown in subsequent layers. High tensile stress was developed in the first PZT layer (926 MPa). This high stress is due to thin thickness of the PZT film and its higher thermal expansion coefficient than the silicon substrate. This stress was decreased by increasing the PZT thickness and it was 273 MPa after the final layer deposition. This difference indicates that the level of the intrinsic stress in the PZT depends on the underlying material on which it is deposited [181]. Moreover, it clearly shows the possibility of stress controlling in the wafers by variation of film thickness.

After backside etching of silicon with deep reactive ion etching (DRIE), suspended membrane method was used to measure the residual stress of the microdiaphragm. The stress value in each diaphragm depends on some parameters such as, local stress of the previously deposited films at that point, formation of any void or defect during the fabrication process at that area, and the uniformity of DRIE process throughout the wafer. We measured center deflection of diaphragms as a function of different pressures up to 80 kPa. Plotting pa^2/dh versus $(d/a)^2$ yields a straight line. The intercept of this line is 4σ , and the slope of the diagram is $8E/3(1-\nu)$. The measured average stress was around 100 MPa, which is in accordance with previous reports [19, 182, 183]. Figure 3-14 shows results of stress measurements for a diaphragm with $a=600\ \mu m$.

Figure 3-14: Load deflection data of a diaphragm with $a = 0.6$ mm.

3.6 Conclusion

The fabrication process of piezoelectric microdiaphragm based sensors was first explained in this chapter. MEMS technology and sol-gel PZT growth method was implemented in order to achieve high quality sensors. The device was characterized electrically and mechanically. High Q factor and coupling value as high as 197 and 1% were obtained respectively. The residual stress of the device was measured by different technique throughout the fabrication process. It was concluded that high values of stress could be generated in the device layers due to thermal and intrinsic stresses.

Chapter 4: Analytical Modeling of Frequency and Coupling Factor

Theoretical calculation of resonant frequency and electromechanical coupling factor is the subject of this chapter. First, influences of high initial stresses generated during fabrication process are studied on the resonant frequency of the diaphragm. Then, coupling factor of the piezoelectric microdiaphragm is theoretically calculated and compared with the experimental results.

4.1 Introduction

As stated in the previous chapter, piezoelectric microdiaphragm based sensors are excited electrically and therefore vibrate at their resonant frequency. Their sensing capability is based on the change of this frequency upon the change in measurand. Theoretical knowledge of this frequency and the parameters which have influences on it makes the interpretation of experimental results more profound. In the first part of this chapter, we study and investigate the important parameters on the resonant frequency of microdiaphragm based sensors. Another parameter, which has high importance in piezoelectric based sensor, is coupling factor. Coupling factor is defined as the ratio of the stored mechanical energy over the provided electrical energy.

Therefore, the efficiency of a sensor can be related to its coupling factor. In the second part of this chapter, we study the coupling factor of fully clamped microdiaphragm based sensors. The results of this theoretical calculation can be used as a rule of thumbs for better design of these types of sensors.

4.2 Vibrational analysis of diaphragm-based biosensor

In a typical diaphragm based sensor the vibration characteristics of a diaphragm structure depend on whether the structure behaves as a tension dominated membrane or a flexural rigidity dominated plate. In tension dominated membrane the resonant frequency obtains by equation (4.1), while for flexural rigidity dominated plate equation (4.2) is used for calculating the resonant frequency [184].

$$f_0 = A \sqrt{\frac{T}{\rho h}} \quad (4.1)$$

$$f_0 = A \sqrt{\frac{D}{\rho h}} \quad (4.2)$$

Where f_0 is the resonant frequency of the diaphragm (Hz), A is a constant related to the shape and size of diaphragm and the mode shape, h is the diaphragm thickness (*meter*), ρ is the diaphragm density (kg/m^3), T is the initial tension of the diaphragm per unit of length (N/m) and D is the flexural rigidity of the diaphragm ($N.m$).

For the two limiting cases where in-plane tension or stiffness is dominant, equations (4.1) and (4.2) can be used accordingly. However, for the mixed mode where both tension and stiffness are interacting equally, an alternative equation is needed. Several researchers investigated the effects of initial tension on the diaphragm's resonant frequency, either theoretically or by the finite element analysis [20, 21]. They concluded that initial tension

stiffens the diaphragm and increases its resonant frequency. In fact the vibrational behavior of the diaphragm changes from that of a plate with negligible tension to one that is governed by membrane with negligible stiffness, due to development of residual stresses in the diaphragm. This behavior is firstly investigated by Sheplak et al. [22] in static case and then followed by Yu et al. [23] for a sound-pressure measuring sensor in dynamic mode. For a piezoelectric mass sensing biosensor, the sensitivity is the rate of change of the resonant frequency in response to the change of the uniformly distributed mass loading per unit area [24]; therefore a well-defined relation between residual stress and resonant frequency is needed for an accurate mass sensing. In this chapter this expression will be obtained for circular and square diaphragms by means of the classical theory of plate vibrations.

4.2.1 Model description and basic equations for circular diaphragm

By considering a clamped circular or rectangular plate [184] including damping, and the transverse loading per unit area $f(r, \theta, t)$, the nonlinear partial differential equation governing a plate with initial tension can be obtained as equation (4.3).

$$\rho h \frac{\partial^2 w}{\partial t^2} + D \nabla^4 w - T \nabla^2 w = -\eta \frac{\partial w}{\partial t} + f(r, \theta, t) \quad (4.3)$$

Where ρ is the density of the diaphragm material, h the diaphragm thickness, T the initial tension per unit length, $w(r, \theta, t)$ the transverse displacement, η the damping coefficient and D the flexural rigidity of the diaphragm. The boundary conditions of this diaphragm at its edges are shown in equation (4.4), which means its deflection and slope are zero at $r=a$.

$$@ r = a \Rightarrow w(r, \theta, t) = 0; \frac{\partial w(r, \theta, t)}{\partial r} = 0 \quad (4.4)$$

Flexural rigidity for a diaphragm composed of one layer is defined as follows:

$$D = \frac{Eh^3}{12(1-\nu^2)} \quad (4.5)$$

Where E is the Young's modulus and ν the poisson's ratio. In a typical piezoelectric mass sensor, as it is mentioned earlier, the diaphragm is composed of different layers like Si, SiO₂, Si₃N₄, Pt/Ti, and PZT layers. For these type of diaphragms, multilayered, the flexural rigidity calculated by equation (4.6).

$$\begin{aligned} A &= \sum_i \frac{E_i}{1-\nu_i^2} (z_i - z_{i-1}); & B &= \sum_i \frac{E_i}{1-\nu_i^2} \left(\frac{z_i^2 - z_{i-1}^2}{2} \right); \\ C &= \sum_i \frac{E_i}{1-\nu_i^2} \left(\frac{z_i^3 - z_{i-1}^3}{3} \right); & \Rightarrow D &= \frac{AC - B^2}{A} \end{aligned} \quad (4.6)$$

Where i represents the layer number and z illustrates the height from the bottom surface. In the absence of damping and forcing, we will search for a modal solution of the form

$$w(r, \theta, t) = W(r, \theta) e^{i\omega t} \quad (4.7)$$

Where $W(r, \theta)$ is an unknown function and ω is the natural frequency. Substituting (4.7) into equation of motion (4.3), we obtain

$$-\rho h \omega^2 W + D \nabla^4 W - T \nabla^2 W = 0 \quad (4.8)$$

Recall from vector analysis that the Laplacian ∇^2 is the divergence of gradient, $\nabla^2 = \nabla \cdot \nabla$, and in polar coordinates is given by

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \quad (4.9)$$

The equation (4.3) can be expressed as

$$\left(\nabla^2 + \gamma_1^2 \right) \left(\nabla^2 - \gamma_2^2 \right) W = 0 \quad (4.10)$$

Where

$$\gamma_1^2 = \frac{-T + \sqrt{T^2 + 4\rho h\omega^2 D}}{2D}; \gamma_2^2 = \frac{+T + \sqrt{T^2 + 4\rho h\omega^2 D}}{2D} \quad (4.11)$$

Equation (4.10) is satisfied by every solution of the form

$$\left. \begin{aligned} (\nabla^2 + \gamma_1^2)W_1 &= 0 \\ (\nabla^2 - \gamma_2^2)W_2 &= 0 \end{aligned} \right\} \Rightarrow W = W_1 + W_2 \quad (4.12)$$

A possible solution for equation (4.12) can be obtained by separating the variables as follows

$$W(r, \theta) = R(r)\Theta(\theta) \quad (4.13)$$

Substitution of $W(r, \theta)$ into equation (4.12), results into equation (4.14).

$$\begin{aligned} r^2 \left(\left(\frac{\partial^2 R}{\partial r^2} + \frac{1}{r} \frac{\partial R}{\partial r} \right) \frac{1}{R} + \gamma_1^2 \right) &= -\frac{1}{\Theta} \frac{\partial^2 \Theta}{\partial \theta^2} \\ r^2 \left(\left(\frac{\partial^2 R}{\partial r^2} + \frac{1}{r} \frac{\partial R}{\partial r} \right) \frac{1}{R} - \gamma_2^2 \right) &= -\frac{1}{\Theta} \frac{\partial^2 \Theta}{\partial \theta^2} \end{aligned} \quad (4.14)$$

Equation (4.14) is satisfied if and only if each of the four expressions is equaled to the same constant m^2 . Therefore, the equation (4.14) leads to

$$\begin{aligned} \frac{\partial^2 \Theta}{\partial \theta^2} + m^2 \Theta &= 0 & (a) \\ \left(\frac{\partial^2 R}{\partial r^2} + \frac{1}{r} \frac{\partial R}{\partial r} \right) + \left(\gamma_1^2 - \frac{m^2}{r^2} \right) R &= 0 & (b) \\ \left(\frac{\partial^2 R}{\partial r^2} + \frac{1}{r} \frac{\partial R}{\partial r} \right) - \left(\gamma_2^2 + \frac{m^2}{r^2} \right) R &= 0 & (c) \end{aligned} \quad (4.15)$$

The solution of equation (4.15)(a) is as follow

$$\Theta(\theta) = A_{1m} \sin m\theta + A_{2m} \cos m\theta \quad (m = 0, 1, 2, \dots) \quad (4.16)$$

The solution of (4.16) must be continuous, implying that the solution for $\theta = \theta_0$ should be equal to the solution for $\theta = \theta_0 + 2\pi$, and therefore m must be an integer. Equation (4.15)(b) is a

Bessel equation, and therefore its solution is composed of $J_m(\gamma_1 r)$ and $Y_m(\gamma_1 r)$ which are the Bessel functions of order m and of the first and second kind, respectively. Equation (4.15)(c) is a modified or hyperbolic Bessel equation, and therefore its solution is composed of $I_m(\gamma_2 r)$ and $K_m(\gamma_2 r)$ which are the modified Bessel functions of order m and of the first and second kind, respectively. Finally, function $R(r)$ is found as follow:

$$R(r) = B_{1m}J_m(\gamma_{1m}r) + B_{2m}Y_m(\gamma_{1m}r) + B_{3m}I_m(\gamma_{2m}r) + B_{4m}K_m(\gamma_{2m}r) \quad (4.17)$$

Where B coefficients are constants and are to be determined from the boundary conditions. Both $Y_m(\gamma_1 r)$ and $K_m(\gamma_2 r)$ are singular at $r=0$. Therefore, for a plate, which its displacement at plate center is finite, the coefficients B_{2m} and B_{4m} are equal to zero. Applying function $R(r)$ into the boundary condition, equation (4.4), results in the two following equations.

$$\begin{bmatrix} J_m(\gamma_1 a) & I_m(\gamma_2 a) \\ J'_m(\gamma_1 a) & I'_m(\gamma_2 a) \end{bmatrix} \begin{bmatrix} B_{1m} \\ B_{3m} \end{bmatrix} = 0 \quad (4.18)$$

The prime indicates a derivative with respect to r . Two important results are obtained from equation (4.18). Firstly, relation between the coefficients which is depicted in equation (4.19). The second result is that for non-trivial solutions of B_{1m} and B_{3m} the characteristic equation should be equal to zero, equation (4.20).

$$B_{1m} = -\frac{I_m(\gamma_2 a)}{J_m(\gamma_1 a)} B_{3m} \quad (4.19)$$

$$J_m(\gamma_{1m}a)I'_m(\gamma_{2m}a) - I_m(\gamma_{2m}a)J'_m(\gamma_{1m}a) = 0 \quad (4.20)$$

Determining the roots of equation (4.20) and labeling them successively as $n=1,2,\dots$ for each $m=0,1,2,\dots$, gives the eigenvalues of equation (4.18). m and n are integers and represents number of diametrical and circular nodes, respectively. Reordering equation (4.11) and replacing the obtained eigenvalues into that gives the natural frequencies, equation (4.21).

$$\omega_{mn} = \sqrt{\frac{1}{\rho h} (\gamma_{1mn}^4 D + \gamma_{1mn}^2 T)} \quad (4.21)$$

Finally, the mode shape is obtained as follow

$$W_{mn}(r, \theta) = \left[J_m(\gamma_{1mn}r) - \frac{J_m(\gamma_{1mn}a)}{I_m(\gamma_{2mn}a)} I_m(\gamma_{2mn}r) \right] (A_{1m} \sin m\theta + A_{2m} \cos m\theta) \quad (4.22)$$

In summary, the one who is interested in calculating the natural frequency of a circular plate, first should solve the characteristic equation, equation (4.20), numerically and obtain the eigenvalues γ_{1mn} and γ_{2mn} . The natural frequencies obtain by substituting these values into equation (4.21).

4.2.2 Model description and basic equations for square diaphragm

With similar method as it was completely explained for circular diaphragm, natural frequency of clamped square diaphragm could be obtained. First the differential equation changes to equation (4.23) which the transverse displacement $w(x, y, t)$ is function of x and y .

$$\rho h \frac{\partial^2 w}{\partial t^2} + D \nabla^4 w - T \nabla^2 w = -\eta \frac{\partial w}{\partial t} + f(x, y, t) \quad (4.23)$$

Where laplacian in Cartesian coordinate is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \Rightarrow \nabla^4 = \frac{\partial^4}{\partial x^4} + 2 \frac{\partial^4}{\partial x^2 \partial y^2} + \frac{\partial^4}{\partial y^4} \quad (4.24)$$

There are two boundary conditions to be satisfied at any point on the boundary of square diaphragm, which are shown in equation (4.25).

$$\begin{aligned} x=0, a &\Rightarrow w(x, y, t) = 0; \quad \frac{\partial w(x, y, t)}{\partial x} = 0 \\ y=0, a &\Rightarrow w(x, y, t) = 0; \quad \frac{\partial w(x, y, t)}{\partial y} = 0 \end{aligned} \quad (4.25)$$

With similar procedure described in previous section, equation (4.26) can be derived as follow:

$$\left(\nabla^2 + \gamma_1^2\right)\left(\nabla^2 - \gamma_2^2\right)W = 0 \quad (4.26)$$

A possible solution for equation (4.26), which can satisfied the clamped boundary condition is proposed by leissa [185] as equation (4.27)

$$W_{m,n}(x, y) = A \left(\cos\left(\frac{2m\pi x}{a}\right) - 1 \right) \left(\cos\left(\frac{2n\pi y}{a}\right) - 1 \right) \quad (4.27)$$

Where a is the length of square diaphragm, and m and n are the number of nodal points in length and width direction, respectively. By normalizing the natural modes as it is illustrated in equation (4.28) the constant A can be obtained as

$$\begin{aligned} \int_0^a \int_0^a \rho (W_{mn})^2 dx dy &= \int_0^a \int_0^a \rho \left(A \left(\cos\left(\frac{2m\pi x}{a}\right) - 1 \right) \left(\cos\left(\frac{2n\pi y}{a}\right) - 1 \right) \right)^2 dx dy = 1 \\ \Rightarrow A &= \frac{2}{3a\sqrt{\rho}} \end{aligned} \quad (4.28)$$

In addition, the natural frequency can be written as:

$$\omega_{mn} = \sqrt{\frac{1}{\rho h} \left(\gamma_{1mn}^4 D + \gamma_{1mn}^2 T \right)} \quad (4.29)$$

4.2.3 Plate-membrane transition

In order to elaborate the plate-membrane transition, a parameter, which compares the pure membrane behavior, tension dominated, and pure plate behavior, flexural rigidity dominated, is needed. This non-dimensional parameter is defined by Sheplak [22], and it is shown in equation (4.30).

$$k = a \sqrt{\frac{T}{D}} \quad (4.30)$$

With applying the tension parameter on equation (4.21), the natural frequency can be written as equation (4.31), and the resonant frequency as equation (4.32).

$$\omega_{mn} = \sqrt{\frac{\gamma_{1mn}^2 D}{\rho h a^2} \left((a \gamma_{1mn})^2 + k^2 \right)} \quad (4.31)$$

$$f_{mn} = \frac{1}{2\pi} \sqrt{\frac{\gamma_{1mn}^2 D}{\rho h a^2} \left((a\gamma_{1mn})^2 + k^2 \right)} \quad (4.32)$$

4.2.3.1 Pure membrane model

As it is mentioned earlier membrane have no flexural rigidity and therefore the condition, where $D \rightarrow 0$, and $k \rightarrow \infty$ represent the membrane model. It can be concluded from equation (4.11), that at this condition $\gamma_1 \rightarrow \infty$. Finally from equation (4.21), the natural frequency of membrane is obtained which is shown in equation (4.33).

$$\omega_{mn} = \gamma_{1mn} \sqrt{\frac{T}{\rho h}} \quad (4.33)$$

Where the values of $\gamma_{1mn}a$ for a circular membrane are obtained by solving the characteristics equation numerically and are shown in Table 4-1.

Table 4-1: Values of $\gamma_{1mn}a$ for a clamped circular membrane

Diametrical node (m)	Circular node (n)					
	1	2	3	4	5	6
0	2.4048	5.5201	8.6537	11.7915	14.9309	18.0711
1	3.8317	7.0156	10.1735	13.3237	16.4706	19.6159
2	5.1356	8.4172	11.6198	14.796	17.9598	21.117
3	6.3802	9.761	13.0152	16.2235	19.4094	22.5827
4	7.5883	11.0647	14.3725	17.616	20.8269	24.019
5	8.7715	12.3386	15.7002	18.9801	22.2178	25.4303

4.2.3.2 Pure plate model

Pure plate has no tension and therefore $T \rightarrow 0$, $k \rightarrow 0$. Then, from equation (4.11), it is found that $\gamma_1 = \gamma_2 = \omega \sqrt{\frac{D}{\rho h}}$. Finally from equation (4.21), the natural frequency of plate is obtained which is shown in equation (4.34).

$$\omega_{mn} = (\gamma_{1mn})^2 \sqrt{\frac{D}{\rho h}} \quad (4.34)$$

Where the values of $(\gamma_{1mn}a)^2$ for a circular plate are obtained from Table 4-2.

Table 4-2: Values of $(\gamma_{1mn}a)^2$ for a clamped circular plate

Diametrical node (m)	Circular node (n)					
	1	2	3	4	5	6
0	10.2157	39.7707	89.1042	158.1834	247.0052	355.5676
1	21.2604	60.8290	120.0796	199.0526	297.7592	416.2008
2	34.8773	84.5830	153.76	242.7208	351.3375	479.6757
3	51.0296	111.0220	190.3048	289.1802	407.7290	545.9840
4	69.6657	140.1075	229.5494	338.4128	466.9230	615.1144
5	90.7390	171.8039	271.4290	390.3904	528.9034	687.0532

4.2.3.3 Plate-membrane transition

The dependence of each of the first four resonant frequencies ($m=0$, $n=1-4$) on the tension parameter k is shown in Figure 4-1. As expected from equation (4.32), the resonant frequencies are expected to increase as the tension parameter k is increased. When the tension parameter k is less than 2, the resonant frequencies almost remain constant with respect to k . However, when k is larger than 20, the resonant frequencies increase rapidly. So the transition between plate behavior to membrane behavior can be seen in the region $2 \leq k \leq 20$.

Figure 4-1: Variations of the first three resonant frequencies with respect to the tension parameter. In k less than 2 the plate behavior is dominated, while in k more than 20 the membrane behavior is dominated

Figure 4-1 is illustrated for a diaphragm with the layer properties shown in Table 4-3. The radius of this diaphragm is 400. ρh is mass per unit area of the diaphragm and here we call it m , which is obtained by equation (4.35).

$$m = \sum_i \rho_i h_i \quad (4.35)$$

Table 4-3: Material properties of different layers

<i>Material</i>	<i>E</i> (GPa)	<i>ν</i>	ρ $10^3 \text{ Kg} / \text{m}^3$	<i>Thickness</i> (μm)
SiO ₂	72.4	0.16	2.63	0.5
Si	150	0.22	2.32	2
PZT	86.2	0.28	7.62	0.75
Pt	146.9	0.39	21.45	0.2

4.3 Calculation of electromechanical Coupling Coefficient

Electromechanical coupling factor directly depends on the material properties such as e_{31} , and d_{31} . These values in turn depends on the process parameters such as heat treatments [186], the ratio of Zr to Ti [155], growth interface chemistry [187], and deposition technique of the bottom electrode [188]. In addition to these materials properties, the characteristics of the composite structure such as residual stress, side length, aspect ratio, electrode coverage, layer thicknesses, and boundary conditions will also have an impact on electromechanical coupling [183, 189, 190].

In this section, we will theoretically calculate the electromechanical coupling factor for our piezoelectric circular microdiaphragm sensor. The results of this theoretical calculation can be used as a rule of thumbs for better design of these types of sensors. The coupling coefficient k is mostly measured in percentages. However, it is more meaningful to deal with its square k^2 , which corresponds to the energy ratio and is defined as equation.

$$k^2 = \frac{\text{Stored mechanical energy}}{\text{Supplied electrical energy}} \quad (4.36)$$

In order to calculate the stored mechanical energy, we should theoretically derive elastic energy of the diaphragm, stretching energy due to tension forces, and coupling energy by piezoelectric terms. The elastic energy of the diaphragm can be calculated based on the work done on an element during bending of the plate. This value can be found in literature [184] as:

$$U_D = \frac{1}{2} D \int_0^a 2\pi r dr \times \left[\left(\frac{d^2 w}{dr^2} + \frac{1}{r} \frac{dw}{dr} \right)^2 - 2(1-\nu) \frac{1}{r} \frac{dw}{dr} \frac{d^2 w}{dr^2} \right] \quad (4.37)$$

In this equation, w is the deflection profile of the diaphragm in its vibration mode. As was mentioned earlier this value for the first fundamental mode could be stated as follows:

$$\begin{aligned} W_{01}(r, t) &= A \left[J_0(\gamma r) - \frac{J_0(\gamma a)}{I_0(\gamma a)} I_0(\gamma r) \right] e^{i\omega t} = \\ &A \left[J_0\left(\lambda \frac{r}{a}\right) - \frac{J_0(\gamma a)}{I_0(\gamma a)} I_0\left(\lambda \frac{r}{a}\right) \right] e^{i\omega t} = A f\left(\frac{r}{a}\right) e^{i\omega t} \end{aligned} \quad (4.38)$$

Where, $\lambda=3.20$, $J_0(\gamma a)=-0.32$, and $I_0(\gamma a)=5.74$. By replacing r/a with a new variable x . U_D can be obtained as:

$$U_D = \pi D \left(\frac{A}{a} \right)^2 I_D \quad (4.39)$$

Where

$$I_D = \int_0^1 \left[\left(\frac{d^2 f}{dx^2} + \frac{1}{x} \frac{df}{dx} \right)^2 - 2(1-\nu) \frac{1}{x} \frac{df}{dx} \frac{d^2 f}{dx^2} \right] x dx \quad (4.40)$$

For calculating the coupling energy term between the electric field and the mechanical deformation we have employed the work done by Dubois [191]. The stress generated in the piezoelectric layer by the electric field is

$$\sigma_p(E_3) = -e_{31,f} \cdot \Pi_3 \quad (4.41)$$

Where Π is the electric field, and $e_{31,f} = 13.1 \text{ C/m}^2$, which derived from the fact that the thickness of PZT layer is free to move in z-direction and therefore the stress in this direction is zero [21]. The coupling energy per unit volume is the work done by the in-plane strains ε_1 and ε_2 against the piezoelectric stress

$$\begin{aligned} dU_p &= -\sigma_p \cdot \varepsilon_r \\ \varepsilon_r &= -(z - z_s) \left(\frac{d^2 w}{dr^2} + \frac{1}{r} \frac{dw}{dr} \right) \Rightarrow dU_p = \sigma_p \cdot (z - z_s) \cdot \left(\frac{d^2 w}{dr^2} + \frac{1}{r} \frac{dw}{dr} \right) \end{aligned} \quad (4.42)$$

Where z_s is the height of neutral plane and is determined from

$$z_s = \frac{1}{2} \frac{\sum_{i=1}^n E_i \frac{h_i^2 - h_{i-1}^2}{(1 - \nu_i^2)}}{\sum_{i=1}^n E_i \frac{h_i - h_{i-1}}{(1 - \nu_i^2)}} \quad (4.43)$$

The coupling energy then can be derived by integrating from this term.

$$U_p = \sigma_p \cdot \int_{PZT \text{ thickness}} (z - z_s) dz \cdot \int_{electrodes} \left(\frac{d^2 w}{dr^2} + \frac{1}{r} \frac{dw}{dr} \right) 2\pi r dr \quad (4.44)$$

By integrating based on x variable

$$U_p = 2\pi \cdot A \cdot M_p \cdot I_p \quad (4.45)$$

Where

$$M_p = \sigma_p t_{pzt} \left(t_{oth} + \frac{t_{PZT}}{2} - z_s \right)$$

$$I_p = \int_{electrodes} \left(x \frac{d^2 f}{dx^2} + \frac{df}{dx} \right) dx \quad (4.46)$$

In case of a plate with negligible initial tension the stored mechanical energy of the diaphragm is derived as:

$$U_{mech} = U_D + U_p = \pi D \left(\frac{A}{a} \right)^2 I_D + 2\pi A M_p I_p \quad (4.47)$$

In order to make this term a minimum, the coefficient $dU_{mech}/dA = 0$, from which it follows

$$\frac{dU}{dA} = 2\pi \left(\frac{DI_D}{a^2} A + M_p I_p \right) = 0 \quad \Rightarrow A = -\frac{a^2 M_p I_p}{DI_D} \quad (4.48)$$

Therefore the mechanical energy is:

$$U_{mech} \approx -\pi \frac{a^2 (M_p I_p)^2}{DI_D} \quad (4.49)$$

The electrostatic energy is the only source of electrical energy in the structure and it is determined as:

$$U_{ele} = \frac{1}{2} \pi a^2 \cdot \alpha \cdot \epsilon \epsilon_0 \cdot t_{PZT} \cdot \Pi_3^2 \quad (4.50)$$

Where α is the relative coverage area of the electrodes on the diaphragm.

The square of coupling coefficient is finally determined as:

$$k^2 = \left| \frac{U_{mech}}{U_{elec}} \right| = \frac{2(M_p I_p)^2}{(DI_D) \cdot \alpha \cdot \epsilon \epsilon_0 \cdot t_{PZT} \cdot \Pi_3^2} = \frac{2t_{PZT} \left(e_{31,eff} \cdot \left(t_{oth} + \frac{t_{PZT}}{2} - z_s \right) \cdot I_p \right)^2}{(DI_D) \cdot \alpha \cdot \epsilon \epsilon_0} \quad (4.51)$$

The values of I_D , and I_p were numerically calculated by Mathematica software and are 10.708, and -0.98418, respectively. The value of I_p , which depends on the electrode area is calculated for electrode coverage of 50% ($r = 0$ to $0.7a$). As it is clear through equation (4.51) the coupling coefficient does not depend on the diaphragm radius. The coupling coefficient derived from equation (4.51) was calculated for different Silicon device layer and is demonstrated in Figure 4-2. Moreover, the coupling coefficient was drawn for different PZT thicknesses. The maximal value achievable does not increase with PZT film thickness, and saturates at about $k^2=2.85\%$. However, the maximum becomes broader with increasing of Silicon thickness.

Figure 4-2: Analytical modeling of coupling coefficients of a stress free diaphragm.

Following equation was used to experimentally calculate the electromechanical coupling factor [171]. In this equation f_r and f_a are resonance and the anti-resonance frequency, which are calculated from the impedance spectrum of the piezoelectric microdiaphragm measured by impedance analyzer.

$$k^2 = 1 - \left(\frac{f_r}{f_a} \right)^2 \quad (4.52)$$

The experimental values of electromechanical coupling factor of the fabricated piezoelectric microdiaphragms are around 1%. For instance, Figure 4-3 demonstrates the electromechanical coupling factor of four different samples with the values 0.93%, 1.27%, 0.95%, and 1.51%. These values are smaller than the theoretical values, which could reach around 2.75% as it is depicted in previous figure. One reason of this deviation is presence of stress in the fabricated diaphragm. Stretching energy is calculated and incorporated into the electromechanical coupling factor term in the next part of this chapter.

Figure 4-3: Electromechanical coupling factor of four different samples

In cases where the tension in the diaphragm cannot be neglected, the stretching energy generated by this stress also should be included in the total mechanical energy of the diaphragm.

The stretching energy can be written as [184, 191]:

$$U_s = \frac{1}{2} S \int_0^a 2\pi r \left(\frac{dw}{dr} \right)^2 dr = \pi \cdot S \cdot A^2 \cdot I_s \quad (4.53)$$

Where

$$I_s = \int_0^1 x \left(\frac{df}{dx} \right)^2 dx \quad (4.54)$$

Therefore, the complete mechanical energy of the diaphragm is

$$U_{mech} = U_D + U_p + U_s = \pi D \left(\frac{A}{a} \right)^2 I_D + 2\pi A M_p I_p + \pi S A^2 I_s \quad (4.55)$$

The amplitude A acquired for minimizing energy is

$$\begin{aligned} \frac{dU}{dA} &= 2\pi \left(\frac{DI_D}{a^2} A + SI_s A + M_p I_p \right) = 0 \\ \Rightarrow A &= -\frac{a^2 M_p I_p}{DI_D + a^2 SI_s} \end{aligned} \quad (4.56)$$

Hence

$$U_{mech} = -\pi \frac{a^2 (M_p I_p)^2}{D I_D + a^2 S I_s} \quad (4.57)$$

Finally, the square of coupling coefficient is determined as:

$$k^2 = \left| \frac{U_{mech}}{U_{elec}} \right| = \frac{2 (M_p I_p)^2}{(D I_D + a^2 S I_s) \cdot \alpha \cdot \varepsilon \varepsilon_0 \cdot t_{PZT} \cdot \Pi_3^2} = \frac{2 t_{PZT} \left(e_{31,eff} \cdot \left(t_{oth} + \frac{t_{PZT}}{2} - z_s \right) \cdot I_p \right)^2}{(D I_D + a^2 S I_s) \cdot \alpha \cdot \varepsilon \varepsilon_0} \quad (4.58)$$

The coupling values for the diaphragm with initial tension are also demonstrated in Figure 4-4. The same material properties were used for this figure. Here, The value of I_s is 0.70595, and was calculated numerically by Mathematica software. The figure illustrates the coupling behavior for two different stresses 50 and 100 *Mpa*. Comparing these curves with Figure 4-2 shows that existence of stress in the film reduces the peak in the coupling coefficient curves. The reduction in the amplitude of vibration due to stress could be stated as the main source of this fall on the maximum of the coupling factor.

Figure 4-4: Analytical modeling of coupling coefficients of a diaphragm with initial tension.

The effect of radius on the electromechanical coupling coefficient for three different residual stresses is shown in Figure 4-5. In general, as the radius increases the electromechanical coupling coefficient decreases. For a given radius, membranes with lower residual stress result in higher values.

Figure 4-5: Coupling coefficients of a diaphragm with initial tension versus radius.

4.4 Conclusion

Resonant frequency and coupling coefficient as the two main parameters of piezoelectric microdiaphragm based sensors were investigated in this chapter. It was found that the microdiaphragms show the transition from plate behavior to membrane behavior for the tension parameter $2 \leq k \leq 20$. Existence of stress in the diaphragms decreases the coupling coefficients of the microdiaphragm. The reduction in the amplitude of vibration due to stress can be stated as the main source of this fall on the maximum of the coupling factor.

Chapter 5: Analysis and Visualization of Vibration Modes

Different vibration modes of piezoelectric microdiaphragms are visualized in this chapter. The influences of different parameters such as excitation voltages will also be investigated in the frequency response of diaphragms. Finally, the chapter will come to an end by theoretical and experimental analysis of nonlinear response of piezoelectric microdiaphragms.

5.1 Introduction

One of the advantages of piezoelectric microdiaphragms over the acoustic wave sensors is their lower resonant frequency. This advantage makes characterization of these sensors cheaper and easier. The reason of their lower resonant frequency compared to bulk or surface acoustic wave devices is that they vibrate in their first bending vibration modes. In this chapter, the visualization of these mode shapes by a reflection digital holograph microscope is reported. Throughout this visualization some other interesting phenomena such as non-degeneracy in the modes with at least one nodal diameter, nonlinear vibration of the diaphragm in higher vibration amplitude, and stress stiffening behavior was observed. We have tried to justify these phenomena theoretically and experimentally in this chapter.

5.2 Vibration measurements

In this work, in order to observe the frequency modes of the diaphragm we employ the Reflection digital holography microscope [192]. The schematic of optical geometry of reflection digital holographic microscope, based on Michelson interferometer, is shown in Figure 5-1. A single mode fiber is coupled to a HeNe laser. The laser beam coming from the other end of the fiber is focused using a focusing lens and split into two parts by the beam splitter. The microscopic objective is placed at one side of beam splitter and the focusing lens is adjusted such that the object beam (coming from microscopic objective) becomes collimated. The other beam focused on a plane mirror and reflects back. The tilt screws of the mirror control the angle of reference wave (reflected by the mirror). The object beam and reference beam, after reflection, interfere (hologram) and recorded by the CCD. The main advantage of this method is its capability of fast detection of different vibration modes without perturbing the device operation. In this work, we also used a commercially available laser doppler vibrometer (Polytec PSV 300) and an Impedance analyzer (Agilent 4294A) to characterize the frequency response of the PCM. The resonant frequencies of the diaphragm were measured by two methods, impedance and laser vibrometry measurements. For impedance measurement, an Agilent 4294A impedance analyzer was connected through wiring pads and probe station to the sensor. The diaphragm was excited with an ac 20 mV signal, and the frequency spectrum was divided into 601 lines. In order to evaluate these frequencies a scanning laser Doppler vibrometer (Polytec PSV 300) was used. In this method, a Helium-neon laser beam was directed to the resonating diaphragm, and scattered light from that was collected and interfered with the reference beam on a photodetector. The

output of the photodetector was a standard frequency spectrum representing the velocity or displacement of the resonating diaphragm.

Figure 5-1: Reflection digital holography microscopy system design

5.3 Resonant Frequencies

The frequency spectrum of the device measured by the laser doppler vibrometer is shown in Figure 5-2. The diaphragm was excited by applying a periodic chirp signal on the electrodes. This electric stimulus consists of a superposition of sinusoidal signals which allows the excitation of all the natural frequencies in the desired frequency band [159]. The excitation voltage was 50 mV. The first nine resonances are marked in this figure. As it was stated earlier, the modes are named based on the number of their nodal diameters and circles.

Figure 5-2: The frequency response of the diaphragm measured by scanning laser vibrometer, showing the first nine resonances of the diaphragm.

The ratios of the frequency of the different modes to the first fundamental mode of the diaphragm are summarized in Figure 5-3. These values are compared with the corresponding amounts of the well-known plate and membrane theory for the different modes explained in the chapter four. The figure clearly indicates that the diaphragm is vibrating in between the plate and the membrane behavior. This frequency response clearly demonstrates the plate-membrane transition which was explained in previous chapter [193]. In cases where T is greater than (D/a^2) , the usual case in thin film multilayered piezoelectric microstructures [19, 170, 194, 195], the diaphragm behaves more like a membrane than a plate. This behavior of the piezoelectric microdiaphragms always occurs in the fundamental resonance mode and it is experimentally

verified by many researches [21, 196]. In higher frequency modes, influences of stiffness on the frequency increases. For instance, in a diaphragm with $a\sqrt{T/D}=10$, corresponding to $a=0.4$ mm, $D=4.57\times 10^{-7}$ N.m, and $T=285$ N/m, the contribution of the diaphragm stiffness in the first resonant frequency is just about 6%, however this contribution is around 46% in the mode (0,3). The reason of this increase is that the stiffness contribution to the frequency is related to γ^4 while this relation is γ^2 for the tension. Therefore, in higher modes which γ increases the contribution of stiffness in frequency also increase.

Figure 5-3: The ratios of the frequency of the different modes to the first fundamental mode of the diaphragm.

5.4 Mode Shapes

The first nine mode shapes of the diaphragm captured by reflection digital holographic microscope are shown in Figure 5-4. As it was stated earlier, the modes are called based on the number of their nodal diameters and circles, which are created in the resonating diaphragm. The nodes are the points where do not move while the rest of diaphragm is vibrating. Therefore, they are not sensitive to mass loading. These diagonal and circular nodes can be clearly distinguished in figure as the white areas. The dark fringes in this figure represent the deflected area at the desired mode. These deflections can be in upward or downward direction. For better understanding we used the commercial software ANSYS (ANSYS8.0, ANSYS Inc., Canonsburg, PA) to extract the vibrational modes of our diaphragm. The diaphragm was built as a homogeneous, isotropic, 3-D structure, and it was meshed by using available element (Solid45). The diaphragm was clamped at the sidewalls and the modal analysis was conducted. The first nine simulated modes are presented in Figure 5-5. The simulated results clearly explain the deflection direction in each mode and there are in a good agreement with the experimental results.

Among these modes, the (0,1) mode acts more like a monopole source, and radiates sound very effectively into the surrounding medium. Therefore the surrounding medium, especially liquid loading, will affect the vibrational behavior of this mode more than the other modes. In the modes (1,1), (2,1), (3,1), and (4,1) one portion of the diaphragm pushes air up while the other portion sucks air down resulting in air being pushed back and forth from side to side of the diaphragm. Therefore, these modes radiate sound less effectively than the (0,1) mode which means that they do not transfer their vibrational energy into radiated sound energy as quickly as

the (0,1) mode does. In the physics of musical sound, it is believed that because these modes "rings" for a while to decay, they contribute to the musical sound or pitch of a drum [197]. However, due to their lower vibration amplitude they are harder to characterize in the sensing applications. The decay time of the (0,2) and (0,3) modes is longer than the (0,1) mode, but shorter than the (1,1) mode, and therefore they are affected from the surrounding medium less than (0,1) mode, but more than the modes with one nodal circles. The (1,2) and (2,2) modes also do not radiate sound very effectively. Thus, they are less affected by the surrounding medium compared to modes without any nodal diameter.

Figure 5-4: The first nine modes of the PCM extracted by Reflection digital holograph microscope.

Figure 5-5: The finite element modeling of the first nine modes of the PCM.

5.5 Non-degenerated Modes

Referring to equations (4.21) and (4.22), which are also brought here for simplicity; it can be concluded that the mode (m,n) has m nodal diameters [resulting from the trigonometric terms $\sin(m\theta)$ or $\cos(m\theta)$] and n nodal circles, [resulting from the Bessel function terms]. The equation (5.2) states that for each frequency f_{mn} there are two modes, except when $m=0$, for which we obtain only one mode. It follows that for $m \neq 0$ the natural modes are degenerate, which means that in one exact frequency, there is one mode shape consisted of a linear superposition of sine and cosine functions.

$$f_{mn} = \frac{1}{2\pi} \sqrt{\frac{1}{\rho h} (\gamma_{mn}^4 D + \gamma_{mn}^2 T)} \quad (5.1)$$

$$W_{mn}(r, \theta) = \left[J_m(\gamma_{mn}r) - \frac{J_m(\gamma_{mn}a)}{I_m(\gamma_{mn}a)} I_m(\gamma_{mn}r) \right] (A_{1m} \sin m\theta + A_{2m} \cos m\theta) \quad (5.2)$$

In another words, in the vibration of the diaphragm each normal mode should be a twofold degenerate in its angular solution, except when $m=0$. However, in real case it was observed that during the frequency sweep the nodal diameters in some modes would rotate between the two orthogonal orientations, which clarifies that the two orthogonal solutions are not degenerated in frequency. Figure 5-6 shows the non-degenerated shapes for the modes (1,1), (2,1), and (1,2). The non-degenerated modes have previously found applications in the development of MEMS ring gyroscopes [198], and MEMS mass sensors [199]. Recalling Figure 5-2, the corresponding peaks of the different orientation of these modes can be distinguished. These non-degenerated frequencies for the three sample modes are shown in Table 5-1. Sarvart was the first one who observed the non-degenerated modes during the vibration of a plate clamped at its center in 1827. Afterwards, in 1887 Lord Rayleigh explain this phenomenon by stating that the two orthogonal solutions would not be degenerate in frequency if the plate is not perfectly symmetric [200]. Finally, Deutsch et al. [201] theoretically and experimentally demonstrates that the degeneracy can be broken by small density perturbations in the plate. In our diaphragm due to lack of symmetry imposed mainly by the top electrode shape these modes are not degenerated and therefore the aforementioned shapes were observed.

Table 5-1: The non-degenerated frequencies of the modes (1,1), (2,1), (1,2).

Mode	f_1	f_2
(1,1)	151.822	156.800
(2,1)	251.377	263.111
(1,2)	471.111	477.866

Figure 5-6: The Non-degenerated modes of the piezoelectric resonating diaphragm

5.6 Excitation Voltage Influences

During the visualization of the modes with the reflection digital holograph microscope, we used an impedance analyzer (Agilent 4294A) to excite and characterize the piezoelectric layer. An AC voltage was applied through the connecting wires to the top and bottom electrodes and the piezoelectric layer was excited through the converse piezoelectric effect. The value of this excitation voltage will affect the vibration behavior of the diaphragm. The impedance of the diaphragm was measured in three different AC voltages, which is demonstrated in Figure 5-7. As it is clear through this figure the excitation voltage equals 100 mV just can excite a few vibration modes mainly the axisymmetrical modes. Two main reasons can be stated for this null changes in the phase and impedance of the diaphragm in the hidden modes; first, the small displacement of the diaphragm at those resonances, and secondly, the anti-symmetrical shape of the modes, shown in Figure 5-5, which results compensation of the charges at the piezoelectric layer [159].

The charge is the integral of the electric displacement over the effective electrode surface. This integral includes the second derivative of the corresponding mode shape, i.e. curvature. If the electrode covers areas with opposite curvature in a way that results the net charge of zero for the mode under study, the displacement will be cancelled out [159, 202]. By increasing the excitation voltage to 500 mV and 900 mV more vibration modes are excited. This phenomenon is clearly demonstrated in Figure 5-7. The reason of this phenomenon is higher displacement values of the diaphragm in higher excitation voltages. Moreover, the nonlinearity arises in higher excitation voltages also may contribute in the excitation of these hidden modes. The relation between the excitation voltages and the nonlinearity is the subject of the next paragraphs of this chapter. We measured the displacement values for the first resonance mode in different excitation voltages and the results are shown in Figure 5-8. The time-averaged fringes of the diaphragm at different excitation voltages for the first mode are also shown in Figure 5-9. As it is shown in this figure the number of fringes increases by using of higher excitation voltages, which implies higher deflection at the desired mode [203].

Figure 5-7: The phase variation for the piezoelectric diaphragm in different AC voltages.

Figure 5-8: Vibration amplitude variation with applied voltage for the piezoelectric diaphragm

Figure 5-9: Vibration fringes of the piezoelectric diaphragm as a function of applied voltages vibrating at the first fundamental mode (The values are in mV)

The higher vibration amplitude in the diaphragm also results the nonlinearity in the vibration of the diaphragm. The results of the study and correlation of these two phenomena is summarized in next part of this chapter. In general, the nonlinearity in the diaphragm structure comes from a change in the restoring force, such as the flexural rigidity or membrane tension,

due to large vibration amplitude [196]. These higher vibration amplitudes also make the diaphragm stiffer (spring hardening effects [204]) and therefore increase the resonance frequency of the diaphragm. One of the sources of this higher vibration amplitude is higher excitation voltages. The impedance and phase response of the piezoelectric diaphragm to different excitation voltages for the first vibration mode are shown in Figure 5-10. The figure clearly demonstrates that in higher excitation voltages the nonlinear response appeared in both of the impedance and phase spectrum. Moreover, the higher displacement in higher excitation voltages induces additional tension in the diaphragm and therefore increases the resonant frequency of the device. This increase in frequency is also demonstrated in Figure 5-10.

Figure 5-10: Nonlinear vibration of the first resonance of the piezoelectric diaphragm at different excitation voltages; A) Phase, B) Impedance.

For further investigating of the correlation between vibration amplitude and nonlinearities observed, we have tested the piezoelectric microdiaphragm in different ambient pressure. The diaphragm was placed inside a vacuum chamber, and its vibration characteristics were studied in different ambient pressure. The pressure in the chamber was monitored using a pressure gauge and is controlled by a flow rate valve. For this measurement, a chip containing an array of several diaphragms was packaged by a Patterned PMMA sheet with spacers between the package and the testing floor to prevent the diaphragms from being sealed. Figure 5-11 shows the setup of this experiment. Using this setup, resonance measurements were conducted at chamber pressures ranging from 1 atmosphere to 0.05 *atm*.

Figure 5-11: The setup for characterization of PCMSs in different ambient pressures.

Figure 5-12 shows the response of the same microdiaphragm under different pressure. By moving from atmosphere to vacuum, the displacement amplitude of the diaphragm increases and therefore the nonlinear vibration behavior appeared in the frequency response of the diaphragm. The reason for increase of vibration amplitude in vacuum is the reduction of the added mass effect induced by surrounded air around the diaphragm. These nonlinearities in the vibration of the diaphragm are clearly shown in Figure 5-12.

5.7 Nonlinear Analysis

In order to explain the nonlinearities observed in the vibration of the diaphragm, we simplified the piezoelectric diaphragm as a single degree of freedom simple harmonic oscillator with mass (m) attached to a spring (k) and damper (c) with the equation of motion as follows:

$$m\ddot{y}(t) + c\dot{y}(t) + ky(t) = f(t) \quad (5.3)$$

For a piezoelectric diaphragm the external force $f(t)$ can be determined as

$$f(t) = -e_{33} \cdot \Pi_3 = -e_{33} \frac{V_{dc} + V_{ac} \cos \omega t}{g} = A_{dc} + A_{ac} \cos \omega t \quad (5.4)$$

Figure 5-12: Nonlinear vibration of the first resonance of the piezoelectric diaphragm at different ambient pressure; A) Phase, B) Impedance.

Where g is the distance between two electrodes, and V_{dc} and V_{ac} are the magnitudes of the direct and alternative current voltages. As proposed by Marzencki et al. [205] elastic nonlinearities can be introduced in the system by relating the spring stiffness to the nonlinear terms of deflection. For instance, this relation can be introduced as [205]:

$$k = k_0 \left(1 + k_1 y^2(t) \right) \quad (5.5)$$

The reason of even square of y is the symmetry of oscillator around its rest position. The parameters k_0 and k_1 are just two constants. By assuming a sinusoidal excitation and replacing the new stiffness term, equation (5.3) changes to

$$\ddot{y}(t) + 2\mu\dot{y}(t) + \omega_0^2 y(t) + \alpha y^3(t) = A_{dc} + A_{ac} \cos(\omega t) \quad (5.6)$$

$$\omega_0 = \sqrt{\frac{k_0}{m}}, \quad \mu = \frac{c}{2m} = \frac{1}{2Q}, \quad \alpha = \frac{k_0 k_1}{m}$$

This equation is known as the Duffing's equation, and its solution is reported in literatures [206]. Duffing's equation clarifies that the increase in the displacement values will gain higher dominance to nonlinear term. The first effect of this nonlinear term is the change in the resonance frequency of the resonator, as it is shown in equation (5.7).

$$\frac{\omega_r}{\omega_0} = \left(1 + \frac{3}{8} \alpha \frac{Y^2}{\omega_0^2} \right) \pm \left(\left(\frac{A}{2\omega_0 Y} \right)^2 - \mu^2 \right) \quad (5.7)$$

The response of a system with $\alpha/\omega_0=1$, $A/2\omega_0=1$, and $Q=50$ is demonstrated in Figure 5-13. The figure clarifies that the nonlinear term bended the response of the system toward higher frequency for $\alpha>0$, stress stiffening case. This is exactly the theoretical explanation of the phenomenon previously was demonstrated in Figure 5-10 and Figure 5-12. The behavior of the nonlinear system depends on the excitation frequency sweep. In positive frequency sweep, starts

from point A, the amplitude of oscillation increases slowly as the frequency ratio passes the point B and reaches point C. At point C there is a discontinuity (known as jump), which the amplitude falls till reaches point D, and then continue the DE branch. In negative sweep (starts from point E), the amplitude slowly increase by decreasing the frequency ratio and passes through point D and then reach point F. At point F there is another jump to point B with a sharp increase in the oscillation amplitude. From point B the amplitude value follows the BA path. In the frequency zone BCDF (Fig. 2) the frequency response move in the BCD path in positive frequency sweep and DFB branch in negative sweep. Hence, the oscillator response never follows FC branch. In fact, it is shown that The FC branch is theoretically unstable and therefore cannot be produced experimentally.

Figure 5-13: Numerical simulation results of nonlinear system response (normalized displacement amplitude) with hysteresis in the frequency domain with $\alpha/\omega_0=1$, $A/2\omega_0=1$, and $Q=50$.

Figure 5-14 demonstrates influences of positive and negative frequency sweep on the response of piezoelectric microdiaphragm. This experiment was conducted on a sample with 0.6 mm diameter under 800 mV alternative current excitation voltages. Figure clearly demonstrates that the experimental up and down frequency sweep follow the explained theoretical calculation shown in Figure 5-13.

Figure 5-14: Positive and negative frequency sweep of piezoelectric microdiaphragm with diameter 0.6 mm excited with 800 mV AC voltages.

The parameters, which determine the bending of the response, are the Q -factor, α the nonlinear term, and the magnitude of the external force. The responses of the resonator to these parameters are demonstrated in the following figures. As it was expected by increasing the values of Q -factor the sharpness of the resonance peak increases (Figure 5-15), increase of the

nonlinear term (α) bends the graphs toward right side (Figure 5-16), and finally the magnitude of excitation voltages increase the amplitude of the vibration (Figure 5-17).

Figure 5-15: Influence of Q -factor on the nonlinear vibration of piezoelectric microdiaphragm

Figure 5-16: Influence of nonlinear term α on the nonlinear vibration of piezoelectric microdiaphragm

Figure 5-17: Influence of external force on the nonlinear vibration of piezoelectric microdiaphragm

5.8 Conclusion

Frequency spectrum of the resonating diaphragm with peaks corresponding to various modes of vibration was obtained. Comparing these results with the theoretical calculation of the resonant frequency of different modes demonstrate that the contribution of stiffness in the resonant frequency of the diaphragm increases by a factor of 7 from mode (0,1) to mode (0,3). Different frequency modes were visualized by reflection digital holography microscope, and good agreement was found between them and the 3-D modes obtained by finite element simulation. During the visualization of the modes, due to lack of symmetry, imposed by the fabrication issue and mainly arises due to the top electrode configuration, the degeneracy of the modes with at least one nodal diameter was broken. The higher excitation voltages result higher deflection of the piezoelectric microdiaphragm, which in turn induce geometrical nonlinearities in the device. The higher displacement in the device induces spring hardening which results the increase of the resonant frequency. The correlation between the higher displacement values and the stress hardening issue was theoretically shown in the last section of this chapter.

Chapter 6: Medium Damping Influences on the Resonant Frequency and Quality Factor

Medium damping influences on the resonant frequency and quality factor of piezoelectric microdiaphragm sensors are investigated theoretically and experimentally in this chapter. The focus of the chapter would be on the two main sources of energy dissipation in medium, which are acoustic radiation and viscosity damping.

6.1 Introduction

The acoustic radiation and viscosity damping as the two main sources of energy dissipation in medium virtually added the mass of the diaphragm and therefore decrease the frequency and Q -factor of the diaphragm. The magnitude of medium damping inversely depends on the radius over thickness ratio of the diaphragm. Increase of this ratio is the trend in fabrication of thin microdiaphragms by MEMS fabrication processes, which implies the higher influence of medium damping in dynamic behavior of microdiaphragms. The fabricated diaphragms were tested in vacuum, air, and in ethanol. Obtained results are compared with their theoretical counterparts, and fairly good correlation was observed.

6.2 Quality factor (Q -factor) definition

Q -factor always plays an important role in determining the sensitivity of a sensor. For instance, in a mass sensitive biosensor the mass sensitivity alone does not determine the minimum detectable mass of the device or whether the device can identify one single organism. The Q -factor is a merit factor in determining this value. In most of applications, Q -factor represents the sharpness of the resonance peak. However, there are several definitions for the Q -factor in literatures, which are almost identical for systems with slight damping.

6.2.1 First definition for Q -factor

One common method of determining Q is from the steady-state frequency response plot of a resonator excited by a harmonic force with constant amplitude

$$Q = \frac{f_0}{\Delta f_{bw}} \quad (6.1)$$

Where f_0 is the resonance frequency defined as the frequency of maximum amplitude response, and Δf_{bw} is the full-width at half maximum of the resonance peak [207]. Based on this formula Q -factor reflects the sharpness of the resonance peak, in other word; it represents the resolution in determining resonance frequency, as it is shown in Figure 6-1.

Figure 6-1: A graph of energy versus frequency. The Q -factor is defined as $f_0/\Delta f_{bw}$. The higher the Q , the narrower and sharper the peak is.

6.2.2 Second definition for Q-factor

Quality factor is commonly used to quantify energy dissipation in MEMS devices. It is a measure of the energy losses of the resonator or, in other words, a measure of the mechanical damping [208]. In this case it defines as [84]

$$Q = 2\pi \frac{W_0}{\Delta W} \quad (6.2)$$

Where W_0 and ΔW are, respectively, the mechanical energy accumulated and dissipated in the device per vibration cycle.

6.2.3 Third definition for Q-factor

By expressing the energy dissipation as a function of time as follows:

$$W(t) = W_i e^{-t/\tau} \quad (6.3)$$

Where W_i is the initial energy in the resonator and τ is the $1/e$ decay time constant. The Q -factor of this system is obtained as follows: [209]

$$Q = \pi \tau f_0 \quad (6.4)$$

6.3 Dissipation mechanisms

The main energy dissipation mechanisms for a mechanical resonator can be identified as (a) medium loss which is the losses into the surrounding (fluid) medium due to acoustic radiation [210] or viscous drag [211] (b) clamping or support losses which is dissipation of energy through the support used to mount the resonator results from vibration of resonator [212, 213], and (c) bulk losses which is composed of variety of physical mechanisms, such as internal friction, thermoelastic dissipation (TED), phonon-phonon scattering, and motion of lattice defects [209]. All of these mechanisms and the possible reasons of their formations are summarized in Table 6-1.

Table 6-1: Different energy dissipation mechanisms in microdiaphragm based resonators

Dissipation source	Dissipation Mechanism	Description
Medium-device interactions	Acoustic radiation losses	Radiation of sound waves propagating in a direction normal to the surface
	Viscous damping	Viscosity of fluid cause to shear forces
Support-device interactions	Clamping loss	Energy propagation through supports into substrate
	Thermoelastic Dissipation (TED)	Irreversible conversion of mechanical energy into thermal energy
Intrinsic damping	Surface loss	Thin surface layer that exhibits enhanced dissipation
	Volume losses	Intrinsic defects inside the bulk material

Each of these energy dissipation mechanisms or losses, contributes to the quality factor of the oscillator and the overall Q -factor can be found from [214]

$$\frac{1}{Q_{tot}} = \frac{1}{Q_{medium}} + \frac{1}{Q_{bulk}} + \frac{1}{Q_{clamping}} + \frac{1}{Q_{others}} \quad (6.5)$$

These energy dissipation mechanisms are not equally contribute to the total energy lost of the system. Size and ambient pressure are the two main parameters, which clarify the contribution of these terms. Size reduction from macro to micro scale increases the resonator's surface to volume ratio, hence signifies effect of surface forces, and dominates them over the body forces. Therefore, bulk losses are negligible in microscale regions compared to medium damping terms. For a resonator vibrates in air, the medium damping is heavily dependent to the ambient pressure [215]. Generally, the pressure range from atmosphere to high vacuum is divided to three different regions [216]. In atmospheric region, air acts as a viscous fluid and the medium damping is dominant. In high vacuum region due to the elimination of surrounding air the bulk losses regain their significance and become the dominant dissipation mechanism. In between there is molecular region which the surface dissipation due to independent collision of non interacting air molecular with the moving surface of the resonator is the dominant lost.

Based on aforementioned notes, the dominant damping mechanism for piezoelectric microdiaphragm sensors working in normal atmosphere or in aqueous environment is the medium damping. Therefore, in this work we theoretically and experimentally investigate influences of this damping, which is composed of acoustic radiation and viscous terms, in the resonant frequency and quality factor of piezoelectric diaphragms.

6.4 Theory

6.4.1 Medium damping

Medium damping refers to the damping exerted by the surrounding medium on structure and it is the most profound damping mechanisms for miniaturized device [217]. The fluid force, F ,

exerted by a surrounding fluid on an oscillating diaphragm with velocity u can be divided into two parts as follows:

$$F = -\beta_1 u - \beta_2 \frac{du}{dt} \quad (6.6)$$

The first term is related to drag force and this force is proportional to the velocity. Second term is the additional mass which is proportional to acceleration. The drag force is obtained by solving the Navier-Stokes equation, while inertial term is obtained by solving the energy emission in the form of sound waves.

6.4.2 Plate vibrating in vacuum

Let us consider a thin circular plate made of linear elastic, homogeneous and isotropic material having radius a , mass density ρ_p , and thickness h . The plate is clamped around its edges and is vibrating in vacuum. Moreover, the effects of shear deformation and rotary inertia are neglected. Lamb [210] in 1920, approximated the normal displacement profile of this plate by an assumed mode shape¹

$$w(r,t) = X(t) \left(1 - \frac{r^2}{a^2} \right)^2 \quad (6.7)$$

Where $w(r,t)$ is the transverse displacement, and $X(t)$ is a function of time. This assumed mode shape was previously proved that is an adequate approximation [218].

¹ The exact solution of vibration of fully clamped circular plate is obtained in previous chapter, and it is:

$$W_{mn}(r, \theta) = \left[J_m(\gamma_{1mn}r) - \frac{J_m(\gamma_{1mn}a)}{I_m(\gamma_{2mn}a)} I_m(\gamma_{2mn}r) \right] (A_{1m} \sin m\theta + A_{2m} \cos m\theta)$$

Based on this mode shape, the maximal kinetic and potential energies of the diaphragm vibrating in vacuum are

$$T_p = \frac{\pi \rho_p h a^2}{10} u_0^2; \quad V_p = \frac{8 \pi E h^3}{9(1-\nu^2) a^2} X^2 \quad (6.8)$$

Where E is the Young's modulus, $u_0 = (dX/dt)_{max}$, and ν is the poisson's ratio. Applying the Rayleigh-Ritz method, the first resonant frequency of the diaphragm is obtained as

$$f_{vac} = 0.4745 \frac{h c_p}{a^2}; \quad c_p = \sqrt{\frac{E_p}{(1-\nu^2) \rho_p}} \quad (6.9)$$

Where c_p is the velocity of propagation of waves in plate.

6.4.3 Plate in contact with an inviscid fluid (Acoustic radiation damping)

For a plate in contact with an inviscid and incompressible fluid with the density ρ_f on one side, the presence of the fluid has the effect of lowering the frequency on account of the increased inertia, and damping of the vibrations owing to the energy carried off in the form of sound waves. Therefore, this type of damping is known as acoustic radiation or added mass effect. The kinetic energy of the fluid in contact with plate was expressed by Lamb [210] as follows

$$T_f = 0.2102 \rho_f a^3 u_0^2 \quad (6.10)$$

The effect of fluid is virtually to increase the inertia in the ratio of β . Where, β is known as the added virtual mass factor.

$$\frac{T_p + T_f}{T_p} = 1 + \beta; \quad \beta = 0.6689 \frac{\rho_f a}{\rho_p h} \quad (6.11)$$

Therefore, the resonant frequency of plate in fluid is lowered by a factor of

$$f_f = \frac{f_{vac}}{\sqrt{1+\beta}} \quad (6.12)$$

The rate of damping is estimated by calculating the emitted energy in the form of sound waves into the fluid [210], and it is obtained as

$$\alpha = \frac{5\pi^2}{9} \frac{\rho_f}{\rho_p} \frac{f_f^2 a^2}{(1+\beta)hc_f} \quad (6.13)$$

Hence, the Q -factor of acoustic radiation is

$$Q_{ar} = \frac{\pi f_f}{\alpha} = 1.20 \frac{\rho_p c_f}{\rho_f c_p} (1+\beta)^{1.5} \quad (6.14)$$

6.4.4 Plate in contact with a Newtonian fluid (Acoustic radiation and viscous damping)

It was mentioned earlier that beside acoustic radiation term, viscous damping is also a significant part of energy dissipation in microsystems. The viscous damping can be divided in two parts, damping in free space (also called drag force damping) [211], and squeeze film damping which occurs in narrow gaps [219, 220]. The squeeze film damping aroused when the membrane vibrates in parallel with a wall. The air film between the plate and the wall is squeezed so that some of the air flows in and out of the gap. This flow dissipates the vibrational energy of the membrane and therefore acts as a damper. Obviously, this damping depends on the gap between the diaphragm and the wall. When the plate is very far away from the wall, the damping force will be reduced to the drag force only. In experimental application of the PCMS the gap between the resonating diaphragm and the wall is at least two times of the diaphragm radius and therefore the squeeze film term can be neglected [219].

Viscous damping is exerted on the device because of friction between fluid and surface of the resonator. The fluid flow around the resonator is described by Navier-Stokes equation. The simplified Navier-Stokes equation for incompressible flow with constant viscosity is

$$\rho_f (\mathbf{v} \cdot \nabla) \mathbf{v} + \rho_f \frac{\partial \mathbf{v}}{\partial t} = \mu \Delta \mathbf{v} - \nabla p \quad (6.15)$$

Where p , μ , $\mathbf{v}$ are the pressure, dynamic viscosity, and velocity. This equation cannot be solved analytically, and some approximations should first introduce. Kozlovsky [221] employed the stream function method [222] to analytically calculate the medium damping. He defined a scalar stream function $\psi(r, z)$, from which the velocity is derived

$$v_r = -\frac{1}{r} \frac{\partial \psi}{\partial z}, \quad v_z = \frac{1}{r} \frac{\partial \psi}{\partial r} \quad (6.16)$$

The advantage of this approach is that the continuity equation of an incompressible fluid is automatically satisfied

$$\frac{1}{r} \frac{\partial}{\partial r} (r v_r) + \frac{\partial}{\partial z} v_z = 0 \quad (6.17)$$

The vorticity ($\omega = \nabla \times \mathbf{V}$) in axisymmetrical flow only has one component in θ direction, which is denoted by Ω . The relation between the vorticity and the stream function is written as

$$-\Omega = \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial \psi}{\partial r} \right) + \frac{1}{r} \frac{\partial^2 \psi}{\partial z^2} \quad (6.18)$$

Rewriting the Navier-Stokes equation with the vorticity term

$$\frac{\partial}{\partial t} \omega = \left[-(\mathbf{v} \cdot \nabla) \omega + (\omega \cdot \nabla) \mathbf{v} \right] + \nu \nabla^2 \omega \quad (6.19)$$

Where $\nu = \mu/\rho$ is the kinetic viscosity. The nonlinear terms in square brackets are negligible compared to the diffusion term in case of small plate velocity ($u_0 \ll \nu/a$). They are also

negligible compared to the time-derivative term, if $u_0 \ll \omega a$. Denoting the plate velocity amplitude as $u_0 = \omega A$, where A is the amplitude of the vertical displacement of the plate, and recalling that plate elastic theory requires that $A \ll a$, the condition is verified. By neglecting those nonlinear terms and solving the new linear equation the vorticity Ω , and the stream function ψ are obtained. Subsequently, the kinetic energy of the fluid surrounding the diaphragm obtains as [221]

$$T_f = \rho a^3 u_0^2 \left(0.06689\pi + \frac{\pi}{10} \frac{1}{\sqrt{2}} \xi + O(\xi^3) \right) \quad (6.20)$$

Where ξ is a nondimensional parameter

$$\xi = \sqrt{\frac{\nu}{\omega a^2}} \quad (6.21)$$

With recruiting equation (6.11), the added virtual mass due to both acoustic radiation and viscosity term is

$$\beta = 0.6689 \frac{\rho_f a}{\rho_p h} \left(1 + 1.057 \xi + O(\xi^3) \right) \quad (6.22)$$

Kozlovsky [221] also calculated the dissipated energy by viscosity as

$$U_{vis} = 0.44\pi\xi \quad (6.23)$$

And therefore, the Q -factor of viscosity term obtains as

$$Q_{vis} = 2\pi \frac{T_p + T_f}{U_{vis}} = \frac{0.95}{\xi} \left(\frac{1}{\beta} + 1 \right) \quad (6.24)$$

In cases where $\beta \gg 1$, the energy stored in the fluid is much larger than the energy stored in the plate, therefore the kinetic energy of the plate T_p can be neglected. This assumption

eliminates the term $1/\beta$ in the Q_{vis} term. The total Q -factor (Q_{tot}) of the resonator is calculated by help of equations (6.5), (6.14), and (6.24)

$$\frac{1}{Q_{tot}} = \frac{1}{Q_{ar}} + \frac{1}{Q_{vis}} = \frac{1}{1.20} \frac{\rho_f c_p}{\rho_p c_f} \frac{1}{(1+\beta)^{1.5}} + \frac{\xi}{0.95} \left(\frac{\beta}{\beta+1} \right) \quad (6.25)$$

6.5 Measurement Procedure

The dynamic behavior of the piezoelectric circular microdiaphragm based sensors (PCMS) in different medium was first examined by measuring its resonant frequency in vacuum and then subsequently in air and liquid. An Agilent 4294A impedance analyzer was used to characterize the resonant frequency behavior of the PCMS. In vacuum, the frequency was recorded in different ambient pressures using a vacuum chamber. The pressure in the chamber was monitored using a pressure gauge and is controlled by a flow rate valve. For this measurement, a chip containing an array of several diaphragms was packaged by a Patterned PMMA sheet with spacers between the package and the testing floor to prevent the diaphragms from being sealed. Figure 5-11 shows the setup of this experiment. Using this setup, resonance measurements were conducted at chamber pressures ranging from 1 atmosphere to 0.05 *atm*.

In order to study the behavior of the PCMS in ethanol, the fluidic cell was connected through capillary tubes (1 mm inner diameter) and adaptive ports to a syringe pump. The fluidic cell was consisted of two patterned PMMA sheets thermally bonded to each other, and the PCMS glued to the PMMA sheet. This setup, which is shown in Figure 6-2 allows the liquid to continuously stream across the piezoelectric membranes with a constant velocity fixed by the syringe pump.

Figure 6-2: The setup for characterization of PCMSs in fluid

6.6 Resonant frequency behavior

We tested the frequency response of the Piezoelectric microdiaphragm at different ambient pressure from normal atmosphere ($1\text{ atm} = 760\text{ torr}$) to 0.05 atm . The results of these measurements are shown in Figure 6-3. As it was expected the resonant frequency of the diaphragm decreases from vacuum to normal atmosphere due to added mass effect. We observed a frequency change around 4.7% from air to 0.05 atm pressure. In lower pressures the peaks also demonstrates nonlinear behavior in their vibration. This nonlinearity which was fully explained in our previous paper [223], originally comes from a change in the restoring force, such as the flexural rigidity or membrane tension, due to large vibration amplitude [196]. In vacuum due to elimination of the added mass effect the vibration amplitude increases and therefore, the nonlinearity in vibration of the PCMS was observed.

Figure 6-3: Phase response of a 1 mm diameter diaphragm in different pressure from normal atmosphere to 0.05 atm.

We employed equation (6.12) to calculate the frequency shift of the sensor in each different pressure. In these calculations, the material properties of different layers and the air properties listed in Table 4-3 and Table 6-2 were used. The average density of the diaphragm and the total thickness of the plate are ($\rho_p = \sum_i \rho_i h_i / h_p = 5548 \text{ kg/m}^3$) and $h_p = 3.65 \text{ }\mu\text{m}$, respectively. The density of air is pressure dependent and it was calculated by

$$\rho_f = 1.18 \times 10^{-5} p / p_0 \quad (6.26)$$

Where $p_0 = 1 \text{ pa}$ and p is the ambient pressure. The value of velocity of sound in air which is independent of pressure is shown in Table 4-3. The comparison between the theoretical and experimental values of resonant frequency in different pressures is summarized in Table 6-3. We choose the frequency of the diaphragm at 0.05 atm as the resonant frequency in vacuum

($f_{vac}=58.045\text{ kHz}$), and the subsequent values of frequencies calculated based on this frequency.

Table 6-3 clearly demonstrates a good agreement between the proposed theoretical values by Lamb method and the experiment.

Table 6-2: Air and ethanol properties

<i>Fluid</i>	<i>Dynamic viscosity μ (Pa.s)</i>	<i>Density ρ (Kg/m³)</i>	<i>Kinetic viscosity ν (m²/s)</i>	<i>Speed of sound c_f (m/s)</i>
<i>Air</i>	1.8×10^{-5}	1.18	1.53×10^{-5}	343
<i>Ethanol</i>	1.2×10^{-3}	789	1.52×10^{-6}	1144

Table 6-3 Comparison of the theoretical and experimental frequency in different pressures.

<i>Pressure</i>	<i>$f_{the}(\text{error}\%)$</i>	<i>f_{exp}</i>	<i>Pressure</i>	<i>$f_{the}(\text{error}\%)$</i>	<i>f_{exp}</i>
0.1atm	58.039(1.3)	57.309	0.6atm	58.011(3.5)	56.071
0.2atm	58.033(1.9)	56.958	0.7atm	58.005(3.9)	55.838
0.3atm	58.028(2.2)	56.774	0.8atm	58.000(4.2)	55.687
0.4atm	58.022(2.6)	56.522	0.9atm	57.994(4.4)	55.536
0.5atm	58.017(3.1)	56.255	1atm (Air)	57.988(4.8)	55.319

We theoretically investigated the frequency behavior of a PCMS in different mediums for a radius range ($300\mu\text{m} \leq r \leq 325\mu\text{m}$), and the results are summarized in Figure 6-4. For radius= $300\mu\text{m}$, the diaphragm frequency decreases by almost 0.58% from vacuum to air. For that diaphragm vibrates in ethanol, Lamb (Inviscid fluid) and Kozlovsky (Viscous fluid) models estimate the frequency shift of around 66.32% and 66.63% from the vacuum condition. The small difference in the values predicted by these two models is due to low kinetic viscosity of the ethanol ($\nu=1.2 \times 10^{-6}\text{ m}^2/\text{s}$). For higher viscosities, for instance, 10 or 100 times of the ethanol viscosity this frequency shift is 67.27% and 69.07% , respectively. (For having a sense of viscosity values, the blood viscosity is $\nu=3\text{-}4 \times 10^{-6}\text{ m}^2/\text{s}$, and the olive oil viscosity is $\nu=9 \times 10^{-5}\text{ m}^2/\text{s}$.)

Figure 6-4: Frequency of a PCMS in a radius rang working in different medium

In order to compare the ratio of contribution of the viscosity over the acoustic radiation terms on frequency shift of a PCMS, Figure 6-5 was drawn. In this figure the ratio of viscous term over acoustic radiation term ($\beta_{vis}/\beta_{ar}=1.057\xi$) is plotted over kinematic viscosity. The vertical axis in this figure as stated earlier is proportional to nondimensional parameter ξ .

$$\xi = \sqrt{\frac{\nu}{\omega a^2}}; \quad \omega \propto \frac{hc_p}{a^2}$$

By replacing the natural frequency ω in ξ , it was found that, the viscosity effect is mainly dependent to $(\nu/hc_p)^{0.5}$. This means, besides the kinematic viscosity, the thickness and the sound velocity in the plate are also two significant parameters in viscosity influences on the frequency shift. For instance, for constant sound velocity and viscosity, the influence of viscous term

increases by decreasing the thickness h . This is the trend in microfabrication technology to reduce the sizes, which shows that the viscosity influences gain higher importance in lower sizes. For our fabricated PCMS, the velocity of sound in the diaphragm was $c_p=5277 \text{ m/s}$, which was calculated by material properties listed in Table 4-3. Figure 6-5 demonstrates that the viscosity influences reach 4.8% in the viscosity of hundred times of ethanol; however, in ethanol range viscosity this contribution can be neglected. This is in agreement with the experimental observations of Ayela and Nicu [17] that only high viscosities (higher than 10 cp) have a significance influence on frequency shift of the piezoelectric sensor.

Figure 6-5: Relative contribution of viscosity to acoustic radiation term on frequency as a function of kinematic viscosity.

6.7 Q -factor analysis

The discussion focused so far was on frequency analysis of a PCMS as a function of surrounding fluid. However, as the effect of the added mass and liquid viscosity on the behavior

of the PCMS was our primary interest in this study, it would be worthy of studying these parameters on the Q -factor values. As it was mentioned earlier, the Q -factor in the experimental part is defined as $Q=f_0/\Delta f$, where the values of f_0 and Δf are obtained by fitting the measured phase peak using Lorentz function. Figure 6-6 demonstrates the calculated Q values of the frequency peaks shown in Figure 6-3. As it was expected in lower pressures the air damping reduces and therefore the Q -factor increases. Experimental results show that the Q -factor of the PCMS in 0.05 atm is around seven times higher than the time it works in normal atmosphere. We also theoretically calculate the Q -factor of the device in air using equations (6.14) and (6.24). The calculation demonstrates that for a diaphragm with radius $a=500\text{ }\mu\text{m}$, Q_{ar} and Q_{vis} are 377 and 2979, respectively. This result clarifies that the viscosity of the air doesn't play an important role in the Q_{tot} of the diaphragm which vibrates in the air.

Figure 6-6: The Q -factor of PCMS with radius $500\text{ }\mu\text{m}$ in different pressure from 1 to 0.05 atm .

The theoretical Q_{tot} of the PCMS in air for a radius range of $300\mu\text{m} \leq r \leq 700\mu\text{m}$ is illustrated in Figure 6-7. This curve is an upper bound of the device Q -factor in air, because other damping sources, such as intrinsic or support damping, were neglected in the theoretical section. The Q -value for this radius range was between 324 and 346. The highest measured experimental value of Q -factor was 137. The Q -factors of nine different samples are depicted in Figure 6-7. The Q -factors vary from device to device, even for the same radius. The reason is that the Q -factor is dependent to the physical and chemical quality of piezoelectric layer, the thickness of layers, and stress issues in different layers, which may vary case by case. The measured Q -values define a rectangular which confines the Q -values between the highest and the lowest Q -factor measured experimentally.

Figure 6-7: The theoretical upper bound of Q -factor in air and the measured Q -factors of nine different samples in air

The Q -factor of a PCMS was also investigated in ethanol. Figure 6-8 shows the phase response of a PCMS in air and in ethanol. The Q -factor of that device in air was 111.195, and this amount reduces to 23.908 in ethanol. This is 4.687 times reduction in Q -value. It should be outlined that this Q -factor is higher than the Q -factors of most of state-of-the-art micromachined cantilevers used for specific applications in liquid media. The higher Q value in liquid is main advantage of microdiaphragms over microcantilevers [16]. The theoretical calculation of the Q -factor in ethanol for a diaphragm with $a=400\mu\text{m}$ results $Q_{ar}=70.64$, $Q_{vis}=123.53$, and therefore $Q_{tot}=44.94$. It is worth emphasizing that the theoretical Q -factor calculation in this work is just an estimation of the total Q of the device. Therefore, the high difference in Q -values is reasonable.

Figure 6-8: The phase response of a PCMS in air and ethanol.

Figure 6-9 demonstrates the contribution of viscosity and acoustic radiation on the Q -factor of a PCMS with radius $300\mu\text{m} \leq r \leq 700\mu\text{m}$ working in ethanol. For this radius range the added virtual mass factor changes in the range of $7.88 \leq \beta \leq 18.43$. This value is between 0.012 and 0.028 for a diaphragm working in air. Figure demonstrates that the predominant parameter in Q_{tot} is the acoustic radiation term. Q_{ar} is between 47.90 and 154.42, while the Q_{vis} is between 135.64 and 104.36. The Q_{tot} value is between 35.40 and 62.27. The Figure also shows that the Q_{medium} increases in larger radiuses, which implies that the medium influences have less significance in Q_{tot} of the device in bigger sizes. This in accordance with experimental observations that in macro scale region the intrinsic dissipation mechanisms are the predominant factor in calculation of Q -factor of the resonating device.

Figure 6-9: The contribution of viscosity and acoustic radiation terms on Q -value of PCMS in radius range from 300 to 700 μm .

6.8 Conclusion

In this chapter, the dynamics behavior of piezoelectric microdiaphragm under medium damping was fully investigated. The contribution of viscosity over acoustic radiation damping is inversely related to the thickness of the diaphragm. Hence, the viscosity has more significance in thinner diaphragms. It was shown that the viscosity influences on frequency reach 4.8% in the viscosity of hundred times of ethanol; however, in ethanol range viscosity this contribution can be neglected. The added virtual mass factor (β) varies from 0.028 in air to 18.43 in ethanol for a PCMS with radius $a=700\mu m$, which clearly shows significant effect of medium on frequency shift of the microdiaphragm. High Q -factor as high as 137 was measured in air. Theoretical calculations of Q for a PCMS with radius $a=400\mu m$ in ethanol results $Q_{ar}=70.64$, $Q_{vis}=123.53$, and therefore $Q_{tot}=44.94$. These values are higher than the Q -factor of most of state-of-the-art micromachined cantilevers. This high Q value in liquid is the main advantage of microdiaphragms over microcantilevers

Chapter 7: Piezoelectric Microdiaphragm based Mass Sensor

In this chapter, piezoelectric microdiaphragms have been employed as physical and biological mass sensors. The diaphragms' mass sensitivity is characterized by deposition of thin gold layers, and immobilization of bioentities.

7.1 Introduction

In this chapter, we have employed piezoelectric microdiaphragm as a mass sensor. In the first part of the chapter, the mass sensitivity of the device and the parameters, which may have influences on that including the diaphragm flexural rigidity, induced stress, and non uniform immobilization of the measurand are analyzed. In the experimental part, the piezoelectric microdiaphragm was first tested as a physical sensor by measuring its response to deposition of thin gold layer. This experiment is followed by characterizing the piezoelectric microdiaphragm behavior under immobilization of bioentities. Overall, the piezoelectric microdiaphragms demonstrate high mass sensitivity and fast response, which either of these characteristics highlights the great potential of piezoelectric microdiaphragms as mass sensors.

7.2 Mass sensitivity analysis

7.2.1 Mass sensitivity definition and measurement

The sensor sensitivity S_m is defined as equation (7.1), and it is the rate of change of the resonant frequency in response to the change of the uniformly distributed mass loading per unit area of the sensor [24].

$$S_m = \lim_{\Delta m \rightarrow 0} \frac{\Delta f}{f_0} \frac{1}{\Delta m} \quad (7.1)$$

Where Δm is the mass loading per unit area added to the surface of the sensor, f_0 is the resonant frequency, and $\Delta f = f_1 - f_0$ is the frequency shift in response to the mass loading. Recalling equations (4.21), and differentiating from that with respect to m , we obtain the mass sensitivity as below:

$$S_m = \frac{1}{f_0} \frac{df}{dm} = -\frac{1}{2f_0} \cdot \frac{1}{2\pi} \sqrt{\frac{1}{m}(\gamma_1^4 D + \gamma_1^2 T)} \cdot \frac{1}{m} = -\frac{1}{2m} \quad (7.2)$$

Equation (7.2) demonstrates that if the flexural rigidity changes and stress changes of the sensor are negligible compared to the mass change; the mass sensitivity is just related to mass per unit area of the diaphragms. In another word, it is the mass per unit area of the diaphragm that determines the mass sensitivity. This result is quite significant in quantitative mass analysis of such a sensor. It can be concluded that as the layers of the sensor get thinner and lighter, the sensitivity of the sensor increases. Based on this result, there is a great attention among researchers to use the MEMS and NEMS for fabrication of these types of sensors. Moreover, this result would give rise to use of new materials and finer fabrication process for achieving higher sensitivities for sensors.

By considering the mentioned assumptions, once the sensor has been fabricated, the S_m can be easily calculated from (7.2), effects of all the other factors, such as T or D , on the sensor are solely exhibited in the resonant frequency f_0 . The relation between the frequency shift Δf , and the total mass change ΔM of the uniformly distributed analyte on the sensor can thus be determined quantitatively from equation (7.3) as:

$$\Delta M = \frac{A}{S_m f_0} \Delta f \quad (7.3)$$

Where A is the active area of the diaphragm. Table 7-1 shows the results, which are obtained by solving the resonant frequency equation. First, the resonant frequency of the diaphragm f_0 is obtained. Then a uniformly distributed additional layer with density of $1.22 \times 10^3 \text{ kg/m}^3$, which is density of protein [224] and thickness of $0.1 \text{ }\mu\text{m}$ is added on top of the diaphragm as the added mass, corresponding to a mass loading of $1.22 \times 10^{-4} \text{ kg/m}^2$. The resonant frequency with this layer is also obtained f_1 . Finally, the sensitivity is obtained as it is shown in the table.

Table 7-1: Theoretical mass sensitivity analysis of multilayered diaphragm

Radius (mm)	f_0 (kHz)	f_1 (kHz)	Δf (Hz)	$\Delta f / \Delta m$ (Hz.m²/kg)	S_m (m²/kg)
0.3	86.317	86.050	-267	-21.930 e5	-25.4059
0.4	48.553	48.403	-150	-12.335 e5	-25.4059
0.5	31.074	30.978	-96	-7.8947 e5	-25.4059
0.6	21.579	21.512	-67	-5.4824 e5	-25.4059

The same set of analysis was also conducted by finite element simulation and results are presented in Table 7-2. As it is evident through these two tables, theoretical and finite element analyses are in good agreement.

Table 7-2: Finite element simulation of mass sensitivity of multilayered diaphragm

Radius (mm)	f_0 (kHz)	f_1 (kHz)	Δf (Hz)	$\Delta f/\Delta m$ (Hz.m ² /kg)	S_m (m ² /kg)
0.3	86.649	86.413	-236	-19.590 e5	-22.3249
0.4	48.746	48.613	-133	-10.901 e5	-22.3641
0.5	31.200	31.115	-85	-6.9672 e5	-22.3308
0.6	21.668	21.608	-60	-4.9180 e5	-22.6972

Figure 7-1 shows the effect of radius on the $\Delta f/\Delta m$. The presented trend in this figure is reasonable, because by reducing the size of the device the sensitivity of it to mass changes increases.

Figure 7-1 Variations of $\Delta f/\Delta m$ with respect to sensor radius by theoretical and finite element analysis

7.2.2 Flexural rigidity effects on the mass Sensitivity

As it was mentioned earlier, the sensitivity is inversely proportional to the active mass of the resonator, and therefore scaling the size of biosensor down is the best way for reducing the detection limits of the sensor. However, by further reduction of the size, the detection limits could achieve unprecedented values [225, 226]. In other word, a discrepancy is found in many cases between the added mass calculated by the theory and the mass adsorbed on the sensor. One source of this discrepancy is maybe due to the flexural rigidity variation by capturing biomolecules on the surface of the sensor [227-229]. In order to investigate effects of flexural rigidity changes on the resonant frequency and therefore the sensitivity of biosensor, Table 7-3 is presented.

Table 7-3: Variation of resonant frequency by considering variation of flexural rigidity due to biomolecules immobilization. In this table, h is the thickness of biomolecules layer. D and D_b are the flexural rigidity with and without biomolecules layer. $\Delta f = f_1 - f_0$; $\Delta f_b = f_{1b} - f_0$

h (nm)	D (N.m)	f_0 (kHz)	f_1 (kHz)	Δf (Hz)	D_b (N.m)	f_{1b} (kHz)	Δf_b (Hz)
5	4.5046e-7	86.317	86.304	-13	4.5048e-7	86.305	-12
10	4.5046e-7	86.317	86.290	-27	4.5050e-7	86.293	-24
50	4.5046e-7	86.317	86.183	-134	4.5063e-7	86.199	-118
100	4.5046e-7	86.317	86.050	-267	4.5080e-7	86.082	-234
Radius =300 μ m							
5	4.5046e-7	48.553	48.546	-7	4.5048e-7	48.547	-6
10	4.5046e-7	48.553	48.538	-15	4.5050e-7	48.540	-13
50	4.5046e-7	48.553	48.478	-75	4.5063e-7	48.487	-66
100	4.5046e-7	48.553	48.403	-150	4.5080e-7	48.421	-132
Radius =400 μ m							
5	4.5046e-7	31.074	31.069	-5	4.5048e-7	31.070	-4
10	4.5046e-7	31.074	31.064	-10	4.5050e-7	31.066	-8
50	4.5046e-7	31.074	31.026	-48	4.5063e-7	31.032	-42
100	4.5046e-7	31.074	30.978	-96	4.5080e-7	30.989	-85
Radius =500 μ m							

In this table D_b and f_{lb} represent the flexural rigidity by considering the biomaterial as an affective layer on rigidity and the resonant frequency after bioentities immobilization, respectively. By comparing the columns of D , D_b and Δf , Δf_b , it turns out that the assumption of negligible change in flexural rigidity due to biomolecules immobilization is reasonable.

7.2.3 Residual stress effects on the mass Sensitivity

As it was stated in chapter 2, the adsorption-induced stress in static sensing mode of microcantilever based biosensor results into a measurable deflection of cantilever. This stress is induced due to biochemical reactions which happened in active layer of the sensor, and mostly because of evaporation process of bioentetise in liquid media [84]. For a diaphragm based sensor, which works in dynamic mode this stress may also exist. However, effect of this stress is reversible. It basically increases the resonant frequency of the sensor due to measurand immobilization on the surface of the sensor. In another words, it is possible that while the measurand is captured on the surface of the sensor instead of frequency depression due to the mass of it, an increase in frequency is observed, or maybe the reported mass was not accurate because of the role of stress in increasing the resonant frequency.

Recently, there are a few works on modeling the effect of induced stress on the resonant frequency of micro and nano cantilevers [71]. However, we are not aware of any prior investigation of this phenomenon in diaphragm based sensors. In all the aforementioned works, the effort was to relate the induced stress with stiffness of the cantilever and replace the stiffness with the new term in equation (7.4).

$$f = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (7.4)$$

For example Chen et. al. [229] proposed the equation (7.5), where s_1 and s_2 are surface stress and $n=0.24$.

$$k = \frac{\pi^2}{4n} (s_1 + s_2) \quad (7.5)$$

Here we investigate effect of this stress on the resonant frequency shifts of the piezoelectric microdiaphragm based sensors by the developed equation (equation (4.21)) for resonant frequency. In pursuit of this aim, the stress induced from measurand immobilization for diaphragm with initial tension is varied and the resonant frequency after immobilization process is calculated. The results of this analysis, which illustrates frequency depression with respect to induced stress changes, are summarized in Figure 7-2. We have used the material properties listed in Table 4-3 for this figure. In this figure, T_0 is the initial tension in the membrane, and the surface stress which varies from 0 to 1 N/m is the stress due to deposited or immobilized layer. It should be mentioned that the induced stress of 1 N/m corresponds to 100 MPa stress in the 10 nm thickness deposited layer. The inset of this figure shows how the equivalent system for the diaphragm with surface stress was made.

Figure 7-2: Frequency depression variation with respect to stress changes due to immobilization process. The figure clarifies that the induced stress can even result into frequency increase. The inset shows the equivalent system for the diaphragm with surface tension.

This figure exactly shows the frequency increase by induced stress. This phenomenon is reported firstly by Chen et al [230] and then by Gupta et al [226] for microcantilever. Gupta and his colleagues observed this phenomenon in ultra-small dimensions (length $L \sim 3\text{--}5 \text{ }\mu\text{m}$, width $W \sim 1.4\text{--}1.5 \text{ }\mu\text{m}$ and thickness $t \sim 30 \text{ nm}$).

7.2.4 Mass Sensitivity Analysis in Higher Frequency Modes

In order to investigate the sensing characteristics of the microdiaphragm based sensors in higher frequency modes we simulate the frequency response of the device to an added layer of gold using the commercial software ANSYS. We add two layers of gold with thicknesses equal

100 nm and 150 nm at the top surface of the diaphragm. We used the following bulk material properties for the Gold layer. (Young's modulus=80 Gpa, Poisson's ratio=0.42, and density $\rho=19320 \text{ Kg/m}^3$) The resonant frequency before and after adding the gold layers to the diaphragm were calculated. Figure 7-3 demonstrates the absolute and relative value of the frequency shift of the sensor after adding the gold layers. As it is clear through that figure the frequency shift increases by going to higher frequency modes. For instance, the frequency shift in mode (0,3) is 8.5 times higher than the frequency shift of the first mode. However, the relative frequency shift is almost constant for all the frequency modes.

Figure 7-3: The absolute and relative frequency shift of the diaphragm after adding Gold layers with thicknesses equal 100 nm and 150 nm calculated by finite element analysis.

7.2.5 Effect of non-uniform immobilization

Another point, which may affect the sensor sensitivity, is the shape of immobilized material on the sensor's surface. In all the analysis conducted in previous section, we assume a uniform

distribution of measurand on the surface of the sensor. Here, in order to understand whether the assumption of evenly distributed load on the surface of sensor is correct or not we conducted some simulation with commercial finite element software, ANSYS. The membrane was modeled as an axisymmetric structure. The model consisted of the two thicker layers, SiO_2 and PZT. The membrane is modeled by plane82 and in the $Z=0.0$ plane. The global Cartesian Y-axis is assumed to be the axis of symmetry, and all the degree of freedoms are clamped at $X=a$. The shape, which is considered for non-uniform immobilization, is ring shape as it is shown in Figure 7-4. The reason for choosing this shape is great inclination of proteins molecules to approach the walls of reaction chamber during the bioentities immobilization. This assumption also is testified by a sensor, which was immobilized with $1\mu\text{l}$ of analyte labeled with Cy-3 in the last step of immobilization. The fluorescent image of the captured analyte could be observed using fluorescence microscopy with the images recorded by CCD camera (Nikon, Japan). The reaction chamber was totally black under the fluorescence microscopy before the analyte was added. Figure 7-4 shows the distribution of analyte on the surface of membrane under a fluorescence microscope. It is evident that the density at the edge of the membrane was higher than the center, and the distribution is more like a ring than a uniform loading, which verified our first assumption.

Figure 7-4: a) Fluorescence image of one sensor after Cy-3 labeled IgG was absorbed. b) Analyte distribution over the surface of biosensor in non-uniform adsorption (the thickness of analyte on the uniform case is t).

For the protein layer, the Young's modulus and the density are taken as 1 *GPa* and 1220 kg/m^3 respectively [231]. The thickness of this layer was assumed to be 50 nm, estimated from the known size of IgG and protein A [226]. In the non-uniform case the shape of the protein layer on the sensor surface changes as it is illustrated in Figure 7-4 while the mass of this layer is kept constant. This mass for uniform and non-uniform case is presented in the left and right hand side terms in following equation.

$$\pi R^2 t \rho = \pi \rho \left((R-L)^2 t_1 + \left(R^2 - (R-L)^2 \right) H \right) \quad (7.6)$$

The geometric parameters (H , R , L , t_1) in equation are indicated in Figure 7-4b. The protein layer assumes a circular profile with step increase in thickness towards the clamped edge. The thickness of the inner circular region is t_1 and the outer annulus layer has a thickness H and width L . Upon dividing both sides of equation (3) by $R^2 t_1$ the following dimensionless expression is obtained.

$$\frac{t}{t_1} = \left(1 + \left(\frac{L}{R} \right)^2 - 2 \frac{L}{R} \right) + \left(2 \frac{L}{R} - \left(\frac{L}{R} \right)^2 \right) \frac{H}{t_1} \quad (7.7)$$

Increasing H/t_1 or decreasing L/R implies that more bioentities are captured at the outer annulus region of the diaphragm compared to its central region. As an illustration, Figure 7-5 exhibits the relative frequency shifts of non-uniform adsorption shapes for the case where more biomolecules are captured at the outer edge of the diaphragm (i.e. lower L/R). It is demonstrated that this ratio could be as low as 0.42 for $L/R=1/5$. It means that if the relative frequency shifts for uniform case is 7%, it is 2.9% for $L/R=1/5$. This justification clearly explains the irreproducibility of experimental measurements. The main reason is that at the first resonant frequency the highest mass sensitive point is the center of the diaphragm, which is equivalent to the cantilever tip in case of the microcantilever mass sensing mode [228, 232]. This means that by keeping the biomolecules away from the center the sensitivity reduces.

Figure 7-5: Relative frequency shift for different distributions of analyte while the total mass is kept constant. The simulations are conducted for $L/R=0.16, 0.2, 0.25, 0.33, 0.5$.

7.3 Piezoelectric Diaphragm as a Physical Mass Sensor (Gold deposition)

In order to study the capability of piezoelectric microdiaphragm as a mass sensor, its frequency response under deposition of gold with different thicknesses is investigated. The gold depositions were conducted in the gold sputter coating machine (Emitech, K500X) at the vacuum level of 0.05 Torr with deposition rate of 25nm/min . The gold layers with thickness of 50 nm were deposited successively on the sensors and their frequency changes due to these depositions were measured. The resonant frequencies of the diaphragm were measured by laser Doppler vibrometer (Polytec PSV 300).

Figure 7-6: Frequency depression of the sensor after deposition of 150 nm gold layer. The Inset shows the comparison of experimental and theoretical frequency measurements.

The velocity of the diaphragm center was first measured. Then layers of 50 nm gold (distributed load of $965\text{fg}/\mu\text{m}^2$) were deposited on the backside of the sensors in three different steps, successively. The frequency measurement was conducted after each deposition steps. The frequency spectrums of the unloaded sensor and the sensor coated with 150 nm gold layer are shown in Figure 7-6. The detailed frequency shifts in all the first ten peaks for the three different gold layers are plotted in Figure 7-7. The graphs clearly indicate that for each layer of gold, the change in resonant frequency increases with the increase in mode number. For example, the frequency shift of the sensor after deposition of 150 nm gold for the first mode is 4.852 kHz, while this frequency for the ninth mode is 13.386 kHz. This higher frequency shift in higher modes also implies that the sensitivity increases with the increase in mode number as illustrated in Figure 7-8. The added mass corresponding to deposition of 150 nm gold on the diaphragm with radius 0.6 mm is 3277ng. With considering the definition of mass sensitivity ($\Delta f/\Delta m$), therefore the corresponding mass sensitivity values are 1.48 Hz/ng for the first peak and 4.08 Hz/ng for ninth peak.

Figure 7-7: Frequency shift measured at various modes for 50, 100 and 150 nm gold layer deposited on the diaphragm with 0.6 mm radius.

Figure 7-8: The increase of sensitivity with the mode number.

The Q -factor was also investigated in different frequency modes. These measurements for different peaks are shown in Figure 7-9. The figure clearly shows the increase in quality factor by increasing the mode number. The Q -factor of the first peak is 23.57, while it is 241.80 in the ninth peaks. However, in some peaks such as peak's number 6 and 8, due to small displacement of the diaphragm at those resonances, or, the anti-symmetrical shape of the modes, which results compensation of the charges at the piezoelectric layer [159], there is a little changes in the phase and impedance of the diaphragm, which in turn lessen the sharpness of the peak and therefore the quality factor of the resonator.

Figure 7-9: The increase of Q -factor with the mode number.

7.4 Piezoelectric Diaphragm as a Mass Sensitive Biosensor

7.4.1 Biomaterial immobilization

The coupling effect between antigen-antibody is actually a key-lock reaction, in which an individual antibody-combining site can only react with one antigenic determinant. Due to this high degree of specificity, antigen-antibody reaction is one of the most popular techniques for immunosensor applications [26]. In this part of this chapter, this type of immobilization was used to verify the feasibility of applying PCM as an immunosensor. Among the numerous reported immobilization methods, immobilizing proteins onto gold surface via physical adsorption, due to their hydrophobic properties, is undoubtedly the simplest and quickest way [233, 234]. Since the bonding between the gold film and protein is of a non-covalent nature, it allows for multiple washing and makes the sensing device reusable [234]. The schematic of biological material immobilization is depicted in Figure 7-10, and it is implemented by a simple yet reliable dip and dry process [235].

Figure 7-10: Schematic processes of immobilizing. (a) Thin gold film was deposited onto the diaphragm. (b) Different antigens were immobilized onto the diaphragm. (c) Blocking the open surface by Blocker Casein in TBS. (d) Hybridization of antigens and antibodies .

To realize multi-detecting capability of the developed piezoelectric sensor array, three different antigens, HBsAg, HBcAg and α -Fetoprotein (AFP), which are purchased from Sigma (US Biological), were used as the probe molecules. The main immobilization processes are described in Figure 7-10. For this test, we have used an array of eight sensors. First, gold film was deposited on the backside of the diaphragms. Then, the diaphragms were cleaned by isopropanol (IPA) and dried out by nitrogen (N_2) gas. Afterwards, antigens such as HBsAg, HBcAg and AFP in PBS (pH7.4) were applied into the individual reaction chambers with the same concentration (100 $\mu\text{g/ml}$) in sensors 1 and 2, 5 and 6, 3 and 4, respectively. One pair of sensors was immobilized with the same biomaterial and concentration, to ensure the accuracy and repeatability of the measurements.

To investigate the effect of the washing processes and the non-specific biomaterial absorption on the resonant frequencies of the sensors; the unused one pair of sensors (7 and 8), without any biomaterial, was used as the reference. After 30 minutes of deposition at room temperature, the reaction chambers were carefully washed by TBS washing buffer (pH8.0, Pierce, Germany) and DI water followed by N_2 drying. In the third step, BlockerTM Casein in TBS (1 $\text{mg}/\mu\text{l}$) was added to block the open space around the immobilized proteins. The excess blockers were washed away by TBS and DI water. To evaluate the specificity and selectivity of the immunochip, in the last step, a mixed solution containing anti-AFP (10 $\mu\text{g/ml}$) and anti-HBsAg (10 $\mu\text{g/ml}$) was added into all the reaction chambers in the sensor array for the hybridization between the antigens and antibodies. This step is similar to the practical clinic or laboratory diagonal process, where the solution to be tested generally contains more than one analyte. This inter-reaction process took about 45 min and the unbonded or excess antibodies

were again washed away by TBS and DI water, and then followed by N₂ air flow drying. To have a detailed study on this relationship, the resonant frequencies of the sensors were measured immediately after each immobilization or reaction process. Although mass deposit on the sensing surface is the dominant factor affecting the resonant frequency of piezoelectric sensor, it has been reported that the resonant frequency is also influenced by the external environmental factors including medium types, viscosity and humidity of the medium, incubation temperature [236, 237]. Hence, in order to ensure that the immunochip has a good performance and minimize the external effect on the frequency, all the measurements were conducted in gas phase in a class-100 clean room to avoid any tiny particles depositing onto the sensing surface. Inside the clean room, the temperature and relative humidity was kept at 23 °C and 35%, respectively.

7.4.2 Characterization

The resonant frequencies of the sensors were again measured by an impedance analyzer after each immobilization process. Figure 7-11 shows the resonant frequency spectrum of sensor 2 at each process. The figure shows that the frequency was continuously shifted to the lower frequencies, which implies increase of accumulated mass after each immobilization or hybridization process. Sensors 3 and 4 for detecting anti-AFP also have a similar frequency spectrum after completing all the processes.

For the convenience of record, the original frequency of a sensor was noted as f_1 , and frequencies after depositing gold film, adding antigens, blockers and antibodies were recorded as f_2, f_3, f_4, f_5 , respectively. Detailed frequency changes after each immobilization process for the sensor array is presented in Figure 7-12. The data shown in the figure were calculated based on the average frequency values of one pair of sensors after 3 measurements.

Figure 7-11: Frequency spectrum of sensor 2. The frequency continues shift to low frequency domain.

The first measurements showed that the variation of basic resonant frequencies of the 4 pairs of sensors with plain surfaces were very small, which indicate that the performance of the individual sensors within the array was uniform. For the sensors with HBsAg and AFP, the frequency continuously decreased after each step. However, for the reference sensor, a significant frequency decrease was only observed after the gold deposition. As there were no biomaterials fixed on the sensing surfaces in the subsequent process, the slight frequency decrease might be caused by the external contaminants during the washing processes. Comparing the frequency depression values for the sensors with HBsAg and AFP, $\Delta f_{12}=f_1-f_2$ is the largest, which means that the deposited gold mass is the highest due to the high density of gold, and $\Delta f_{34}=f_3-f_4$ is the smallest, which implies that most of the spaces were occupied by the antigens in

the second step and only a small amount of blockers were captured. This is also the reason why the slope of the curve at this step shown in Figure 7-12 is the smallest as well.

Figure 7-12: Detailed frequencies of the sensors in the immunochip after each immobilization process.

Although the concentration and volume of the immobilized probe proteins, such as HBsAg, AFP and HBcAg, were the same in the second step, the depressions of the frequency (Δf_{23}) in the second measurement have some variations. This implied that the amount of proteins successfully fixed onto the individual sensor surface was different due to the different physical properties of the proteins, such as density and mobility.

In the last process, because the applied mixed solution only contains anti-HBsAg and anti-AFP, the results presented in Figure 7-12 showed significant resonant frequency depression in the sensors with HBsAg and AFP. The frequency change in the sensors with HBcAg was

negligible as no anti-HBcAg was contained in the added analyte solution. These results indicated that the frequency depression of the biosensors with HBsAg and AFP in the last step were mainly due to the mass of the captured antibodies by the antigens. It also demonstrated that the immunochip has a very good specificity. The very small frequency variations of the reference sensors during the whole immobilization processes showed that the washing processes and the non-specific biomaterials absorption had negligible effect on the sensor resonant frequency.

A typical single HBV diagnosis through polymer chain reaction (PCR) normally takes 9 to 12 h or even longer time [238]. However, as discussed above, the total experiment time for detecting HBsAg and AFP via this immunochip was less than 2 h, which is much shorter than the previously reported time. The current immunochip consists of 8 individual sensors. Even if one pair of sensors is used to detect the same analyte, it is still 4 times faster than the single immunosensor.

7.5 Conclusion

In this chapter, we have tested piezoelectric microdiaphragm as a physical and biological mass sensors. In the first set of experiment, the mass sensitivity and Q -factor of the device in its frequency response was characterized with deposition of gold. The experimental results demonstrate that the mass sensitivity and the quality factor of the device are 4.08 Hz/ng and 241.80 at the ninth peak. In the second part of this chapter, we have investigated capability of piezoelectric microdiaphragms as a biosensing element by implementing coupling effect between antigens and antibodies. Three different antigens, HBsAg, HBcAg and α -Fetoprotein (AFP), were immobilized on the piezoelectric diaphragm. It was demonstrated that piezoelectric microdiaphragms are able of characterization of the bioentities in less than 2 hours.

Chapter 8: Piezoelectric Microdiaphragm based Pressure Sensors

This chapter reports on the application of piezoelectric microdiaphragm as physical pressure sensors. A high value of pressure sensitivity, as high as 280 Hz/mbar, has been achieved.

8.1 Introduction

Pressure influences on the vibration characteristics of piezoelectric microdiaphragm based pressure sensors are investigated theoretically and experimentally in this chapter. It was demonstrated that only Bessel function of zero order, $m=0$, participates in the vibration modes of the microdiaphragm symmetrically loaded by pressure. This means that anti-symmetrical vibration modes eliminates while the diaphragm is vibrating under pressure loading. A high value of pressure sensitivity, as high as 280 Hz/mbar, has been achieved; this value is 2.43 times higher than the currently reported sensitivity (i.e., 115 Hz/mbar) in the literature [29].

8.2 Theory

8.2.1 Free Vibration of Circular Diaphragm

Aforementioned in chapter four, the sensor is modeled as a clamped circular diaphragm with initial tension and rigidity as shown in Figure 8-1, with radius a , thickness h , Young's modulus E , and Poisson's ratio ν . The nonlinear partial differential equation of that diaphragm with a transverse loading per unit area, is governed as equation [23, 184].

$$\rho h \frac{\partial^2 w}{\partial t^2} + D \nabla^4 w - T \nabla^2 w = f(r, \theta, t) \quad (8.1)$$

Where ρ is the diaphragm density, w is the transverse displacement which is function of (r, θ, t) , $D = Eh^3/12(1-\nu^2)$ is the flexural rigidity, ∇^2 is the Laplacian, and T is the initial tension of the diaphragm per unit of length. By solving this equation which was fully explained in chapter four for the free vibration case, $f(r, \theta, t) = 0$, the resonant frequencies and their corresponding deflection profile at different modes obtain as follows :

$$f_{mn} = \frac{1}{2\pi} \sqrt{\frac{1}{\rho h} (\gamma_{mn}^4 D + \gamma_{mn}^2 T)} \quad (8.2)$$

$$\begin{aligned} W_{0n}(r, \theta) &= A_{0n} \left[J_0(\gamma_{0n} r) - \frac{J_0(\gamma_{0n} a)}{I_0(\gamma_{0n} a)} I_0(\gamma_{0n} r) \right], \quad n = 1, 2, \dots \\ \left. \begin{aligned} W_{mnc}(r, \theta) \\ W_{mns}(r, \theta) \end{aligned} \right\} &= A_{mn} \left(J_m(\gamma_{mn} r) - \frac{J_m(\gamma_{mn} a)}{I_m(\gamma_{mn} a)} I_m(\gamma_{mn} r) \right) \begin{Bmatrix} \cos m\theta \\ \sin m\theta \end{Bmatrix}, \quad m, n = 1, 2, \dots \end{aligned} \quad (8.3)$$

In these equations, $J_m(\gamma_{mn} r)$, and $I_m(\gamma_{mn} r)$ are the Bessel and the modified Bessel functions of the first kind, the subscripts m and n represent the number of nodal diameters and nodal circles of the vibrating mode, respectively. The γ values for each different mode will obtain by solving the characteristics equation which is completely explained in chapter four [193]. In equation

(8.3), for $m=0$, we obtained only one mode shape; however, for $m \neq 0$, for each resonance frequency ω_{mn} there are two mode shapes, which are shown with the separation of sine and cosine function in that equation. This statement shows that for $m \neq 0$, the natural modes are degenerated, which means in one exact frequency, there are two different mode shapes linearly combined by each other. In other words, in the vibration of the diaphragm each normal mode is twofold degenerated in its angular solution, unless $m=0$ [201].

8.2.2 Pressure loaded microdiaphragm

While the diaphragm is subjected to a time-dependent uniform pressure $f(r, \theta, t) = p \cdot f(t)$, p is uniform pressure over the surface and $f(t)$ is a function of time, the general formulation for the response of undamped continuous systems developed by Meirovitch [239] can be applied to study the vibration characteristics of the diaphragm. The response of the diaphragm is written in the form of a series, using the expansion theorem by multiplying the normal modes W_{mn} obtained previously for free vibration of the clamped diaphragm by their corresponding time-dependent generalized coordinates, η_{mn} .

$$w(r, \theta, t) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} W_{mn}(r, \theta) \eta_{mn}(t) \quad (8.4)$$

The generalized coordinates are given by

$$\eta_{mn}(t) = \frac{1}{\omega_{mn}} \int_0^t N_{mn}(\tau) \sin \omega_{mn}(t - \tau) d\tau \quad (8.5)$$

Where N_{mn} denotes a generalized force associated with the generalized coordinate η_{mn} .

$$N_{mn}(t) = \int_0^{2\pi} \int_0^a w_{mn}(r, \theta) p_0 f(t) r dr d\theta \quad (8.6)$$

As it was stated earlier all the frequency modes are degenerated, except for $m=0$; therefore, integration of the trigonometric function ($\sin(m\theta)$ or $\cos(m\theta)$) over domain $0 \leq \theta \leq 2\pi$, eliminates the N_{mn} with $m \neq 0$. Hence, the solution of equation (8.6) is obtained as:

$$N_{0n}(t) = \int_0^{2\pi} \int_0^a w_{0n}(r, \theta) p_0 f(t) r dr d\theta =$$

$$2\pi A_{0n} p_0 f(t) \left(\frac{a}{\gamma_{0n}} \right) \left(J_1(\gamma_{0n}a) - \frac{J_0(\gamma_{0n}a)}{I_0(\gamma_{0n}a)} I_1(\gamma_{0n}a) \right) \quad (8.7)$$

thus

$$\eta_{0n}(t) = A_{0n} p_0 \frac{2\pi}{\omega_{0n}} \left(\frac{a}{\gamma_{0n}} \right) \left(J_1(\gamma_{0n}a) - \frac{J_0(\gamma_{0n}a)}{I_0(\gamma_{0n}a)} I_1(\gamma_{0n}a) \right) \int_0^t f(\tau) \sin \omega_{0n}(t-\tau) d\tau \quad (8.8)$$

The transverse displacement of the diaphragm is obtained by introducing (8.8) in the series(8.4):

$$w(r, \theta, t) = \frac{2\pi}{\omega_{0n}} A_{0n}^2 p_0 f(t) \left(\frac{a}{\gamma_{0n}} \right) \left(J_1(\gamma_{0n}a) - \frac{J_0(\gamma_{0n}a)}{I_0(\gamma_{0n}a)} I_1(\gamma_{0n}a) \right)$$

$$\sum_{n=1}^{\infty} \left[J_0(\gamma_{0n}r) - \frac{J_0(\gamma_{0n}a)}{I_0(\gamma_{0n}a)} I_0(\gamma_{0n}r) \right] \int_0^t f(\tau) \sin \omega_{0n}(t-\tau) d\tau \quad (8.9)$$

Equation (8.9) states that only Bessel function of zero order, $m=0$, participates in the vibration modes. Two physical reasons can be mentioned for this behavior. First, symmetrical nature of load bans participation of any antisymmetric modes in the vibration of the diaphragm (The modes with $m \neq 0$ are antisymmetric with respect to the vertical through $r=0$). Moreover, the pressure loading prevents the participation of the modes with nodes at the center in the vibration motion of the diaphragm (The Bessel functions of order higher than zero have a zero at $r=0$).

8.2.3 Pressure Sensitivity

The pressure sensitivity of the piezoelectric circular microdiaphragm can be estimated by assuming that the mechanism causing the frequency shift is the tension generated in the diaphragm by pressure loading. The pressure sensitivity S_p is defined as

$$S_p = \frac{1}{f} \frac{df}{dp} = \frac{1}{f} \frac{df}{dT} \frac{dT}{dp} \quad (8.10)$$

In multilayered piezoelectric microdiaphragm, during the fabrication processes high residual stresses generated in the diaphragm [183]. The contribution of these stresses in resonance frequency usually is much higher than the stiffness term, especially in the first fundamental mode [19, 193]. Therefore, the resonant frequency can be estimated by equation(8.11) instead of equation (8.2):

$$f_{01} = \frac{\gamma_{01}}{2\pi} \sqrt{\frac{T}{\rho h}} \quad (8.11)$$

The stress induced due to pressure loading can be calculated by classical theory of plates. The maximum stress induced on the diaphragm due to the pressure loading is [184]

$$(\sigma_r)_{max} = \frac{3}{4} \frac{pa^2}{h^2}; \quad T = \sigma_r h \quad (8.12)$$

By introducing equations (8.12) and (8.11) in (8.10), the pressure sensitivity is obtained as

$$S_p = \frac{1}{f} \frac{df}{dp} = \frac{1}{f} \frac{df}{dT} \frac{dT}{dp} = \frac{3}{8} \frac{a^2}{hT} = \frac{3}{8\sigma_r} \left(\frac{a}{h} \right)^2 \quad (8.13)$$

Figure 8-1: (A) Illustration of the clamped diaphragm

8.3 Experiments

8.3.1 Experimental Setup

In order to measure the frequency response of the sensor at different pressures, the setup shown in Figure 8-2 was used. The specimen was mounted on the vacuum chuck, which was machined from a solid aluminum block. To avoid air leakage, the membrane was glued with wax on the holder. The vacuum chuck was connected to the rotary vacuum pump by vacuum tubes. The pressure in the backside of the membrane was controlled by a flow rate valve and a pressure gauge. The resonant frequencies of the diaphragm were measured by two methods, impedance and laser vibrometry measurements. For impedance measurement, an Agilent 4294A impedance analyzer was connected through wiring pads and probe station to the sensor. In order to evaluate these frequencies a scanning laser Doppler vibrometer (Polytec PSV 300) was used. The vibration modes are also visualized by reflection digital holography microscope [192]. The main advantage of this method is its capability of fast detection of different vibration modes without perturbing the device operation.

Figure 8-2: The setup for pressure sensing measurement.

8.4 Frequency Shift and Pressure Sensitivity

By applying pressure at the bottom side of the membrane, the resonance frequency increases due to the generated stress in the diaphragm. For instance, an increase in resonance frequency from 86.93 kHz to 116.65 kHz is shown in Figure 8-3 due to pressure difference increase from zero (atmospheric pressure at both sides of the diaphragm) to 10 kPa. The pressure sensitivity was measured over the pressure operating range equal 90 kPa; however the sensor response was just linear in the first 10 kPa region. This response is demonstrated in Figure 8-4. The average sensitivity calculated for this region was 280 Hz/mbar, which is 2.43 times higher than the sensitivity reported by Defay [29]. Moreover, Defay was only able to see the frequency peak only in the range of 15-140 mbar, while our sensor shows the peak till 900 mbar. Table 8-1 compares these two sensors in their relevant metric of performance.

Table 8-1: Comparison of the fabricated sensor by previous reported work

Sensor	Pressure Range (mbar)	Size		Sensitivity (Hz.mbar ⁻¹)	Resonant frequency (kHz)
		Area	Thickness (μm)		
Defay [29]	15-140	Square: 3mm*3mm	15	115	18.6
This work	0-100	Diameter: 0.8 mm	3.65	280	86.93

The theoretical normalized sensitivity of the sensor can be calculated from equation (8.13). The sensor was tested here has $a=400\ \mu\text{m}$ and $h=3.65\ \mu\text{m}$. As it was stated earlier, by assuming stress around 100MPa which correlates to tension per unit of length $T=365\ \text{N/m}$ [193]. The theoretical normalized sensitivity is 4503.66 ppm/mbar. The experimental results show that this sensitivity is around 3256 ppm/mbar, which is in a fairly good agreement with the value obtained by the developed theoretical calculation.

Figure 8-3: Frequency shift due to increase in pressure difference from zero (atmospheric pressure at both sides of the diaphragm) to 10 kPa (atmospheric pressure, 100 kPa, at top side and 90 kPa at bottom side).

Figure 8-4: The average sensitivity calculated for the linear region (0-10 kPa pressure differences) was 280 Hz/mbar

Aforementioned, the radially symmetric pressure loading prevents the modes with diametrical nodes to participate in the vibration modes of the diaphragm. Therefore, only the modes with zero nodal diameters, $m=0$, participate in the motion. This phenomenon was also observed through the phase response of the piezoelectric layer during experiments as it is shown in Figure 8-5. The peaks corresponding to modes (0,1) and (1,1) are shown in different pressures in this figure. It can be seen that by increasing the pressure differences, these two peaks join together and form one fundamental peak, which is the mode (0,1).

Figure 8-5: By increasing the pressure difference the antisymmetric mode (1,1) eliminates and only mode (0,1) remains.

8.5 Conclusion:

In this chapter, piezoelectric circular microdiaphragm based pressure sensors were studied. A high normalized sensitivity (3256 ppm/mbar) was achieved. This sensitivity is in fairly good agreement with the theoretical calculated sensitivity 4503.66 ppm/mbar. In the free vibration of the diaphragm, the first four modes were visualized. However, by applying the pressure load to the diaphragm, owing to the symmetrical nature of the pressure load, the modes with trigonometric functions would not participate on the vibration modes, and therefore, the modes with $m \neq 0$ eliminated due to pressure loading. This was experimentally observed through the phase response of the sensor, where mode (1,1) eliminated by increasing the pressure at the backside of the diaphragm.

Chapter 9: Conclusion and Future Work

Try not to become a man of success but rather try to become a man of value.

Albert Einstein

9.1 Introduction

Piezoelectric microdiaphragms have been studied as a platform for physical and biological sensing in this thesis. The microdiaphragms were first designed and fabricated by MEMS fabrication methods. Then their different characteristics such as their frequency behavior, mode shapes, coupling factor, and their quality factor were studied theoretically and experimentally. Finally, they have been applied for two different schemes of sensing, mass sensing and pressure sensing. In the following paragraphs, the major contributions of this work together with recommendations for further study of this type of sensors in future are discussed.

9.2 Concluding remarks and research contributions

The major findings and contributions of this study are summarized in the following points:

- Significant amount of residual stresses generated in different layers of the piezoelectric microdiaphragm based sensors during their fabrication process. These stresses are mainly induced due to high temperature processes (annealing process in sol-gel method with the temperature of 600°C), different thermal and elastic properties of the consecutive layers and some other fabrication issues. Stress values were characterized in the device based on three different methods. Micro-Raman technique was used to measure the stress of the upper silicon in SOI wafer. The stress of the device layer of SOI wafer (Si 2 μm /SiO₂ 0.5 μm /Si 300 μm) was around 50 MPa. Wafer curvature method has employed to calculate the stress inside each different layer during the fabrication processes. High tensile stress was developed in the first PZT layer (926 MPa). This high stress is due to thin thickness of the PZT film and its higher thermal expansion coefficient than the silicon substrate. This stress was decreased by increasing the PZT thickness and it was 273 MPa after the final layer deposition. Finally, the average stress of the diaphragm was calculated by suspended membrane method. The measured average stress was around 100 MPa, which is in accordance with previous reports.
- The dynamic behavior of the fabricated sensor under high stresses developed during the fabrication processes was investigated. It was concluded that both flexural rigidity and tension contribute to the resonant frequency of the diaphragm sensor. In another words, the vibrational behavior of the piezoelectric microdiaphragm is in the transition region between plate and membrane. The applied model simplify the issues of choosing the

appropriate model for resonating diaphragm with introducing one general formula for resonant frequency based on both tension and rigidity. It was found that the microdiaphragms show the transition from plate behavior to membrane behavior for the tension parameter $2 \leq k \leq 20$. Experimental measurements clearly indicate that the diaphragm is vibrating in between plate and membrane behavior, which agrees with previously obtained theoretical results.

- In order to demonstrate that the microdiaphragms vibrate in their flexural vibration modes, the first nine mode shapes of the microdiaphragm were characterized by reflection digital holography microscope. It was also experimentally observed that during the frequency sweep the nodal diameters in the modes with $m \neq 0$ will rotate between the two orthogonal orientations, which clarifies that the two orthogonal solutions are not degenerated in frequency. It was concluded that the degeneracy of the modes is broken due to small density perturbations in the microdiaphragm. These perturbations are imposed by the lack of symmetry mainly due to the top electrode shape.
- The effective electromechanical coupling coefficient k^2 of the device obtained from its impedance response, was around 1%. For better understanding of electromechanical coupling factor of piezoelectric microdiaphragms and the parameters, which have influences on it, this parameter was studied theoretically. Calculated theoretical results are in good agreement with the experimental values. It was concluded that existence of stress in the diaphragms decreases the coupling coefficients of the microdiaphragm. The reduction in the amplitude of vibration due to stress is the main source of this fall on the maximum of the coupling factor. The results of this theoretical calculation can be used as a rule of thumbs for better design of these types of sensors.

- In higher excitation voltages, piezoelectric microdiaphragms demonstrate nonlinear vibration behavior. Observation of these nonlinearities was correlated to higher displacement values of the diaphragm in higher voltages by help of Duffing's equation. For further understanding of this behavior, the microdiaphragms were tested in vacuum. The measurement results indicate the same nonlinear behavior, which clarifies that the nonlinearity arouses in the system by higher displacement amplitudes in vacuum. These nonlinearities induce spring hardening which results the increase of the resonant frequency of the microdiaphragm.
- Based on a comprehensive modeling, medium damping influences on the resonant frequency and quality factor of piezoelectric microdiaphragm sensors were investigated theoretically and experimentally. The acoustic radiation and viscosity damping as the two main sources of energy dissipation in medium virtually added the mass of the diaphragm and therefore decrease the frequency and Q -factor of the diaphragm. The magnitude of medium damping inversely depends on the radius over thickness ratio of the diaphragm. Increase of this ratio is the trend in fabrication of thin microdiaphragms by MEMS fabrication processes, which implies the higher influence of medium damping in dynamic behavior of microdiaphragms. The fabricated diaphragms were tested in vacuum, air, and in ethanol. Obtained results are compared with their theoretical counterparts, and fairly good correlation was observed.
- In order to study the mass sensing capability of the sensor, gold layers with different thicknesses were deposited on the sensor's surface. The frequency shift due to this mass deposition in different frequency modes was measured. An increase in the sensitivity and the quality factor was found with the increase in the vibration mode number of the sensor.

The experimental results demonstrate that the mass sensitivity and quality factor of the device are 4.08 Hz/ng and 241.80 at the ninth peaks. These are 2.76 and 10.26 times higher than the mass sensitivity and the Q -factor of the device at the first peak. The observation is in accordance with the conducted finite element simulations. This result may lead to this conclusion that the sensitivity of microdiaphragm resonating sensors can be increased by working in higher modes without changing their physical parameters.

- Antigen-antibody reaction immobilization which is one of the most popular techniques for immunosensor applications implemented by a simple yet reliable dip and dry process to verify the feasibility of applying piezoelectric microdiaphragm as an immunosensor. It was demonstrated that the sensor chip, which was composed of eight sensors, was able to simultaneously detect HBsAg, AFP and HBcAg. The total experiment time for detecting these bioentities via the immunochip was less than 2 h, which is much shorter than the current reported time for the conventional detection methods.
- Pressure influences on the vibration characteristics of piezoelectric microdiaphragm based sensors were investigated theoretically and experimentally. It was demonstrated that only Bessel function of zero order, $m=0$, participates in the vibration modes of the microdiaphragm symmetrically loaded by pressure. A high value of pressure sensitivity, as high as 280 Hz/mbar, has been achieved; this value is 2.43 times higher than the currently reported sensitivity (i.e., 115 Hz/mbar) in the literature.

9.3 Future works

Although there have been several achievements in this research, there is always scope for further research in this area. A lot of work is still needed especially in the area of design,

modeling, and fabrication of novel piezoelectric microdiaphragm based sensors. As it was mentioned earlier in chapter six, the sensitivity and Q -factor of piezoelectric microdiaphragm based sensors reduce while working in liquid medium. One possible method for increasing these two parameters is implementing of the idea of suspended microchannel resonator [102, 106]. In this method, instead of submerging the device inside a fluid, the fluid flows through microchannels, which are placed inside the resonator itself. This design makes the sensitivity and Q -factor of the device almost unchanged in different medium. Hence, the main recommendation for future work is to incorporate the idea of suspended microchannel resonators in the piezoelectric microdiaphragms sensors.

High sensitivity to surface bound mass in the vibrating channel on top of the sensor requires a large ratio of surface area to channel volume and wall thickness. The resonating microchannel with a height up to $1\ \mu\text{m}$ and a width higher than $10\ \mu\text{m}$ can be fabricated to achieve high sensitivity. One plausible method for fabrication of these types of microchannels is based on wafer-to-wafer bonding process. The fabrication process can be summarized as follows:

The first step of realization of the microfluidic enhanced piezoelectric microdiaphragm based sensors is fabrication of microchannels. Microchannel fabrication process is composed of anisotropic silicon etching and growth of silicon nitride on the surface of the sensor. Figure 9-1 (a) and (b) show this process for microchannel and inlet section, respectively. Piezoelectric microdiaphragms will be fabricated by the methods previously explained in chapter three. The last step of the sensor fabrication is bonding of the two wafers and etching the membrane and inlet and outlet of microfluidic channels as it is illustrated in Figure 9-2.

Figure 9-1: The microchannel fabrication process for (a) channel section (b) inlet and outlet of solution.

(b)

Figure 9-2: The bonding and final etching process for (a) channel section (b) inlet section

This fabrication method can results high sensitive, high Q -factor sensors in air and liquid medium, with the capability of online mass sensing of chemical and biological entities.

References

- [1] P. Muralt, "PZT thin films for microsensors and actuators: Where do we stand?," *IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control*, vol. 47, pp. 903-915, Jul 2000.
- [2] P. Muralt, "Piezoelectric thin films for MEMS," *Integrated Ferroelectrics*, vol. 17, pp. 297-307, 1997.
- [3] S. Trolier-McKinstry and P. Muralt, "Thin film piezoelectrics for MEMS," *Journal of Electroceramics*, vol. 12, pp. 7-17, Jan-Mar 2004.
- [4] D. J. Laser and J. G. Santiago, "A review of micropumps," *Journal of micromechanics and microengineering*, vol. 14, p. R35, 2004.
- [5] M. Koch, N. Harris, A. G. R. Evans, N. M. White, and A. Brunnenschweiler, "A novel micromachined pump based on thick-film piezoelectric actuation," *Sensors and Actuators a-Physical*, vol. 70, pp. 98-103, Oct 1998.
- [6] P. Muralt, M. Kohli, T. Maeder, A. Kholkin, K. Brooks, N. Setter, and R. Luthier, "Fabrication and characterization of PZT thin film vibrators for micromotors," *Sensors and Actuators a-Physical*, vol. 48, pp. 157-165, May 1995.
- [7] A. M. Flynn, L. S. Tavrow, S. F. Bart, R. A. Brooks, D. J. Ehrlich, K. R. Udayakumar, and L. E. Cross, "Piezoelectric micromotors for microrobots," *Microelectromechanical Systems, Journal of*, vol. 1, pp. 44-51, 1992.
- [8] W. S. Lee and S. S. Lee, "Piezoelectric microphone built on circular diaphragm," *Sensors and Actuators A: Physical*, vol. 144, pp. 367-373, 2008.
- [9] G. Percin and B. T. Khuri-Yakub, "Micromachined droplet ejector arrays for controlled ink-jet printing and deposition," *Review of Scientific Instruments*, vol. 73, pp. 2193-2196, May 2002.
- [10] P. J. Stephanou, G. Piazza, C. D. White, M. B. J. Wijesundara, and A. P. Pisano, "Piezoelectric aluminum nitride MEMS annular dual contour mode filter," *Sensors and Actuators A: Physical*, vol. 134, pp. 152-160, 2007.
- [11] J. J. Bernstein, S. L. Finberg, K. Houston, L. C. Niles, H. D. Chen, L. E. Cross, K. K. Li, and K. Udayakumar, "Micromachined high frequency ferroelectric sonar transducers," *Ieee Transactions on Ultrasonics Ferroelectrics and Frequency Control*, vol. 44, pp. 960-969, Sep 1997.
- [12] P. D. Mitcheson, E. M. Yeatman, G. K. Rao, A. S. Holmes, and T. C. Green, "Energy harvesting from human and machine motion for wireless electronic devices," *Proceedings of the Ieee*, vol. 96, pp. 1457-1486, Sep 2008.
- [13] S. B. Horowitz, M. Sheplak, L. N. Cattafesta, and T. Nishida, "A MEMS acoustic energy harvester," *Journal of micromechanics and microengineering*, vol. 16, pp. S174-S181, Sep 2006.
- [14] E. K. Hong, S. Trolier-McKinstry, R. L. Smith, S. V. Krishnaswamy, and C. B. Freidhoff, "Design of MEMS PZT circular diaphragm actuators to generate large

- deflections," *Journal of Microelectromechanical systems*, vol. 15, pp. 832-839, Aug 2006.
- [15] S. J. Gross, S. Tadigadapa, T. N. Jackson, S. Trolrier-McKinstry, and Q. Q. Zhang, "Lead-zirconate-titanate-based piezoelectric micromachined switch," *applied physics letters*, vol. 83, pp. 174-176, Jul 2003.
 - [16] L. Nicu, M. Guirardel, F. Chambosse, P. Rougerie, S. Hinh, E. Trevisiol, J.-M. Francois, J.-P. Majoral, A.-M. Caminade, E. Cattani, and C. Bergaud, "Resonating piezoelectric membranes for microelectromechanically based bioassay: detection of streptavidin-gold nanoparticles interaction with biotinylated DNA," *Sensors and Actuators B: Chemical*, vol. 110, pp. 125-136, 2005.
 - [17] C. Ayala and L. Nicu, "Micromachined piezoelectric membranes with high nominal quality factors in newtonian liquid media: A Lamb's model validation at the microscale," *Sensors and Actuators B: Chemical*, vol. 123, pp. 860-868, 2007.
 - [18] T. Xu, Z. Wang, J. Miao, L. Yu, and C. M. Li, "Micro-machined piezoelectric membrane-based immunosensor array," *Biosensors and Bioelectronics*, vol. 24, pp. 638-643, 2008.
 - [19] E. Hong, R. Smith, S. V. Krishnaswamy, C. B. Freidhoff, and S. Trolrier-McKinstry, "Residual stress development in $\text{Pb}(\text{Zr,Ti})\text{O}_3/\text{ZrO}_2/\text{SiO}_2$ stacks for piezoelectric microactuators," *Thin Solid Films*, vol. 510, pp. 213-221, 2006.
 - [20] S. Lee, T. Tanaka, K. Inoue, J.-M. Kim, Y.-E. Shin, and M. Okuyama, "Stress influences on the ultrasonic transducers," *Sensors and Actuators A: Physical*, vol. 119, pp. 405-411, 2005.
 - [21] P. Murali, A. Kholkin, M. Kohli, and T. Maeder, "Piezoelectric actuation of PZT thin-film diaphragms at static and resonant conditions," *Sensors and Actuators A: Physical*, vol. 53, pp. 398-404, 1996.
 - [22] K. Sheplak and J. Dugundji, "large deflection of clamped circular plate under initial tension and transitions to membrane behavior," *Journal of applied mechanics*, vol. 65, pp. 107-115, 1998.
 - [23] M. Yu and B. Balachandran, "Sensor diaphragm under initial tension: Linear analysis," *Experimental Mechanics*, vol. 45, pp. 123-129, Apr 2005.
 - [24] S. W. Wenzel and R. M. White, "Analytical comparison of the sensitivities of bulk-wave, surface-wave, and flexural plate-wave ultrasonic gravimetric sensors," *applied physics letters*, vol. 54, pp. 1976-1978, , 1989.
 - [25] G. Sauerbrey, "VERWENDUNG VON SCHWINGQUARZEN ZUR WAGUNG DUNNER SCHICHTEN UND ZUR MIKROWAGUNG," *Zeitschrift Fur Physik*, vol. 155, pp. 206-222, 1959.
 - [26] A. Janshoff, H. J. Galla, and C. Steinem, "Piezoelectric mass-sensing devices as biosensors - An alternative to optical biosensors?," *Angewandte Chemie-International Edition*, vol. 39, pp. 4004-4032, 2000.
 - [27] T. Nomura and M. Okuhara, "FREQUENCY-SHIFTS OF PIEZOELECTRIC QUARTZ CRYSTALS IMMERSSED IN ORGANIC LIQUIDS," *Analytica Chimica Acta*, vol. 142, pp. 281-284, 1982.
 - [28] F. S. Wagoner and H. G. Craighead, "Micro and nonomechanical sensors for environmental, chemical, and biological detection," *Lab on a chip*, vol. 7, pp. 1238-1255, 2007.

- [29] E. Defay, C. Millon, C. Malhaire, and D. Barbier, "PZT thin films integration for the realisation of a high sensitivity pressure microsensor based on a vibrating membrane," *Sensors and Actuators A: Physical*, vol. 99, pp. 64-67, 2002.
- [30] C. Ayela, T. Leichle, C. Bergaud, L. Nicu, E. Cattani, C. Soyer, M. Pugnieri, and Ieee, "High quality factors of silicon membranes with piezoelectric actuation and detection scheme for biosensing purpose in liquid media," in *IEEE International Frequency Control Symposium and Exposition*, Miami, FL, 2006, pp. 123-128.
- [31] Available: <http://en.wikipedia.org/wiki/Sensor>
- [32] B. R. Eggins, *Chemical sensors and biosensors*. chichester: john wiley and sons, 2002.
- [33] J. H. Seo, "Silicon-based resonant microsensor platform for chemical and biological application," Ph. D., Georgia Institute of Technology, 2007.
- [34] R. E. Sonntag and G. J. Van Wylen, *Introduction to Thermodynamics, Classical and Statistical*, 3rd ed. New York: John wiely and sons, 1991.
- [35] A. P. F. Turner, I. Karube, and G. S. Wilson, *Biosensors: Fundamental and applications*: Oxford university press, 1987.
- [36] P. Krebs and A. Grisel, "Low power integrated catalytic gas sensor," *Sensors and Actuators, B: Chemical*, vol. 13, pp. 155-158, 1993.
- [37] M. Zanini, J. H. Visser, L. Rimai, R. E. Soltis, A. Kovalchuk, D. W. Hoffman, E. M. Logothetis, U. Bonne, L. Brewer, O. W. Bynum, and M. A. Richard, "Fabrication and properties of a Si-based high-sensitivity microcalorimetric gas sensor," *Sensors and Actuators, A: Physical*, vol. 48, pp. 187-192, 1995.
- [38] K. Ramanathan, B. R. Jönsson, and B. Danielsson, "Sol-gel based thermal biosensor for glucose," *Analytica Chimica Acta*, vol. 427, pp. 1-10, 2001.
- [39] P. Gründler, *Chemical Sensors [electronic resource] : An Introduction for Scientists and Engineers* Springer-Verlag Berlin Heidelberg, 2007.
- [40] J. Janata, *Principle of chemical sensors*. Salt lake city: Plenum, 1990.
- [41] P. Bataillard, "Calorimetric sensing in bioanalytical chemistry: Principles, applications and trends," *TrAC Trends in Analytical Chemistry*, vol. 12, pp. 387-394, 1993.
- [42] K. Ramanathan, M. Rank, J. Svitel, A. Dzgoev, and B. Danielsson, "The development and applications of thermal biosensors for bioprocess monitoring," *Trends in Biotechnology*, vol. 17, pp. 499-505, 1999.
- [43] B. Xie, K. Ramanathan, and B. Danielsson, "Mini/micro thermal biosensors and other related devices for biochemical/clinical analysis and monitoring," *TrAC Trends in Analytical Chemistry*, vol. 19, pp. 340-349, 2000.
- [44] S. J. Dixon-Warren, M. Kovar, C. E. Wartnaby, and D. A. King, "Pyroelectric single crystal adsorption microcalorimetry at low temperatures: oxygen on Ni{100}," *Surface Science*, vol. 307-309, pp. 16-22, 1994.
- [45] M. Kovar, L. Dvorak, and S. Cerny, "Application of pyroelectric properties of LiTaO3 single crystal to microcalorimetric measurements of the heat of adsorption," *Appl. Surf. Sci*, vol. 74, pp. 51-59, 1994.
- [46] J. P. Hall, R. W. Whatmore, and F. W. Ainger, "A black platinum catalyst/pyroelectric gas sensor," *Ferroelectrics* vol. 54, pp. 211-214, 1984.
- [47] M. Schreiter, R. Gabl, J. Lerchner, C. Hohlfeld, A. Delan, G. Wolf, A. Blüher, B. Katzschner, M. Mertig, and W. Pompe, "Functionalized pyroelectric sensors for gas detection," *Sensors and Actuators B: Chemical*, vol. 119, pp. 255-261, 2006.

- [48] J. Janata, "Electrochemical Microsensors," in *Proceedings of the IEEE*, 2003, pp. 864-869.
- [49] E. Lindner and R. P. Buck, "Microfabricated potentiometric electrodes and their in vivo applications," *Anal. Chem.*, vol. 72, pp. 336A-345A, 2000.
- [50] J. Janata and M. Josowicz, "A fresh look at some old principles: The Kelvin probe and the Nernst equation," *Anal. Chem.*, vol. 69, pp. 293A-296A, 1997.
- [51] M. Andersson, M. Holmberg, I. Lundström, A. Lloyd-Spetz, P. Mårtensson, R. Paolesse, C. Falconi, E. Proietti, C. Di Natale, and A. D'Amico, "Development of a ChemFET sensor with molecular films of porphyrins as sensitive layer," *Sensors and Actuators B: Chemical*, vol. 77, pp. 567-571, 2001.
- [52] J. A. Covington, J. W. Gardner, D. Briand, and N. F. de Rooij, "A polymer gate FET sensor array for detecting organic vapours," *Sensors and Actuators B: Chemical*, vol. 77, pp. 155-162, 2001.
- [53] S. M. Sze, *Semiconductor devices: physics and technology*: John Wiley and sons, 2001.
- [54] J. Janata, "Potentiometric microsensors," *Chemical Reviews*, vol. 90, pp. 691-703, 1990.
- [55] I. Lundstrom, M. S. Shivaraman, L. Stibler, and C. Svensson, "Hydrogen in smoke detected by the palladium-gate field-effect transistor," *Rev. Sci. Instrum.*, vol. 47, pp. 738-740, 1976.
- [56] I. Lundstrom, S. Shivaraman, C. Svensson, and L. Lundkvist, "Hydrogen-sensitive MOS field-effect transistor," *Appl. Phys. Lett.*, vol. 26, pp. 55-57, 1975.
- [57] M. S. Shivaraman, I. Lundstrom, C. Svensson, and H. Hammarsten, "Hydrogen sensitivity of palladium-thin oxide-silicon Schottky barriers," *Electron. Lett.*, vol. 12, pp. 483-484, 1976.
- [58] L. D. Mello and L. T. Kubota, "Review of the use of biosensors as analytical tools in the food and drink industries," *Food chemistry*, vol. 77, p. 237, 2002.
- [59] T. Matsumoto, S. Saito, and S. Ikeda, "A multilayer membrane amperometric glucose sensor fabricated using planar techniques for large-scale production," *Journal of Biotechnology*, vol. 122, pp. 267-273, 2006.
- [60] J. Wang, "Electrochemical glucose biosensors," *Chem. Rev.*, vol. 108, pp. 814-825, 2008.
- [61] N. Nikolaus and B. Strehlitz, "Amperometric lactate biosensors and their application in (sports) medicine, for life quality and wellbeing," *Microchim. Acta.*, vol. 160, pp. 15-55, 2008.
- [62] S. K. Arya, M. Datta, and B. D. Malhotra, "Recent advances in cholesterol biosensor," *Biosens. Bioelectron.*, vol. 23, pp. 1083-1100, 2008.
- [63] R. Bashir, "BioMEMS: state-of-the-art in detection, opportunities and prospects," *Advanced Drug Delivery Reviews*, vol. 56, pp. 1565-1586, 2004.
- [64] S. A. Andreescu, C. Bala, V. Măgăru, and J. L. Marty, "Detection of organophosphorus insecticides with immobilized acetylcholinesterase - comparative study of two enzyme sensors " *analytical and bioanalytical chemistry*, vol. 374, pp. 39-45, 2002.
- [65] Z. Muhammad-Tahir and E. C. Alocilja, "A conductometric biosensor for biosecurity," *Biosensors and Bioelectronics*, vol. 18, pp. 813-819, 2003.
- [66] H. Suzuki, H. Arakawa, and I. Karube, "Fabrication of a sensing module using micromachined biosensors," *Biosensors and Bioelectronics*, vol. 16, pp. 725-733, 2001.

- [67] X. Fan, I. M. White, S. I. Shopova, H. Zhu, J. D. Suter, and Y. Sun, "Sensitive optical biosensors for unlabeled targets: A review," *Analytica Chimica Acta*, vol. 620, pp. 8-26, 2008.
- [68] L. Gorton, *Biosensors and modern biospecific analytical techniques* vol. 44. Boston: Elsevier, 2005.
- [69] B. Liedberg, C. Nylander, and I. Lunström, "Surface plasmon resonance for gas detection and biosensing," *Sensors and Actuators*, vol. 4, pp. 299-304, 1983.
- [70] J. Homola, S. S. Yee, and G. Gauglitz, "Surface plasmon resonance sensors: review," *Sensors and Actuators B: Chemical*, vol. 54, pp. 3-15, 1999.
- [71] !!! INVALID CITATION !!!
- [72] X. Yao, X. Li, F. Toledo, C. Zurita-Lopez, M. Gutova, J. Momand, and F. Zhou, "Sub-attomole oligonucleotide and p53 cDNA determinations via a high-resolution surface plasmon resonance combined with oligonucleotide-capped gold nanoparticle signal amplification," *Analytical Biochemistry*, vol. 354, pp. 220-228, 2006.
- [73] C. Cao, J. P. Kim, B. W. Kim, H. Chae, H. C. Yoon, S. S. Yang, and S. J. Sim, "A strategy for sensitivity and specificity enhancements in prostate specific antigen-[alpha]1-antichymotrypsin detection based on surface plasmon resonance," *Biosensors and Bioelectronics*, vol. 21, pp. 2106-2113, 2006.
- [74] J. W. Chung, R. Bernhardt, and J. C. Pyun, "Additive assay of cancer marker CA 19-9 by SPR biosensor," *Sensors and Actuators B: Chemical*, vol. 118, pp. 28-32, 2006.
- [75] J. Wei, Y. Mu, D. Song, X. Fang, X. Liu, L. Bu, H. Zhang, G. Zhang, J. Ding, W. Wang, Q. Jin, and G. Luo, "A novel sandwich immunosensing method for measuring cardiac troponin I in sera," *Analytical Biochemistry*, vol. 321, pp. 209-216, 2003.
- [76] A. Leung, P. M. Shankar, and R. Mutharasan, "A review of fiber-optic biosensors," *Sensors and Actuators B: Chemical*, vol. 125, pp. 688-703, 2007.
- [77] J. O. Spiker and K. A. Kang, "Preliminary study of real-time fiber optic based protein C biosensor," *Biotechnol. Bioeng.*, vol. 66, pp. 158-163, 1999.
- [78] L. Tang, H. J. Kwon, and K. A. Kang, "Theoretical and experimental analysis of analyte transport in a fiber-optic protein C immuno-biosensor," *Biotechnol. Bioeng.*, vol. 88, pp. 869-879, 2004.
- [79] L. Tang, Y. J. Ren, B. Hong, and K. A. Kang, "Fluorophore-mediated, fiber-optic, multi-analyte, immunosensing system for rapid diagnosis and prognosis of cardiovascular diseases," *J. Biomed. Opt.*, vol. 11, 2006.
- [80] F. Kleinjung, F. F. Bier, A. Warsinke, and F. W. Scheller, "Fibre-optic genosensor for specific determination of femtomolar DNA oligomers," *Anal. Chim. Acta* vol. 350, pp. 51-58, 1997.
- [81] J. Zeng, A. Almadidy, J. Watterson, and U. K. Krull, "Interfacial hybridization kinetics of oligonucleotides immobilized onto fused silica surfaces," *Sens. Actuators B: Chem.*, vol. 90, pp. 68-75, 2003.
- [82] A. Brandenburg and A. Gombert, "Grating couplers as chemical sensors: a new optical configuration," *Sensors and Actuators, B: Chemical*, vol. 17, pp. 35-40, 1993.
- [83] P. V. Lambeck, "Integrated optical sensors for the chemical domain," *Measurement Science and Technology*, vol. 17, pp. 93-116, 2006.

- [84] N. V. Lavrik, M. J. Sepaniak, and P. G. Datskos, "Cantilever transducers as a platform for chemical and biological sensors," *Review of Scientific Instruments*, vol. 75, pp. 2229-2253, 2004.
- [85] J. Fritz, M. K. Baller, H. P. Lang, H. Rothuizen, P. Vettiger, E. Meyer, H. Guntherodt, C. Gerber, and J. K. Gimzewski, "Translating Biomolecular Recognition into Nanomechanics " *Science*, vol. 288, pp. 316-318, 2000.
- [86] G. Wu, R. H. Datar, K. M. Hansen, T. Thundat, R. J. Cote, and A. Majumdar, "Bioassay of prostate-specific antigen (PSA) using microcantilevers," *nature biotechnology*, vol. 19, pp. 856-860, 2001.
- [87] M. K. Baller, H. P. Lang, J. Fritz, C. Gerber, J. K. Gimzewski, U. Drechsler, H. Rothuizen, M. Despont, P. Vettiger, F. M. Battiston, J. P. Ramseyer, P. Fornaro, E. Meyer, and H. J. Güntherodt, "A cantilever array-based artificial nose," *Ultramicroscopy*, vol. 82, pp. 1-9, 2000.
- [88] A. Subramanian, P. I. Oden, S. J. Kennel, K. B. Jacobson, R. J. Warmack, T. Thundat, and M. J. Doktycz, "Glucose biosensing using an enzyme-coated microcantilever," *applied physics letters*, vol. 81, pp. 385-387, Jul 2002.
- [89] G. Shekhawat, S. H. Tark, and V. P. Dravid, "MOSFET-embedded microcantilevers for measuring deflection in biomolecular sensors," *Science*, vol. 311, pp. 1592-1595, Mar 2006.
- [90] K. W. Wee, G. Y. Kang, J. Park, J. Y. Kang, D. S. Yoon, J. H. Park, and T. S. Kim, "Novel electrical detection of label-free disease marker proteins using piezoresistive self-sensing micro-cantilevers," *Biosensors and Bioelectronics*, vol. 20, pp. 1932-1938, 2005.
- [91] R. Mukhopadhyay, M. Lorentzen, J. Kjems, and F. Besenbacher, "Nanomechanical Sensing of DNA Sequences Using Piezoresistive Cantilevers," *Langmuir*, vol. 21, pp. 8400-8408, 2005.
- [92] B. Ilic, D. Czaplewski, H. G. Craighead, P. Neuzil, C. Campagnolo, and C. Batt, "Mechanical resonant immunospecific biological detector," *applied physics letters*, vol. 77, pp. 450-452, Jul 2000.
- [93] B. Ilic, D. Czaplewski, M. Zalalutdinov, H. G. Craighead, P. Neuzil, C. Campagnolo, and C. Batt, "Single cell detection with micromechanical oscillators," in *45th International Conference on Electron, Ion, and Photon Beam Technology and Nanofabrication*, Washington, D.C., 2001, pp. 2825-2828.
- [94] N. V. Lavrik and P. G. Datskos, "Femtogram mass detection using photothermally actuated nanomechanical resonators," *applied physics letters*, vol. 82, pp. 2697-2699, Apr 2003.
- [95] B. Ilic, H. G. Craighead, S. Krylov, W. Senaratne, C. Ober, and P. Neuzil, "Attogram detection using nanoelectromechanical oscillators," *Journal of Applied Physics*, vol. 95, pp. 3694-3703, 2004.
- [96] B. Ilic, Y. Yang, and H. G. Craighead, "Virus detection using nanoelectromechanical devices," *applied physics letters*, vol. 85, pp. 2604-2606, Sep 2004.
- [97] L. Johnson, A. K. Gupta, A. Ghafoor, D. Akin, and R. Bashir, "Characterization of vaccinia virus particles using microscale silicon cantilever resonators and atomic force microscopy," *Sensors and Actuators B: Chemical*, vol. 115, pp. 189-197, 2006.

- [98] A. Gupta, D. Akin, and R. Bashir, "Single virus particle mass detection using microresonators with nanoscale thickness," *applied physics letters*, vol. 84, pp. 1976-1978, 2004.
- [99] B. Ilic, Y. Yang, K. Aubin, R. Reichenbach, S. Krylov, and H. G. Craighead, "Enumeration of DNA molecules bound to a nanomechanical oscillator," *Nano Letters*, vol. 5, pp. 925-929, May 2005.
- [100] K. S. Hwang, J. H. Lee, J. Park, D. S. Yoon, J. H. Park, and T. S. Kim, "In-situ quantitative analysis of a prostate-specific antigen (PSA) using a nanomechanical PZT cantilever," *Lab on a chip*, vol. 4, pp. 547-552, 2004.
- [101] T. P. Burg and S. R. Manalis, "Suspended microchannel resonators for biomolecular detection," *applied physics letters*, vol. 83, pp. 2698-2700, Sep 2003.
- [102] T. P. Burg, M. Godin, S. M. Knudsen, W. Shen, G. Carlson, J. S. Foster, K. Babcock, and S. R. Manalis, "Weighing of biomolecules, single cells and single nanoparticles in fluid," *nature*, vol. 446, pp. 1066-1069, Apr 2007.
- [103] G. Y. Kang, G. Y. Han, J. Y. Kang, I.-H. Cho, H.-H. Park, S.-H. Paek, and T. S. Kim, "Label-free protein assay with site-directly immobilized antibody using self-actuating PZT cantilever," *Sensors and Actuators B: Chemical*, vol. 117, pp. 332-338, 2006.
- [104] Y. T. Yang, C. Callegari, X. L. Feng, K. L. Ekinci, and M. L. Roukes, "Zeptogram-scale nanomechanical mass sensing," *Nano Letters*, vol. 6, pp. 583-586, Apr 2006.
- [105] G. M. Whitesides, "The origins and the future of microfluidics," *nature*, vol. 442, pp. 368-373, 2006.
- [106] T. P. Burg, A. R. Mirza, N. Milovic, C. H. Tsau, G. A. Popescu, J. S. Foster, and S. R. Manalis, "Vacuum-packaged suspended microchannel resonant mass sensor for biomolecular detection," *Journal of Microelectromechanical systems*, vol. 15, pp. 1466-1476, Dec 2006.
- [107] M. Godin, A. K. Bryan, T. P. Burg, K. Babcock, and S. R. Manalis, "Measuring the mass, density, and size of particles and cells using a suspended microchannel resonator," *applied physics letters*, vol. 91, Sep 2007.
- [108] K. Park, J. Jang, D. Irimia, J. Sturgis, J. Lee, J. P. Robinson, M. Toner, and R. Bashir, "'Living cantilever arrays' for characterization of mass of single live cells in fluids," *Lab on a chip*, vol. 8, pp. 1034-1041, 2008.
- [109] J. R. Masters, "HeLa cells 50 years on: the good, the bad and the ugly," *Nature Reviews Cancer*, vol. 2, pp. 315-319, Apr 2002.
- [110] M. J. Bartkovsky, "Development of an acoustic wave mems biosensing device," Ph.D., Chemical engineering department, CARNEGIE MELLON UNIVERSITY, 2006.
- [111] B. Drafts, "Acoustic wave technology sensors," *IEEE Transactions on Microwave Theory and Techniques*, vol. 49, pp. 795-802, Apr 2001.
- [112] D. S. Ballantine, R. M. White, S. Martin, A. J. Ricco, E. T. Zellers, G. C. Frye, and H. Wohltjen, *Acoustic Wave Sensors*: Academic Press, 1997.
- [113] F. Aberl, H. Wolf, C. Kosslinger, S. Drost, P. Woias, and S. Koch, "HIV serology using piezoelectric immunosensors," in *Euroensors VII*, Budapest, Hungary, 1993, pp. 271-275.
- [114] K. A. Marx, "Quartz crystal microbalance: A useful tool for studying thin polymer films and complex biomolecular systems at the solution-surface interface," *Biomacromolecules*, vol. 4, pp. 1099-1120, Sep-Oct 2003.

- [115] L. Rodriguez-Pardo, J. F. Rodriguez, C. Gabrielli, and R. Brendel, "Sensitivity, noise, and resolution in QCM sensors in liquid media," in *2nd IEEE International Conference on Sensors*, Toronto, CANADA, 2003, pp. 1251-1257.
- [116] A. F. Collings and F. Caruso, "Biosensors: recent advances," *Reports on Progress in Physics*, vol. 60, pp. 1397-1445, Nov 1997.
- [117] B. Frey, C. Jordan, S. Kornguth, and R. Corn, "Control of the specific adsorption of proteins onto gold surfaces with poly(l-lysine) monolayers," *Analytical Chemistry*, vol. 67, pp. 4452-4457, 1995.
- [118] C. K. O'Sullivan and G. G. Guilbault, "Commercial quartz crystal microbalances - theory and applications," *Biosensors and Bioelectronics*, vol. 14, pp. 663-670, 1999.
- [119] H. Muramatsu, F. Ohata, Y. Miya, T. Hosokawa, S. Kurosawa, N. Kamo, and H. Ikeda, "Quartz crystal microbalance for the detection of microgram quantites of human serum albumin: Relationship between the frequency change and the mass of protein adsorbed.," *analytical chemistry*, vol. 65, pp. 2293-2937, 1993.
- [120] X. Zhou, L. Liu, L. Wang, and J. Hu, "Detection of hepatitis B virus by piezoelectric biosensor," *Journal of Pharmaceutical and Biomedical Analysis*, vol. 27, pp. 341-345, 2002.
- [121] J. W. Grate and M. Klusty, "Surface acoustic-wave vapor sensors based on resonators devices," *Analytical Chemistry*, vol. 63, pp. 1719-1727, Sep 1991.
- [122] J. C. Pyun, H. Beutel, J. U. Meyer, and H. H. Ruf, "Development of a biosensor for E. coli based on a flexural plate wave (FPW) transducer," *Biosensors and Bioelectronics*, vol. 13, pp. 839-845, 1998.
- [123] P. W. Walton, M. R. Oflaherty, M. E. Butler, and P. Compton, "Gravimetric biosensors based on acoustic-waves in thin polmer-films," *Biosensors & Bioelectronics*, vol. 8, pp. 401-407, 1993.
- [124] C. Hagleitner, A. Hierlemann, D. Lange, A. Kummer, N. Kerness, O. Brand, and H. Baltes, "Smart single-chip gas sensor microsystem," *nature*, vol. 414, pp. 293-296, Nov 2001.
- [125] W. G. Cady, *Piezoelectricity*. New York: McGraw-Hill, 1946.
- [126] T. Ikeda, *Fundamentals of piezoelectricity*. Oxford: Oxford university press, 1990.
- [127] S. D. Sentoria, *Microsystem design*. Boston: Kluwer academic publishers, 2004.
- [128] C. L. Zhao, "Ferroelectric films for MEMS type devices using novel hybrid processing technology," School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, 2003.
- [129] A. RodriguezNavarro, W. OtanoRivera, J. M. GarciaRuiz, R. Messier, and L. J. Pilione, "Preparation of highly oriented polycrystalline AlN thin films deposited on glass at oblique-angle incidence," *Journal of Materials Research*, vol. 12, pp. 1689-1692, Jul 1997.
- [130] F. J. Hickernell, R. X. Yue, and F. S. Hickernell, "Statistical modeling for the optimal deposition of sputtered piezoelectric films," *IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control*, vol. 44, pp. 615-623, May 1997.
- [131] U. Ozgur, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho, and H. Morkoc, "A comprehensive review of ZnO materials and devices," *Journal of Applied Physics*, vol. 98, Aug 2005.

- [132] A. Barker, S. Crowther, and D. Rees, "Room-temperature rf magnetron sputtered ZnO for electromechanical devices," *Sensors and Actuators a-Physical*, vol. 58, pp. 229-235, Mar 1997.
- [133] I. Mayergoyz and G. Bertotti, *The Science of Hysteresis* vol. 3. New York: Elsevier, 2005.
- [134] B. Noheda, D. E. Cox, G. Shirane, R. Guo, B. Jones, and L. E. Cross, "Stability of the monoclinic phase in the ferroelectric perovskite $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$," *Physical Review B*, vol. 63, Jan 2001.
- [135] R. G. Polcawich, "Design, fabrication, test, and evaluation of RF MEMS series switches using lead zirconate titanate (PZT) thin film actuators," The Pennsylvania State University, 2007.
- [136] R. D. Klissurska, K. G. Brooks, I. M. Reaney, C. Pawlaczyk, M. Kosec, and N. Setter, "Effect of Nb doping on the microstructure of sol-gel-derived PZT thin films " *Journal of the American Ceramic Society*, vol. 78, pp. 1513-1520, Jun 1995.
- [137] C. K. Kwok and S. B. Desu, "Low temperature perovskite formation of lead zirconate titanate thin films by a seeding process " *Journal of Materials Research*, vol. 8, pp. 339-344, Feb 1993.
- [138] P. Murali, "Ferroelectric thin films for micro-sensors and actuators: a review," in *10th Micromechanics Europe Workshop (MME 99)*, Gif Sur Yvette, France, 1999, pp. 136-146.
- [139] M. Okada and K. Tominaga, "Preparation and properties of $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ thin films by metal organic chemical vapor deposition " *Journal of Applied Physics*, vol. 71, pp. 1955-1959, Feb 1992.
- [140] T. Maeder, P. Murali, L. Sagalowicz, I. Reaney, M. Kohli, A. Kholkin, and N. Setter, " $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ thin films on zirconium membranes for micromechanical applications," *applied physics letters*, vol. 68, pp. 776-778, Feb 1996.
- [141] C. Kumar, M. Sayer, R. Pascual, D. T. Amm, Z. Wu, and D. M. Swanson, "Lead zirconate titanate films by rapid thermal processing " *applied physics letters*, vol. 58, pp. 1161-1163, Mar 1991.
- [142] R. Bruchhaus, H. Huber, D. Pitzer, and W. Wersing, "Deposition of ferroelectric PZT thin films by planar multitarget sputtering " *Ferroelectrics*, vol. 127, pp. 137-142, 1992.
- [143] Z. Wang, J. Miao, T. Xu, L. Yu, C. M. Li, and X. Chen, "Biosensors Based on Flexural Mode Piezo-Diaphragm," in *Proceedings of the 3rd IEEE Int. Conf. on Nano/Micro Engineered and Molecular Systems*, Sanya, China, 2008.
- [144] Z. H. Wang, J. M. Miao, and W. G. Zhu, "Micromachined ultrasonic transducers and arrays based on piezoelectric thick film," *Applied Physics a-Materials Science & Processing*, vol. 91, pp. 107-117, Apr 2008.
- [145] T. M. Shaw, S. Trolier-McKinstry, and P. C. McIntyre, "The properties of ferroelectric films at small dimensions," *Annual Review of Materials Science*, vol. 30, pp. 263-298, 2000.
- [146] B. A. Tuttle, J. A. Voigt, D. C. Goodnow, D. L. Lamppa, T. J. Headley, M. O. Eatough, G. Zender, R. D. Nasby, and S. M. Rodgers, "Highly oriented chemically prepared $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ thin films " *Journal of the American Ceramic Society*, vol. 76, pp. 1537-1544, Jun 1993.

- [147] G. Arlt, D. Hennings, and G. Dewith, "Dielectric-properties of fine-grained barium-titanate ceramics," *Journal of Applied Physics*, vol. 58, pp. 1619-1625, 1985.
- [148] S. H. Hu, G. J. Hu, X. J. Meng, G. S. Wang, J. L. Sun, S. L. Guo, J. H. Chu, and N. Dai, "The grain size effect of the $\text{Pb}(\text{Zr}_{0.45}\text{Ti}_{0.55})\text{O}_3$ thin films deposited on LaNiO_3 -coated silicon by modified sol-gel process," *Journal of Crystal Growth*, vol. 260, pp. 109-114, 2004.
- [149] H. t. Martirena and J. C. Burfoot, "Grain-size effects on properties of some ferroelectric ceramics," *Journal of Physics C-Solid State Physics*, vol. 7, pp. 3182-3192, 1974.
- [150] O. Auciello and R. Waser, *Science and Technology of Electroceramic Thin Films*. Amsterdam Kluwer Academic Publishers, 1995.
- [151] K. Kakimoto, H. Kakimoto, S. Fujita, and Y. Masuda, "Control of crystal orientation and piezoelectric response of lead zirconate titanate thin films near the morphotropic phase boundary," *Journal of the American Ceramic Society*, vol. 85, pp. 1019-1021, Apr 2002.
- [152] P. Muralt, S. Hiboux, C. Mueller, T. Maeder, L. Sagalowicz, T. Egami, and N. Setter, "Excess lead in the perovskite lattice of PZT thin films made by in-situ reactive sputtering," *Integrated Ferroelectrics*, vol. 36, pp. 53-62, 2001.
- [153] J. H. Park, F. Xu, and S. Trolier-McKinstry, "Dielectric and piezoelectric properties of sol-gel derived lead magnesium niobium titanate films with different textures," *Journal of Applied Physics*, vol. 89, pp. 568-574, Jan 2001.
- [154] T. Yoshimura and S. Trolier-McKinstry, "Growth and piezoelectric properties of $\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - PbTiO_3 epitaxial films," *Journal of Applied Physics*, vol. 92, pp. 3979-3984, Oct 2002.
- [155] M. A. Dubois and P. Muralt, "Measurement of the effective transverse piezoelectric coefficient $e_{(31,f)}$ of AlN and $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films," *Sensors and Actuators a-Physical*, vol. 77, pp. 106-112, Oct 1999.
- [156] P. Muralt, "Ferroelectric thin films for micro-sensors and actuators: a review," *Journal of micromechanics and microengineering*, vol. 10, pp. 136-146, 2000.
- [157] K. G. Brooks, I. M. Reaney, R. Klissurska, Y. Huang, L. Bursill, and N. Setter, "Orientation of rapid thermally annealed lead-zirconate-titanate thin-films on (111) pt substrates," *Journal of Materials Research*, vol. 9, pp. 2540-2553, Oct 1994.
- [158] S. Y. Chen and I. W. Chen, "Temperature-time texture transition of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ thin-films, 2. heat-treatment and compositional effects," *Journal of the American Ceramic Society*, vol. 77, pp. 2337-2344, Sep 1994.
- [159] P. Sanz, J. Hernando, J. Vazquez, and J. L. Sanchez-Rojas, "Laser vibrometry and impedance characterization of piezoelectric microcantilevers," *Journal of micromechanics and microengineering*, vol. 17, pp. 931-937, May 2007.
- [160] P. Muralt and J. Baborowski, "Micromachined ultrasonic transducers and acoustic sensors based on piezoelectric thin films," *Journal of Electroceramics*, vol. 12, pp. 101-108, Jan-Mar 2004.
- [161] H. N. Al-Shareef, K. D. Gifford, S. H. Rou, P. D. Hren, O. Auciello, and A. I. Kingon, "Electrodes for ferroelectric thin films," *Integrated Ferroelectrics: An International Journal*, vol. 3, pp. 321 - 332, 1993.
- [162] D. P. Vijay and S. B. Desu, "Electrodes for $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ferroelectric thin-films," *Journal of The Electrochemical Society*, vol. 140, pp. 2640-2645, Sep 1993.

- [163] R. Ramesh, H. Gilchrist, T. Sands, V. G. Keramidas, R. Haakenaasen, and D. K. Fork, "Ferroelectric La-Sr-Co-O/Pb-Zr-Ti-O/La-Sr-Co-O heterostructures on silicon via template growth," *applied physics letters*, vol. 63, pp. 3592-3594, Dec 1993.
- [164] G. R. Fox, S. Troliermckinstry, S. B. Krupanidhi, and L. M. Casas, "PT/TI/SIO₂/SI SUBSTRATES," *Journal of Materials Research*, vol. 10, pp. 1508-1515, Jun 1995.
- [165] G. J. Willems, D. J. Wouters, H. E. Maes, and R. Nouwen, "Nucleation and orientation of sol-gel PZT-films on Pt electrodes," *Integrated Ferroelectrics*, vol. 15, pp. 19-28, 1997.
- [166] T. Maeder, L. Sagalowicz, and P. Muralt, "Stabilized platinum electrodes for ferroelectric film deposition using Ti, Ta and Zr adhesion layers," *Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers*, vol. 37, pp. 2007-2012, Apr 1998.
- [167] K. Sreenivas, I. Reaney, T. Maeder, N. Setter, C. Jagadish, and R. G. Elliman, "Investigation of Pt/Ti bilayer metallization on silicon for ferroelectric thin-film integration," *Journal of Applied Physics*, vol. 75, pp. 232-239, Jan 1994.
- [168] K. R. Williams and R. S. Muller, "Etch rates for micromachining processing," *Journal of Microelectromechanical systems*, vol. 5, pp. 256-269, Dec 1996.
- [169] Z. H. Wang, W. G. Zhu, C. L. Zhao, and O. K. Tan, "Dense PZT thick films derived from sol-gel based nanocomposite process," *Materials Science and Engineering B-Solid State Materials for Advanced Technology*, vol. 99, pp. 56-62, May 2003.
- [170] P. Muralt, N. Ledermann, J. Baborowski, A. Barzegar, S. Gentil, B. Belgacem, S. Petitgrand, A. Bosseboeuf, and N. Setter, "Piezoelectric micromachined ultrasonic transducers based on PZT thin films," *IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control*, vol. 52, pp. 2276-2288, Dec 2005.
- [171] *IEEE Standard on Piezoelectricity, ANSI/IEEE Std 176-1987.*
- [172] D. Berlincourt, "Piezoelectric ceramics- characteristics and applications," *Journal of the Acoustical Society of America*, vol. 70, pp. 1586-1595, 1981.
- [173] I. DeWolf, "Micro-Raman spectroscopy to study local mechanical stress in silicon integrated circuits," *Semiconductor Science and Technology*, vol. 11, pp. 139-154, Feb 1996.
- [174] X. Pan, C. W. Tan, J. Miao, J. Kasim, Z. Shen, and E. Xie, "The stress analysis of Si MEMS devices by micro-Raman technique," *Thin Solid Films*, vol. 517, pp. 4905-4908, 2009.
- [175] S. Nakashima, T. Mitani, M. Ninomiya, and K. Matsumoto, "Raman investigation of strain in Si/SiGe heterostructures: Precise determination of the strain-shift coefficient of Si bands," *Journal of Applied Physics*, vol. 99, Mar 2006.
- [176] G. G. Stoney, "The tension of metallic films deposited by electrolysis," *Proceeding of the Royal Society of London, A*, vol. 82, pp. 172-180, 1909.
- [177] E. I. Bromley, J. N. Randall, D. C. Flanders, and R. W. Mountain, "A technique for the determination of stress in thin films," *Journal of Vacuum Science & Technology B*, vol. 1, pp. 1364-1366, 1983.
- [178] M. J. Madou, *Foundamentals of Microfabrication*, 2nd ed. Florida: CRC Press LLC, 2002.
- [179] J. M. Jones, *Mechanics of Composite Materials*, 2nd ed. Philadelphia: Taylor and Francis, Inc, 1999.

- [180] J. Camassel and A. Tiberj, "Strain effects in device processing of silicon-on-insulator materials," *Applied Surface Science*, vol. 212-213, pp. 742-748, 2003.
- [181] G. A. C. M. Spierings, G. J. M. Dormans, W. G. J. Moors, M. J. E. Ulenaers, and P. K. Larsen, "Stresses in Pt/Pb(Zr,Ti)O₃/Pt thin-film stacks for integrated ferroelectric capacitors," *Journal of Applied Physics*, vol. 78, pp. 1926-1933, 1995.
- [182] J. D. Hall, N. E. Apperson, B. T. Crozier, C. Xu, R. F. Richards, D. F. Bahr, and C. D. Richards, "A facility for characterizing the dynamic mechanical behavior of thin membranes for microelectromechanical systems," *Review of Scientific Instruments*, vol. 73, pp. 2067-2072, May 2002.
- [183] O. Al-Hattamleh, J. Cho, R. F. Richards, D. F. Bahr, and C. D. Richards, "The effect of design and process parameters on electromechanical coupling for a thin-film PZT membrane," *Journal of Microelectromechanical systems*, vol. 15, pp. 1715-1725, Dec 2006.
- [184] S. P. Timoshenko and S. Woinowsky-Kringer, *Theory of plates and shells*. New York: McGraw-Hill 1959.
- [185] A. Leissa, *Vibration of plates*. Columbus, Ohio, 1993.
- [186] J. F. Shepard, F. Chu, I. Kanno, and S. Trolier-McKinstry, "Characterization and aging response of the d(31) piezoelectric coefficient of lead zirconate titanate thin films," *Journal of Applied Physics*, vol. 85, pp. 6711-6716, May 1999.
- [187] D. L. Polla and L. F. Francis, "Processing and characterization of piezoelectric materials and integration into microelectromechanical systems," *Annual Review of Materials Science*, vol. 28, pp. 563-597, 1998.
- [188] Z. Song, C. Lin, L. Wang, J. Huang, D. Hesse, N. D. Zakharov, H. Xu, and M. Okuyama, "Microstructure and electrical properties of textured Sr_{0.51}Ba_{0.48}La_{0.01}Nb₂O₆ thin films," *Applied Physics a-Materials Science & Processing*, vol. 70, pp. 355-358, Mar 2000.
- [189] J. Cho, M. Anderson, R. Richards, D. Bahr, and C. Richards, "Optimization of electromechanical coupling for a thin-film PZT membrane: II. Experiment," *Journal of micromechanics and microengineering*, vol. 15, pp. 1804-1809, Oct 2005.
- [190] J. Cho, M. Anderson, R. Richards, D. Bahr, and C. Richards, "Optimization of electromechanical coupling for a thin-film PZT membrane: I. Modeling," *Journal of micromechanics and microengineering*, vol. 15, pp. 1797-1803, Oct 2005.
- [191] M. A. Dubois and P. Muralt, "PZT thin film actuated elastic fin micromotor," *IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control*, vol. 45, pp. 1169-1177, Sep 1998.
- [192] V. R. Singh, J. Miao, Z. Wang, G. Hegde, and A. Asundi, "Dynamic characterization of MEMS diaphragm using time averaged in-line digital holography," *Optics Communications*, vol. 280, pp. 285-290, 2007.
- [193] M. Olfatnia, T. Xu, L. S. Ong, J. M. Miao, and Z. H. Wang, "Investigation of residual stress and its effects on the vibrational characteristics of piezoelectric-based multilayered microdiaphragms," *Journal of micromechanics and microengineering*, vol. 20, p. 5007, 2010.
- [194] S. S. Sengupta, S. M. Park, D. A. Payne, and L. H. Allen, "Origins and evolution of stress development in sol-gel derived thin layers and multideposited coatings of lead titanate," *Journal of Applied Physics*, vol. 83, pp. 2291-2296, Feb 1998.

- [195] N. Ledermann, P. Muralt, J. Baborowski, M. Forster, and J. P. Pellaux, "Piezoelectric Pb(Zr-x,Ti1-x)O-3 thin film cantilever and bridge acoustic sensors for miniaturized photoacoustic gas detectors," *Journal of micromechanics and microengineering*, vol. 14, pp. 1650-1658, Dec 2004.
- [196] E. Hong, S. Trolier-McKinstry, R. Smith, S. V. Krishnaswamy, and C. B. Freidhoff, "Vibration of micromachined circular piezoelectric diaphragms," *IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control*, vol. 53, pp. 697-706, Apr 2006.
- [197] R. E. Berg and D. G. Stork, *The Physics of Sound*, 3rd ed. ed. London: Pearson Prentice Hall, 2005.
- [198] B. J. Gallacher, J. S. Burdess, and A. J. Harris, "Principles of a three-axis vibrating gyroscope," *Aerospace and Electronic Systems, IEEE Transactions on*, vol. 37, pp. 1333-1343, 2001.
- [199] A. K. Isamil, J. S. Burdess, A. J. Harris, C. J. McNeil, J. Hedley, S. C. Chang, and G. Suarez, "The principle of a MEMS circular diaphragm mass sensor," *Journal of micromechanics and microengineering*, vol. 16, pp. 1487-1493, 2006.
- [200] J. W. S. Rayleigh, *The theory of sound*, 2nd ed. New York: Dover Publication, 1945.
- [201] B. M. Deutsch, A. R. Robinson, R. J. Felce, and T. R. Moore, "Nondegenerate normal-mode doublets in vibrating flat circular plates," *American Journal of Physics*, vol. 72, pp. 220-225, Feb 2004.
- [202] J. Hernando, J. L. Sanchez-Rojas, U. Schmid, A. Ababneh, G. Marchand, and H. Seidel, "Characterization and displacement control of low surface-stress AlN-based piezoelectric micro-resonators," *Microsystem Technologies-Micro-and Nanosystems-Information Storage and Processing Systems*, vol. 16, pp. 855-861, May 2010.
- [203] V. R. Singh, "Lensless in-line digital holography for dynamic applications," Ph.D., School of Mechanical and Aerospace Engineering, Nanyang Technological University, 2008.
- [204] W. Weaver, J. S. P. Timoshenko, and D. H. Young, *Vibration Problems in Engineering*. New York: Wiley, 1990.
- [205] M. Marzencki, M. Defosseux, and S. Basrour, "MEMS Vibration Energy Harvesting Devices With Passive Resonance Frequency Adaptation Capability," *Journal of Microelectromechanical systems*, vol. 18, pp. 1444-1453, Dec 2009.
- [206] A. H. Nayfeh, *Nonlinear oscillations*. New York: John Wiley and sons, 1979.
- [207] H. A. C. Tilmans, M. Elwenspoek, and J. H. J. Fluitman, "Micro resonant force gauges," *Sensors and Actuators A: Physical*, vol. 30, pp. 35-53, 1992.
- [208] E. Majorana and Y. Ogawa, "Mechanical thermal noise in coupled oscillators," *Physics Letters A*, vol. 233, pp. 162-168, Aug 1997.
- [209] K. Y. Yasumura, T. D. Stowe, E. M. Chow, T. Pfafman, T. W. Kenny, B. C. Stipe, and D. Rugar, "Quality factors in micron- and submicron-thick cantilevers," *Journal of Microelectromechanical systems*, vol. 9, pp. 117-125, Mar 2000.
- [210] H. Lamb, "On the Vibrations of an Elastic Plate in Contact with Water," *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, vol. 98, pp. 205-216, 1920.
- [211] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics*. London: Pergamon Press, 1959.

- [212] Z. Hao, A. Erbil, and F. Ayazi, "An analytical model for support loss in micromachined beam resonators with in-plane flexural vibrations," *Sensors and Actuators A: Physical*, vol. 109, pp. 156-164, 2003.
- [213] Z. Hao and F. Ayazi, "Support loss in the radial bulk-mode vibrations of center-supported micromechanical disk resonators," *Sensors and Actuators A: Physical*, vol. 134, pp. 582-593, 2007.
- [214] K. L. Ekinci and M. L. Roukes, "Nanoelectromechanical systems," *Review of Scientific Instruments*, vol. 76, p. 061101, Jun 2005.
- [215] J. L. Yang, T. Ono, and M. Esashi, "Energy dissipation in submicrometer thick single-crystal silicon cantilevers," *Journal of Microelectromechanical systems*, vol. 11, pp. 775-783, Dec 2002.
- [216] F. R. Blom, S. Bouwstra, M. Elwenspoek, and J. H. J. Fluitman, "Dependence of the quality factor of micromachined silicon beam resonators on pressure and geometry," *Journal of Vacuum Science & Technology B*, vol. 10, pp. 19-26, Jan-Feb 1992.
- [217] W. E. Newell, "Miniaturization of Tuning Forks," *Science*, vol. 161, pp. 1320-1326, 1968.
- [218] M. Amabili and M. K. Kwak, "Free vibrations of circular plates coupled with liquids: Revising the lamb problem," *Journal of Fluids and Structures*, vol. 10, pp. 743-761, Oct 1996.
- [219] M. H. Bao, *Micro Mechanical Transducers*. Amsterdam: Elsevier, 2000.
- [220] Y.-H. Cho, B. M. Kwak, A. P. Pisano, and R. T. Howe, "Slide film damping in laterally driven microstructures," *Sensors and Actuators A: Physical*, vol. 40, pp. 31-39, 1994.
- [221] Y. Kozlovsky, "Vibration of plates in contact with viscous fluid: Extension of Lamb's model," *Journal of Sound and Vibration*, vol. 326, pp. 332-339, Sep 2009.
- [222] F. M. White, *Fluid Mechanics*, Fifth ed. New York: McGraw-Hill, 2003.
- [223] M. Olfatnia, V. R. Singh, T. Xu, J. M. Miao, and L. S. Ong, "Analysis of the vibration modes of piezoelectric circular microdiaphragms " *Journal of micromechanics and microengineering*, vol. 20, p. 085013, 2010.
- [224] K. M. Andersson and S. Hovmöller, "The protein content in crystals and packing coefficients in different space groups," *Acta Crystallographica Section D-Biological Crystallography*, vol. 56, pp. 789-790, Jul 2000.
- [225] J. Tamayo, D. Ramos, J. Mertens, and M. Calleja, "Effect of the adsorbate stiffness on the resonance response of microcantilever sensors," *applied physics letters*, vol. 89, pp. 224104-3, Nov 2006.
- [226] A. K. Gupta, P. R. Nair, D. Akin, M. R. Ladisch, S. Broyles, M. A. Alam, and R. Bashir, "Anomalous resonance in a nanomechanical biosensor," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 103, pp. 13362-13367, Sep 2006.
- [227] D. Ramos, J. Tamayo, J. Mertens, and M. Calleja, "Photothermal excitation of microcantilevers in liquids," *Journal of Applied Physics*, vol. 99, Jun 2006.
- [228] D. Ramos, J. Tamayo, J. Mertens, M. Calleja, and A. Zaballos, "Origin of the response of nanomechanical resonators to bacteria adsorption," *Journal of Applied Physics*, vol. 100, pp. 106105-3, Nov 2006.

- [229] G. Y. Chen, T. Thundat, E. A. Wachter, and R. J. Warmack, "Adsorption-induced surface stress and its effects on resonance frequency of microcantilevers," *Journal of Applied Physics*, vol. 77, pp. 3618-3622, Apr 1995.
- [230] G. Y. Chen, R. J. Warmack, T. Thundat, D. P. Allison, and A. Huang, "Resonance response of scanning force microscopy cantilevers," *Review of Scientific Instruments*, vol. 65, pp. 2532-2537, Aug 1994.
- [231] A. Ptak, S. Takeda, C. Nakamura, J. Miyake, M. Kageshima, S. P. Jarvis, and H. Tokumoto, "Modified atomic force microscope applied to the measurement of elastic modulus for a single peptide molecule," *Journal of Applied Physics*, vol. 90, pp. 3095-3099, 2001.
- [232] S. Dohn, R. Sandberg, W. Svendsen, and A. Boisen, "Enhanced functionality of cantilever based mass sensors using higher modes," *applied physics letters*, vol. 86, pp. 233501-3, Jun 2005.
- [233] A. A. Karyakin, G. V. Presnova, M. Y. Rubtsova, and A. M. Egorov, "Oriented immobilization of antibodies onto the gold surfaces via their native thiol groups," *Analytical Chemistry*, vol. 72, pp. 3805-3811, Aug 2000.
- [234] S. Tombelli and M. Mascini, "Piezoelectric quartz crystal biosensors: Recent immobilisation schemes," *Analytical Letters*, vol. 33, pp. 2129-2151, 2000.
- [235] K. Ito, K. Hashimoto, and Y. Ishimori, "Quantitative analysis for solid-phase hybridization reaction and binding reaction of DNA binder to hybrids using a quartz crystal microbalance," *Analytica Chimica Acta*, vol. 327, pp. 29-35, Jun 1996.
- [236] I. S. Park, W. Y. Kim, and N. Kim, "Operational characteristics of an antibody-immobilized QCM system detecting Salmonella spp," *Biosensors & Bioelectronics*, vol. 15, pp. 167-172, Jun 2000.
- [237] S. Z. Yao and T. A. Zhou, "Dependence of the oscillation frequency of a piezoelectric crystal on the physical parameters of liquids," *Analytica Chimica Acta*, vol. 212, pp. 61-72, Sep 1988.
- [238] Y. K. Ye, J. H. Zhao, F. Yan, Y. L. Zhu, and H. X. Ju, "Electrochemical behavior and detection of hepatitis B virus DNA PCR production at gold electrode," *Biosensors & Bioelectronics*, vol. 18, pp. 1501-1508, Oct 2003.
- [239] L. Meirovitch, *Analytical methods in vibrations* New york: The Macmillan company, 1967.

Appendix A: Table of Material properties

Material properties of different layers of piezoelectric microdiaphragm			
<i>Material</i>	<i>E</i> (GPa)	<i>ν</i>	<i>ρ</i> 10 ³ Kg / m ³
SiO ₂	72.4	0.16	2.07
Si	150	0.22	2.32
PZT	86.2	0.28	7.62
Si ₃ N ₄	150	0.24	3.24
Ti	102.1	0.3	4.85
Pt	146.9	0.39	21.45