Quartz Crystal Microbalance Technique for Chemical and Biological Applications

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A dissertation submitted for the partial fulfilment of BS-MS dual degree in Science

Indian Institute of Science Education and Research Mohali
April 2020

Certificate of Examination

This is to certify that the dissertation titled **" Quartz Crystal Microbalance Technique for Chemical and Biological Applications "** submitted by **Himanshu Dev** (Reg. No. MS15116) for the partial fulfillment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr. Sharvan Sehrawat	Dr. K. P. Singh	Dr. Ananth Venkatesan (Supervisor)

Dated: June 15, 2020

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Ananth Venkatesan at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Himanshu Dev
(Candidate)

Dated: June 15, 2020

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Ananth Venkatesan
(Supervisor)

Acknowledgment

No work in the laboratory can be executed without assistance, guidance, and support. It has been traditional to thank people for starting from the supervisor, but I would like to express my thanks from the lab members to others.

First of all, I would like to express profound gratitude to Mr. Pankaj Sahu, Mr. Shelender Kumar, Mr. Shayam Sundar Yadav, and Dr. Radhikesh for their unfailing encouragement and being continuously assistive throughout my research work.

I would like to express my sincere thanks to my supervisor. The door to Dr. Ananth Venkatesan's office always remains open whenever I found some troublesome, having questions or doubts concerning my thesis work. Apart from my thesis work, he gave me the freedom to learn nanofabrication and lithography techniques, as well as techniques related to microwave physics. So again, I am thankful to my thesis supervisor for it.

I am also greatly indebted to Dr. K.P Singh from the physical science department and Dr. Sharvan Sehrawat from the department of biological science for being a committee member to evaluate my thesis work and leaving valuable comments.

Ultimately, my most significant and special thanks is for my family for all the support and patience throughout my thesis work. I would also like to thank my friends to put me off from stress through conversation throughout this work.

Abstract

Sauerbrey discovery in 1959 [Sauerbrey 59] of relating mass variation due to frequency shift makes the necessary foundation of sensors based on the quartz in air and vacuum and then Nomura and Okuhara [Rodahl 96] also made it applicable in the liquid medium. All these discoveries attracted a lot of attention of the scientist working in various fields. So in the last 40 years, the quartz crystal(QC) has been of great importance due to its full applications in the electrochemistry, bio-sensors, gas sensors, probing bio-molecular interaction, and microorganism. Thus quartz crystal oscillators(QCOs) have proved themselves to be a unique laboratory for sensing. Moreover, recently the study of magnetic properties and noise measurement could also be possible with a quartz crystal oscillator. Ultimately we can say that QCOs become an indispensable tool for broad applications in physics, chemistry, and biology. The questions that are inquisitive for me that I tried to explore in the thesis are related to the physics of liquid crystal(LC) and the responsible parameters that significantly affect Q factor during its loading, probing bio-molecules with quartz and mass detection of chemicals. This thesis tries to provide a brief overview of the theory and applications of quartz crystal oscillators(QCOs). The piezoelectric nature of quartz, an amazing feature of quartz crystal, and due to its high stability over a wide range of temperatures, quartz crystals have a broad range of applications. The research work in this thesis is at the interface of physics, chemistry, and biology. I focus on the applications of quartz, mainly in the fields chemistry utilizing techniques of microwave physics. I use quartz crystal microbalance technique and developed a system for the mass detection and probing bio-molecular interaction, and Lock in amplifier, signal generator, LabVIEW for the study of physical properties of liquid crystals(LCs) 4-Cyano-4'-pentylbiphenyl(5CB). Moreover, in this thesis, some techniques involved fabrication and lithography are discussed in the appendix section. The mass sensing of Hexamethyldisilazane (HMDS), which turns out to be after calculation from the Sauerbrey equation, is 1.59×10^{-8} grams. I studied the phase transition of 4-Cyano-4'-pentylbiphenyl liquid crystal at temperature 34.2^{o}C, which is close to its transition temperature 35^{o}C. The deviation from its exact transition temperature is due to not having good control over temperature. I also made Wilkinson power divider in EagleCAD software (used in designing PCB and electronic component) is also in the appendix.

Abbreviations

QC	Quartz Crystal
QCO	Quartz Crystal Oscillator
QCM	Quartz Crystal Microbalance
EEC	Equivalent Electrical Circuit
QCH	Quartz Crystal Holder
QCC	Quartz Crystal Cut
QCMw	Quartz Crystal Micro-weighing
PQC	Piezoelectric Quartz Crystal

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Chapter 1

Natural Quartz And Theory of Quartz Crystal(QC)

Abstract

This chapter provides a brief overview of the quartz crystal. Then it sheds light over its amazing properties such as piezoelectricity and anisotropic nature of QC. Moreover, I have made a schematic to explain piezoelectricity more naturally from a molecular point of view. At the end of this chapter, In equivalent electric circuit(EEC) is parallel, and the series resonance frequency is described. This chapter concludes that for having piezoelectricity, crystal lattice of material should contain some polar bonds and lack of center of symmetry or point symmetry.

1.1 Introduction

At the very first, one may think that what is natural quartz and how the crystals of it are achieved? And then what is the reason of its high stability? Therefore the first chapter addresses such question and their answers and much more other qualitative information about QC. At the end, the underlying physics these crystals is given. From the last five decades to till date, quartz crystal are playing and essential role in revolutionizing the electronic industry as quartz has attractive electrical, mechanical and thermal properties.

1.2 Quartz

In nature, silicon dioxide (SiO_2) is found to be in ample amount, and a crystalline form of silicon dioxide (SiO_2) shown in figure 1.1 is known as quartz that is forming about 14% the Earth's crust. The crystalline form of SiO_2 at temperatures below 573°C is known as alpha quartz(or only quartz). The origin of quartz is from the German word "quartz," which has the melting point of quartz is above 1,700°C. The form of SiO_2 is called the beta quartz above

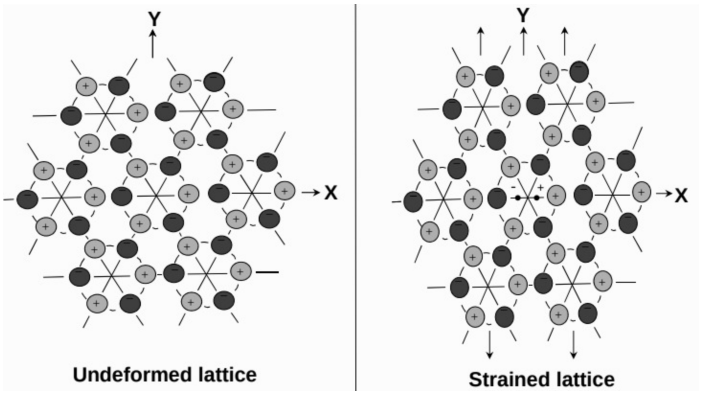

Figure 1.1: Representation of the Lord Kelvin model of charge in quartz. Application of strain in quartz causes displacement of net positive charge in y direction and displacement of net negative charge in x direction.
Image courtesy: Vig, J. R., "Quartz Crystal Resonators and Oscillators," www.ieee-uffc.org, January 2007.

573°C, the Curie temperature of quartz. As alpha quartz transforms into beta quartz, most of the piezoelectric properties are lost. A limited supply of natural quartz and its high cost together resulted in the development of synthetic quartz. Crystals of quartz are achieved by dissolving SiO_2 in an alkaline solution at approximately 400°C and pressure of 10,000 inside a steel autoclave, which is built to combat the extreme conditions required. In the coldest part of the autoclave, seed crystals are mounted in frames, and a solution of hydroxide, and in the warmer portion, fragments of SiO_2, sodium carbonate are placed, The solution moves from the hot place to the coolest place and, in doing so, dissolves the nutrient and deposits on the seed crystal. Temperatures are controlled throughout this process. Large bars of a crystal can be grown in about ten weeks. The conditions of growth play a crucial role in the quality of the crystal, and crystals are grown in such shape and sizes that minimize wastage of time and material. The bars of the crystal is used to obtain wafers. The angle at which it is cut plays a crucial role in determining the frequency and temperature stability of the final crystal. The most widely used cut is the AT-cut, where the blank is cut from the bar of crystal at approximately 35°, allowing a frequency range of 1 MHz to 300MHz. Both natural and synthetic quartz generally have a hexagonal cross-section and are usually capped by hexagonal pyramids with six cap faces at both or either ends, as depicted in Figure 1.3. Three axes identify the various directions within the crystal. The Z or optical axis runs longitudinally through the center of the quartz. The direction of most significant electrical sensitivity is called the electrical, or X-axis which axis joins two points at opposite corners of the hexagon. The Y or mechanical axis joins two opposite faces of the hexagon. As there are six faces, there are three X and Y axes [Cerda 14].

1.3 Discovery of quartz

Jacques Curie and Pierre Curie both discovered in 1880, the direct piezoelectric effect on quartz. They were successful in observing a charge on the surface of natural quartz whose magnitude was proportional to the force per unit area applied on it. Moreover, in 1881, the French physicist Gabriel Lippmann was able to predict the converse piezoelectric effect (a crystal is deformed when a voltage is applied to it) using the principle of conservation of electricity. It was verified by the Curie brothers in the same year. The discovery of the piezoelectric properties of quartz has become a significant factor in the growth of the electronics industry.

1.4 Peizoelectric nature of quartz (piezoelectricity)

The Greek word piezein from where "piezo" is derived has the meaning "to press." Hence, piezo-electricity means "pressure electricity." In 1881, Hankel gave the name to these two phenomena, direct and converse piezoelectric effects as "piezoelectricity"[Buchanan 54]. Professor Walter Guyton Cady [Cady 18] stated (piezoelectricity) in the following manner, that is, "Piezoelectricity is electric polarization that is caused by mechanical strain in crystals belonging to certain classes, the polarization being proportional to the strain and changing direction with it."The highlighted words mean that if applied, the force per unit area is replaced by a stretch(i.e., a reversal in the sign of force per unit area), then the sign of the electric polarization also reverses. Professor Cady also stated: piezoelectric crystal must have a structural'bias' that determines whether a given region on the surface shall show a positive or negative charge on compression(i.e.it must have a certain direction sensitiveness in its internal structure). It is the reversal of a sign of strain with a sign of field that distinguishes piezoelectric materials from the non-piezoelectric materials. By stretching or compressing piezoelectric material, a voltage is generated. In the case of quartz crystals, a voltage is applied, which gives rise to the pressure that is displayed in the form of oscillations at a particular resonant frequency, which depends on the thickness of the quartz crystal. Quartz crystal can be made to oscillate at any frequency by preparing a crystal carefully, and the fundamental frequency is the lowest frequency, which one can supply up to about 45MHz. Operate the crystal at odd overtones; 3rd, 5th, 7th, 9th, and 11th, to obtain higher frequencies (to over 300 MHz) and change the circuit in such a way so that quartz crystal oscillates at the overtone frequency at which it is made.

1.5 Anisotropic nature of quartz

Many properties of crystal properties such as mechanical, electrical, and optical are profoundly affected by direction in the quartz bar. Therefore, quartz is anisotropic, which

is one of the main characteristics of piezoelectric materials which leads to quartz being direction-sensitive (one-wayness), as stated by Cady.

1.6 Understanding of piezoelectricity from the made schematic

I present an excellent way to understand the quartz crystal's piezoelectricity from a molecular point of view. To know how it works, we go to figure 1.1 and take one unit of the molecular structure. See the schematic in the figure, when you press the positive charge ions as I have shown, one can figure out that the center of the net charge goes upward(red color circle) from its center in the undeformed case in the upper side in the leftmost. The same process can use for negative charge ions, and in this case, the center goes downward. So when somebody presses the whole crystal. Net positive charge and net negative charge gather in opposite directions. If you connect to wires to each end and touch them, you will see an electric spark. Do you know why this happens, the answer is SiO_2 is a polar molecule, and it lacks a point symmetry.

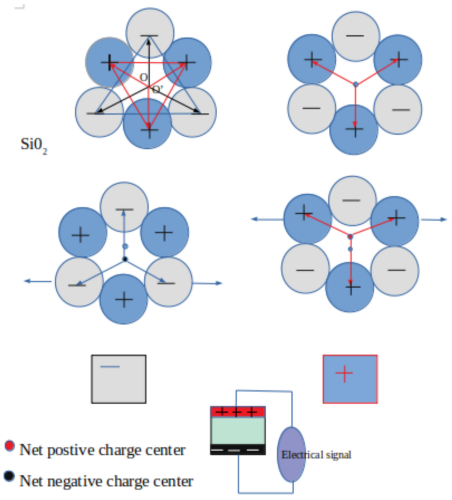

Figure 1.2: Understanding of piezoelectricity via pulling negative and postive charge centers

1.7 Equivalent electrical circuit(EEC) of quartz crystal oscillator

In this section, I am present EEC of the quartz crystal oscillator(QCO). This model is also known as the Van Dyke model consists of shunt capacitance(static arm)and motional arm formed by motional capacitance, inductance, and resistance in series. I first consider two conditions when the crystal is not oscillating, and in the latter one, it is oscillating. The circuit can be regarded as equivalent to the capacitance C_o when the crystal is connected

across the AC source, it is not vibrating and can behave as a tuned motional arm of the electrical equivalent circuit when the crystal vibrates.

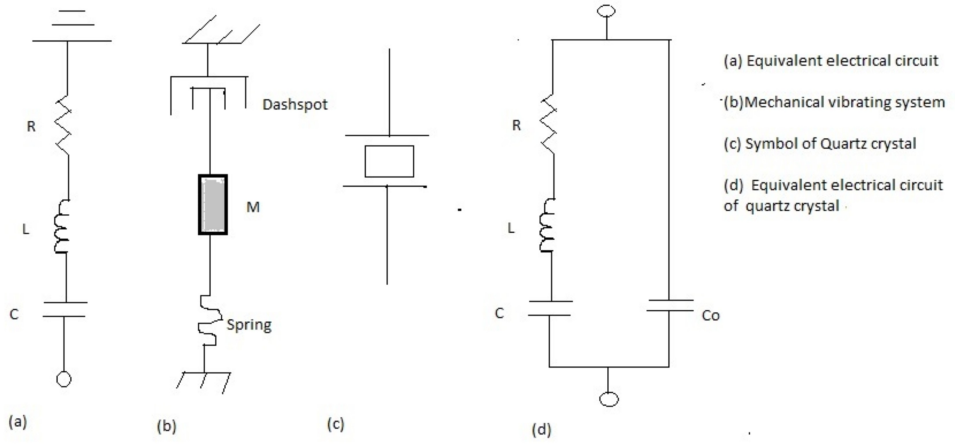

Figure 1.3: (a) Equivalent electrical circuit, (b)Mechanical vibrating system,(c) Symbol of quartz crystal, (d) Equivalent electrical circuit for quartz crystal

1.7.1 Crystal frequency response

If we look at the figure 1.4, it is clear that at the point where reactance of inductance becomes equal to the value of inductance of capacitance, the equivalent circuit behaves as resistance. In this case series resonance frequency occurs which is given by $f_s = \frac{1}{2\pi}.\frac{1}{\sqrt{LC}}$. Parallel resonance frequency occurs when the reactance of motional branch(R-L-C) of equivalent circuit is equal to the reactance of shunt capacitor C_o. The frequency in parallel resonance frequency is given by $f_p = \frac{1}{2\pi}.\frac{1}{\sqrt{L\left(\frac{CC_o}{C+C_o}\right)}}$. It is good to keep in mind is that at f_p, high impedance to the external circuit is provided by the quartz crystal oscillator.

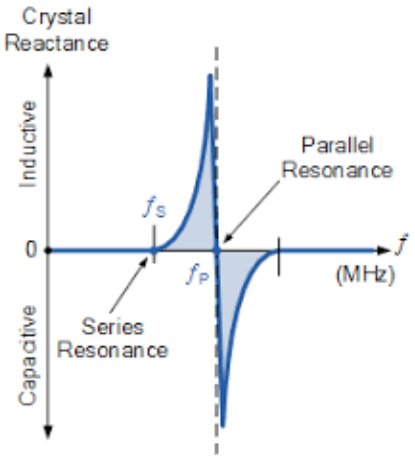

Figure 1.4: Crystal reactance versus frequency
Image courtesy: https://www.electronics-tutorials.ws/oscillator/crystal.html

Chapter 2

Characteristics of Quartz Crystals and Glossary of Terms of Quartz Crystals

Abstract

This chapter will deal more with the details on quartz properties (especially AT-Cut) since different performances are the consequences of the use of different crystal cuts in frequency control applications. This chapter mainly discusses AT-cut and also makes familiar with the pros and cons of the AT-cut quartz crystal. Furthermore, the Glossary of terms is to be familiar with a QC in depth.

2.1 Introduction

First of all, this chapter is an extension of chapter one in which many of the crystal characteristics will be discussed in more detail. In this chapter, I am going to talk about how temperature characteristics of quartz crystal with AT-cut and pros and cons of AT-cut quartz crystal. Then glossary terms for the quartz crystal will be defined. It will deal with the electrical equivalent circuit of quartz and parallel and the series resonance frequency of quartz.

2.2 Temperature characteristics of the AT-cut quartz crystal

The cuts are very important to know because the performances and stability of quartz crystals are different for different cuts. In 1929, the groups in America, Germany, and Japan discovered that at certain temperatures, the temperature coefficient could be brought to zero for a Y-cut plate [Bottom 82]. The cut at which the first zero temperature coefficient was named AT-cut. See figure for AT cut 2.1.

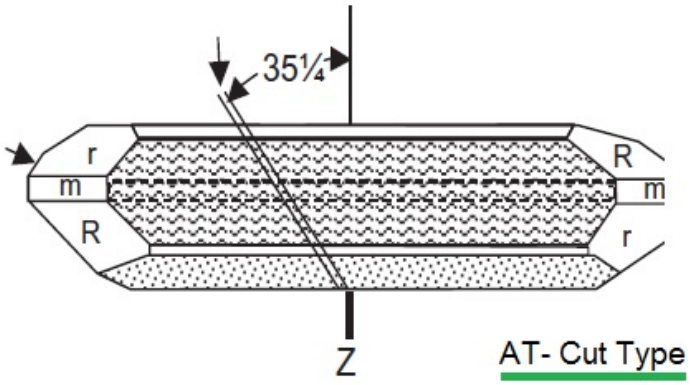

Figure 2.1: AT-cut
Image courtesy: https://www.iqdfrequencyproducts.com/blog/2015/06/29/a-short-primer-on-at-cut-quartz-crystals/

2.2.1 Frequency-Temperature curve family for AT cut quartz crystal

AT-cut QC is the most widely used crystal due to its wonderful performance over a large range of temperatures. To obtain AT-cut, one has to take cut the quartz blank at the angle of $35\left(\frac{1}{4}\right)^{o}$. From figure 2.2, it can be seen that the first zero temperature coefficient is 25^{o}C. One can quickly capture that at the time discovery; good stability can be achieved at near room temperature. If the angle from $35\left(\frac{1}{4}\right)^{o}$ changes to another value, then the whole family of the curve for frequency versus temperature will change.

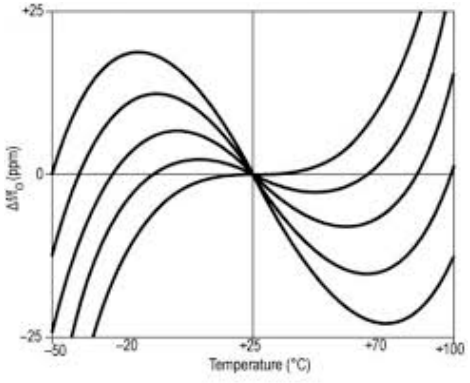

Figure 2.2: AT-cut Frequency vs. Temperature curves
Image courtesy:
https://www.rfwireless-world.com/Terminology/AT-cut-vs-SC-cut-quartz-crystal.html

2.3 Pros and cons of AT cut quartz crystals

The pros and cons for AT cut are [Cerda 14]-

2.3.1 Pros of AT cut Quartz Crystals

- They are cost effective.
- They can be prepared with very high motional capacitance for voltage-controlled crystal oscillator utility purposes.
- Good stability in frequency over wide range of temperature

2.3.2 Cons of AT cut quartz crystals

- They are really very sensitive to vibration, stress, gravity.
- Temperature gradients in these crystals during initial power-up cause long warm up time.
- In small physical and high-frequency designs, there can be perturbations or activity dips in frequency versus temperature graph, which give rise to lowering in the frequency of quartz crystals and an increase in resistance. This is why motional inductance and capacitance deviate from their actual value [Bottom 82].

2.4 Important Glossary of the terms of the quartz crystal oscillator

Glossary of the terms is:

- Quartz Crystal oscillator(QCO): An electrical circuit with two electrodes on top of the quartz crystal to generate high stability in frequency.
- Quartz Crystal Holder: A case housing in which quartz crystal oscillator is put.
- Nominal frequency: It is the ideal frequency of the quartz with no uncertainty.
- Quality factor: It is the quality function of the quartz crystal. If it is high, then sharper the selectivity of the circuit is.
- Ambient temperature: It is the temperature range in for the operation of the quartz crystal.
- Temperature Stability: It tells about the amount of frequency change as a function of temperature.

- Quartz Crystal Cut: Properties of quartz crystal oscillator on which they are much dependent.
- Load capacitance: It is the total amount of capacitance that quartz crystal oscillator exhibits to the two crystal terminals, which has to be on the frequency of the quartz crystal in the circuit.
- Frequency Stability: It is the amount of the frequency deviation from its nominal(or ambient temperature) frequency in the specified temperature range.
- Frequency tolerance: It is a permittable deviation for a quartz crystal from its nominal frequency at room temperature.
- Shunt Capacitance: It is the static capacitance(C_o) between the two electrodes of the quartz crystal.
- Equivalent Series Resistance: It is the value of impedance that quartz crystal shows during the time of operation.
- Series resonance: The condition of resonance at which the impedance is minimum and its equivalent circuit in this resonance condition is a resistor.
- Motional capacitance: It is the capacitance(C) of the motional arm in the electrical equivalent circuit. See figure 1.3.
- Electrical inductance: The capacitance(L) of the motional arm is in the electrical equivalent circuit(EEC). See figure 1.3

Chapter 3

The Quartz Crystal Microbalance: Theory and Applications

Abstract

In chapter 1 and 2, theory and Characteristics of quartz crystal oscillators have already been discussed, therefore in this chapter, I shed light on the theory of quartz crystal microbalance, a thickness-shear mode for QCM and mathematical formulation to establish a relation between frequency shift upon application of foreign mass on the active surface of the quartz crystal oscillator. Note worth features of this relation and its validity condition is also discussed. At the end of this chapter, a general expression for finding mass for QCM is established.

3.1 Introduction

Quartz crystal oscillators due to its high stability in frequency and its piezoelectric property become an indispensable tool for mass sensing. The quartz crystal microbalance(QCM) is an advantageous technique because of its compatibility to function in different environments(i.e., vacuum, liquid, and air) to measure mass deposited on the quartz crystal and its very high surface sensitivity. All the above features make more valuable this technique as it offers many applications in the field of physics, chemistry, biology. Any mechanical object that vibrates has its resonance frequency, which depends on the total mass of that object, including some other physical parameter related to the object—for example, shear velocity, the density of the objects. Therefore, one adds or removes some mass; change in frequency with respect to its resonance frequency will certainly occur, and thus it can be used to determines mass. There must be a set of rules related to the mechanical vibrating object that helps determine mass added or removed.

- A mechanical vibrating object must be that it should be afire upon the applied electric potential and have sharply defined resonant frequencies because this will help in a reasonable period of time to precisely determine the frequency of vibration.
- A system that measures frequency can be attached to it with negligible disturbance. To accurately measure the mass, it necessary that the change in resonance frequency caused by mass must be much larger than the instability of resonance frequency uncertainty in the frequency measurement techniques exploited.
- Moreover, changes in the resonance frequency caused by environmental factors such as temperature, pressure, electric and magnetic field, and mechanical stresses caused by external sources must be minimal compared to mass change.
- There should be an equation that mass changes corresponding to the shift in the resonance frequency of the mechanical vibrating object.

High-frequency resonators made of thin quartz crystal plates with specific crystallographic orientation fulfill most of the above set of requirements. Another good merit of quartz crystal resonators is they are chemically stable and small in size. Furthermore, the piezoelectricity of quartz crystal resonators can be used for two purposes:

- To couple electric signal with the mechanical objects for the applications in sensing and actuation
- To fabricate the oscillators with very high fidelity and frequency standard

High stability, strong piezoelectric response, anisotropic nature, to be abundance, all these make quartz highly applicable for both the purposes and in other fields as well. Among them, the third one is significant (see section 1.5) because in that different cuts of quartz behave differently upon application of temperature and mechanical stress. Apart from this, elasticity constants also show temperature dependence. Utilizing this benefit, we can make temperature-compensated quartz crystals if we cut the in-way that the shift in frequency is less or negligible as a function of temperature at room temperature. Moreover, the vibration frequency spectrum can also be made simple in the vicinity of zero temperature dependence of frequency over a finite temperature range. So quartz crystal can be made putting on the plate of quartz crystal and by coupling the unit of the circuit with the proper gain and feedback. This is how one achieves a quartz crystal resonator whose resonance frequency can be measured by electrical means. There are other piezoelectric materials available in nature, but the most commonly used quartz crystal resonators is because of its amazing properties and availability in ease and abundance.
These crystal resonators have been employed for sensing the mass in micrograms to nanograms in different environments. Even though the scientists are still working on its performance

improvement, taking into account its specific crystallographic orientation for mass sensing purposes.

3.2 Theory of Quartz crystal microbalances

From the last three decades, AT-cut quartz crystal microbalance sensors have been playing a significant role in various applications in different research fields. Precise measurement is a key factor, and the most desired in mass sensing experiments and mass change incurs whenever there is a shift in resonance frequency. So to get accurate results, it is important to know the sources of errors that are responsible for the desired results [Lu 12].

3.2.1 Sources of errors

These are the following sources of errors:

- Errors due to resonance frequency or time measurement techniques used
- Errors due to changes in resonance frequency introduces by factors such as temperature and stress besides mass
- the preciseness of the formula used to convert the resonance frequency change to mass change

An error occurring due to time or resonance frequency techniques employed can be minimized in a considerable amount if long enough time for measurement is allowed, and it happens only when the frequency is stable, nevertheless, on mass loading on the QCM, resonance frequency with time. In some cases, for example, a dynamic study of mass change, we are also concern with the rate of mass. Then resonance frequency or time measurement must be with a short time interval. In this way, the resolution of frequency or time is limited and results in limitation in sensitiveness too. Thus we can conclude that choosing a particular method to determine resonance is entirely a matter of sensitiveness and speed for specific purposes. The errors due to resonance frequency or time measurement techniques can be predicted easily. Errors due to changes in resonance frequency introduces by factors such as temperature and stress besides mass can reduce by taking care of crystallographic orientation and befitting design of quartz crystal resonator, but can not be eliminated. Thus, we conclude that that preciseness in mass determination is how well these factors are controlled. Suppose that a technique has been employed to overcome error and factors in the second source of error are worthy of considering, then preciseness of the formula that converts frequency shift into mass change becomes essential and must be taken account[Lu 12].

3.3 Thickness-shear mode the quartz crystal oscillator for micro-weighing

Thickness-shear mode the quartz crystal oscillator for micro-weighing which acts as a sensor, made of the very thin plate(most often circular, can be rectangular as well) of quartz with AT-cut have two electrodes on alternative sides [Arnau 00]. In general, shear modes are excited in AT-cut quartz, in which displacement is parallel to quartz surfaces. Resonance takes place in these oscillators at the frequencies if the thickness of quartz crystal oscillators is equal half times the odd multiple of the acoustic wavelength. Moreover, in these resonators, frequency ranges from about 1kHz to 500 MHz. This mode has the most common application, which is mass sensing, which helps minimize the energy loss in liquid media [Lucklum 06]. In the ideal sense, this mode can be approximated as a transverse wave traveling wave in the plate's displacement direction. Suppose we take a rectangular plate, then wave equation takes from as follows:

$$\frac{\partial^2 \psi}{\partial^2 t} = v_{qc}\left[\nabla^2 \psi\right] \tag{3.1}$$

where qc stands for quartz crystal and $\nabla^2 = \left[\frac{\partial^2 \psi}{\partial^2 x} + \frac{\partial^2 \psi}{\partial^2 y} + \frac{\partial^2 \psi}{\partial^2 z}\right]$
We can assume the solution for the equation 3.1 as $\psi(x, y, z, t) = \mathrm{X(x)Y(y)Z(z)T(t)}$ and presuming that length l_q in x direction, thickness d_q is in y-direction, and width w_q is in z direction. In equation 3.1, ψ is a displacement function which is normal to the direction of propagation, and v_q is the wave velocity, which depends on the elastic constant and density. Let's consider that plate is anchored and its center is a node that provides appropriate boundary conditions ($\psi(i = 0) = 0$ at midpoint of the crystal plate, where i is x, y, and z.) for the solution

$$\psi_{pqr}(x, y, z, t) = sin\left(\frac{p\pi x}{d_{qc}}\right) sin\left(\frac{q\pi y}{l_{qc}}\right) sin\left(\frac{r\pi z}{w_{qc}}\right) sin(\omega_{pqr} t) \tag{3.2}$$

where p,q, and r belong to odd number indices and d_{qc}, l_{qc},w_{qc} are thickness, length, width of the plate.[Bottom 82] Substituting equation (3.2) in equation (3.1) we obtain frequencies

$$\omega_{pqr} = \pi v_{qc} \sqrt{\frac{p^2}{d_{qc}^2} + \frac{q^2}{l_{qc}^2} + \frac{r^2}{w_{qc}^2}}$$

Assuming that length l_q and width w_q have very large values then ω_{pqr} can be approximated as [Wang 11]

$$\omega_{pqr} \approx \frac{p\pi v_{qc}}{d_{qc}} \implies f_{qc} \approx \frac{p v_{qc}}{2 t_{qc}} \tag{3.3}$$

We can also get the same expression in last can be obtained for circular plate but we have to take limit of large value of radius to thickness value [Bottom 82, Gerber 85]. At the frequency $f_{qc} \approx \frac{pv_{qc}}{2t_{qc}}$ at drive current, maximum displacement ψ is of the order of few atomic spacings [Vig 92].

3.4 Frequency shift to mass change relation for small mass load for quartz crystal micro-weighing(QCMw)

The quartz crystal resonators for mass sensing, the first and for foremost, introduces by German scientist G. Suaerbrey [Sauerbrey 59]. The most common use for QCRs are gas absorption, thin layer thickness determination, and can also be used as chemical sensors [Vashist 11, Janata 10]. Sauerbrey stated the principle of working a QCM that can be seen as the idealized physical model in the following figures. For p^{th} thickness-shear mode of a quartz crystal plate to oscillate $d_{qc} = \frac{\lambda p}{2}$ where d_{qc}, the thickness of thickness-shear mode and λ, the wavelength of thickness-shear mode elastic wave in thickness direction must be satisfied [Lu 84]. we can write frequency in term of thickness shear mode velocity v_{qc} and λ using the relation $v_{qc} = f_{qc}\lambda$ and we obtain equation

$$f_{qc} = \frac{pv_{qc}}{2d_{qc}} \tag{3.4}$$

which looks exactly as equation 3.3. Note that we completely neglect the effect of electrodes on both sides in this case. Now differentiating equation 3.4 with respect to thickness d_{qc} of thickness shear mode of quartz we obtain equation,

$$df_{qc} = -\frac{pv_{qc}d(d_{qc})}{2d_{qc}^2} \tag{3.5}$$

Dividing equation 3.5 by f_{qc}, we obtain

$$\frac{df_{qc}}{f_{qc}} = -\frac{d(d_{qc})}{d_{qc}} \tag{3.6}$$

If the area A and the density ρ_{qc} of the coating material, we can write $m = \rho_{qc}Ad_{qc}$. Then we can write equation 3.6 in term of mass, i.e.,

$$\frac{df_{qc}}{f_{qc}} = -\frac{dm_{qc}}{m_{qc}} \tag{3.7}$$

At this stage, Sauerbrey assume that for small mass change, the loaded mass can be considered as an equivalent mass change of the quartz crystal itself. So we can write equation

3.7 as

$$\frac{df_{qc}}{f_{qc}} = -\frac{dm}{m_{qc}} \tag{3.8}$$

where dm is an infinitesimal uniformly loaded mass distributed on surface of the quartz crystal. Suppose that this assumption is valid to an arbitrary value but small loaded mass, then it can taken as mass of thin film m_{tf}, and equation 3.8 can be written under this assumption as,

$$\frac{f_{dc} - f_{qc}}{f_{qc}} = -\frac{m_{tf}}{m_{qc}} \tag{3.9}$$

where f_{dc} stands for resonance frequency of quartz crystal with deposited material. Defining m_{tf}^{pa} and m_{qc}^{pa}, masses per unit area for deposited thin film and quartz crystal respectively. Now from 3.9 equation, we obtain

$$\frac{f_{dc} - f_{qc}}{f_{qc}} = -\frac{m_{tf}^{pa}}{m_{qc}^{pa}} \tag{3.10}$$

We can also write above mass in term thickness and mass densities for the materials in which mass density is uniformly distributed. $m_{tf}^{pa} = \rho_{th} d_{th}$ and $m_{qc}^{pa} = \rho_{qc} d_{qc}$, where ρ_{th}, ρ_{qc} , d_{th} and, d_{qc} are density of thin film, density of quartz crystal, thickness of thin film, and thickness of quartz crystal respectively. Substituting $m_{qc}^{pa} = \rho_{qc} d_{qc}$ in the equation 3.10, we obtain

$$\frac{f_{dc} - f_{qc}}{f_{qc}} = -\frac{m_{tf}^{pa}}{\rho_{qc} d_{qc}}$$

$$m_{tf}^{pa} = -\left[\frac{f_{dc} - f_{qc}}{f_{qc}}\right] \rho_{qc} d_{qc} \tag{3.11}$$

Now we use equation 3.4 and writing $f_{dc} - f_{qc}$ as Δf. So we obtain an equation for p^{th} thickness shear mode from equation 3.11

$$m_{tf}^{pa} = -p \left[\frac{\Delta f}{2 f_{qc}^2}\right] \rho_{qc} v_{qc}$$

$$\Delta f = -\frac{1}{pA} \left[\frac{2 f_{qc}^2}{\rho_{qc} v_{qc}}\right] m_{tf} \tag{3.12}$$

The realtion $v = \sqrt{\frac{\mu}{\rho}}$ where μ and ρ are bulk shear modulus and density of material respectively, is very helpful to get very famous the Sauerbrey equation. From this relation we can write, $v_{qc}\rho_{qc} = \sqrt{\mu_{qc}\rho_{qc}}$ where μ_{qc} and ρ_{qc} shear modulus and density of quartz

crystal. In equation 3.12, replacing values of $v_{qc}\rho_{qc}$ by $\sqrt{\mu_{qc}\rho_{qc}}$. We obtain

$$\Delta f = -\frac{1}{pA}\left[\frac{2f_{qc}^2}{\sqrt{\mu_{qc}\rho_{qc}}}\right] m_{tf} \tag{3.13}$$

In equation 3.12 and 3.13 where paramters following meaning

- p: p^{th} thickness shear mode of quartz crystal(p =1 stands for fundamental thickness shear mode)
- A: Active area (Piezoelectrically) of quartz crystal where mass is deposited
- f_{qc}: Resonance frequency of quartz crystal
- μ_{qc}: Shear modulus coefficient for AT-cut quartz crystal ($\mu_{qc} = 2.947\times10^{11} g.cm^{-1}.s^{-2}$)
- ρ_{qc}: density of quartz($\rho^{th} = 2.648$ g.cm^{-3})
- v_{qc} = Shear mode velocity of quartz crystal ($v_{qc} = 33400$ cm.s^{-1})
- m_{tf}: Deposited mass of thin film

Assuming that $C_{fc} = \frac{1}{pA}\left[\frac{2f_{qc}^2}{\sqrt{\mu_{qc}\rho_{qc}}}\right]$. we obtain for fundamental thickness shear mode(i.e., p =1) using equation 3.13.

$$\Delta f = -C_{fc}.m_{tf} \tag{3.14}$$

where C_{fc} is calibration constant for QCM. Taking the values of constant requires to calculate calibration constant per cm^2 area for the crystal of 5 MHz, we get C_{fc}= 0.00566 MHz.cm^2.g^{-1}. Now using equation 3.14, for the detection of the shift of 1 Hz in frequency, the mass that has to add is 17.699 ng. This calculation is for the fundamental thickness-shear mode videlicet p = 1.
We can also find thickness of the film as well. Substitute $m_{tf}^{pa} = \rho_{th}d_{th}$ in the equations 3.12 and equation 3.13.

3.4.1 The Notable features of equation 3.13 or equation 3.14

- Considering that loaded mass of material uniformly covers the active area of a quartz crystal resonator, if it is so, then intrinsic properties and the resonance frequency of quartz crystal are sufficient to get to know the amount deposited from frequency shift.
- The Second feature is that change in mass does not at all depend on the physical properties of loaded material on the surface quartz crystal.

Gunter Sauerbrey and other researchers claimed through their experimental work that is even depositing materials and using different crystals; mass sensing does not depend on the physical of deposited materials within the range of mass load.

3.4.2 Theoretical justification for the validity of equation 3.13

Even though many authors including G. Sauerbrey that for loading small mass data support with theoretical work, but the justification for theoretical work to formulate equation 3.13 requires after loading mass on the surface of the quartz, so for this, we use perturbation formulation used in the book, the theory of sound, by Rayleigh, which was then used to get equation 3.13 by Stockbridge [Warner 62]. An assumption is made, which is that mass loaded on the active surface of QCO in thickness-shear mode does not have potential energy or, in other words, the surface acoustic wave does not propagate. In order to get reasonable justification, we use equation derived for vibrations of a dimensional system.

$$f_{dc}^2 = f_{qc}^2 \left[1 - 2\frac{m_{tf}}{m_{qc}} + 3\frac{m_{tf}^2}{m_{qc}^2} - .....\right] \tag{3.15}$$

$$2\frac{m_{tf}}{m_{qc}} - 3\frac{m_{tf}^2}{m_{qc}^2} = \frac{(f_{qc} + f_{dc})(f_{qc} - f_{dc})}{f_{qc}^2}$$

where we consider only first three terms of the expansion.

$$\frac{m_{tf}}{m_{qc}} - \frac{3}{2}\frac{m_{tf}^2}{m_{qc}^2} = \frac{(f_{qc} - f_{dc})}{f_{qc}} - \frac{(f_{qc} - f_{dc})}{2f_{qc}^2}$$

quadratic terms which if we drop, we have the equation which is same as equation 3.9

$$\frac{m_{tf}}{m_{qc}} = \frac{(f_{qc} - f_{dc})}{f_{qc}} \tag{3.16}$$

The deposited mass in proportion to the thickness of thin-film d_{th}, therefore, one may think the dependence of ρ_{th} in equation 3.13 in the denominator for fundamental thickness-shear mode rather than ρ_{th}. Moreover, the resonant frequency of unloaded quartz entirely depends on the elastic constants such as shear mode velocity or shear modulus of quartz [Miller 68]. But, surprisingly, the frequency shift does not depend on the elastic constant of the thin film. Therefore, this leads to conclude for the validity of equation 3.13 that mass deposited on the active surface of quartz crystal oscillator in thickness-shear mode does not have potential energy, or in other words, the surface acoustic wave does not propagate in the film. Still, this conclusion becomes less acceptable in case of uniform coverage of film of finite thickness and an appreciable amount of deposited foreign material. Therefore, Stockbridge's explanation for the justification of equation 3.13 using Rayleigh formulation for one vibrating dimension system gives a little insight from a physics point of view.

Miller et al., correct the above problem taking into account the deposited film of foreign material in contrast to Stockbridge assumption, they do state acoustic wave traverses in the film. They use a coplanar wave acoustic analysis to the quartz crystal(composite)oscillator

with crystal oscillator density ρ_{qc}., shear mode velocity of quartz v_{qc} and thickness of film d_{qc}, a film of density ρ_{th}, the acoustic phase velocity of film v_{qc}, and thickness d_{th} is deposited. They stated in their article that given that acoustic loss in quartz and thin film are considerably small, then the frequency of quartz can found from the following equation [Miller 68]

$$2r\left[cos\left(\frac{2\pi f}{f_{th}}\right)-cos\left(\frac{2\pi f}{f_{qc}}\right)\right]+(1+r^2)\left[1-cos\left(\frac{2\pi f}{f_{th}}\right)cos\left(\frac{2\pi f}{f_{qc}}\right)\right]+(1-r^2)sin\left(\frac{2\pi f}{f_{th}}\right)sin\left(\frac{2\pi f}{f_{qc}}\right)=0, \quad (3.17)$$

$f_{qc} = \frac{v_{qc}}{2d_{qc}}$, $f_{th} = \frac{v_{th}}{2d_{th}}$, and r is reflection coefficient of acoustic wave at interface of quartz crystal and thin film. f_{th} can be considered as mechanical frequency of film if it is suspended since v_{th} is acoustic wave velocity and d_{th} thickness of the film. To obtain the relation between frequency shift and mass , J. G. Miller, and D. I. Bolef presumed that on the deposition of film the frequency shift is $\delta f = f_{dc} - f_{qc}$ and introduces convenient parameter[Miller 68] $\delta = \frac{\rho_{th} l_{th}}{\rho_{qc} l_{qc}}$(where $\delta \ll 1$) that tells that about how film of foreign material influences the resonant frequency of quartz crystal resonator. Utilizing the definition of r, the reflection coefficient, and after this do Taylor expansion of of sine and cosine in equation 3.17 upto second order, they established the relation for small load of foreign mass.

3.5 General expression to find mass using quartz crystal microbalance

In the previous the section the equation that we obtain work for small load of foreign mass (i.e $\frac{\Delta f}{f} < 0.05$). But if the ratio of Δf and f is greater than 0.05, then acoustic impedance match of quartz crystal resonator and thin film, often used as Z match method [Lu 75, Lu 72] which now become responsible and so using that method equation takes the following form to determine the mass of foreign material

$$\frac{\Delta m}{A} = \left(\frac{N_{qc}\rho_{qc}}{\pi Z f_{dc}}\right) tan^{-1}\left[Z\ tan\left(\pi\frac{f_{qc}-f_{dc}}{f_{dc}}\right)\right] \quad (3.18)$$

where parameters are :

- Δm : Mass change caused by frequency shift
- A : Active area of quartz crystal between gold electrodes
- N_{qc} : Frequency constant for AT-cut of quartz crystal($N_{qc} = 1.668 \times 10^{13} Hz.$Å)
- Z : Z factor of film material (Z = $\sqrt{\frac{\rho_{qc}\mu_{qc}}{\rho_{th}\mu_{th}}}$)
- f_{qc} : Resonance frequency of quartz crystal oscillator(viz. f_{qc} during unloaded mass)

- f_{dc}: Frequency of unloaded quartz crystal resonator
- ρ_{qc}: density of quartz crystal resonator($\rho^{qc} = 2.648$ g.cm^{-3})

Chapter 4

Mass Sensing Using Quartz Crystal Microbalance(QCM)

Abstract

In this chapter, QCM theory in the chapter 3 is made applicable for mass detection of 1,1,1,3,3,3-hexamethyldisilazane. I have calculated the change in frequency in the air just to look at whether it is working properly or not and then moved to deposit HMDS a chemical(liquid form) on the active surface of quartz crystal. I found the mass deposited in nanograms after calculation that is 1.59 $\times 10^{-8}$ grams. I used 6 MHz quartz crystal for my experiments.

4.1 Introduction

The sensors based on QCM have been very attentive in the fields of biology and chemistry apart from its application physics. The QCM sensors have been widely used for the applications in the detection of gases, chemicals, in probing biomolecular interaction and microorganism [Vashist 11]. I will discuss one of the applications in the field of chemistry of QCM based sensors in this chapter. I used 6 MHz quartz to prepare a system to detect the mass of a chemical Hexamethyldisilazane(HMDS). For the determination of mass deposited on the quartz's active surface, a rough vacuum is created in the system, and I use openQCM software to collect frequency versus time data. The vapor pressure of HMDS at room temperature is about 7 Torr, so it will quickly boil under vacuum, and a few drops of HMDS vaporizes at room temperature in a few minutes.

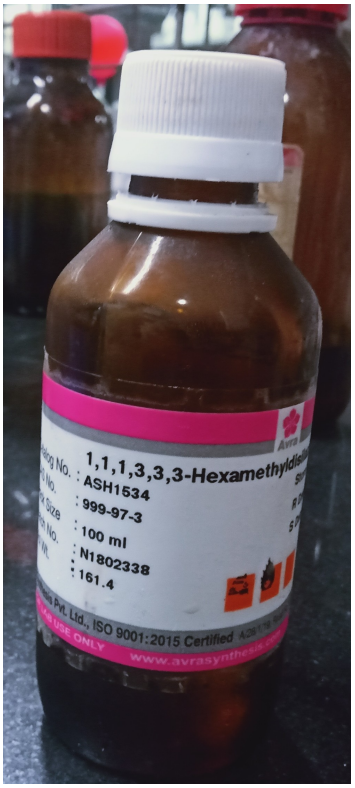

Figure 4.1: 1,1,1,3,3,3-hexamethyldisilazane

Figure 4.2: 6 MHz quartz crystal

4.2 Hexamethyldisilazane(HMDS) and 6 MHZ quartz crystal

Hexamethyldisilazane also is known as Bis(trimethylsilyl)amine is an organosilicon compound with molecular formula $[(CH3)_3Si]_2NH$. 1,1,1,3,3,3-hexamethyldisilazane is its another name [Bradley 78]. It is a colorless compound that is used as a precursor in chemical vapor deposition techniques [Nakamura 08]. It also works as an adhesion promoter for photoresists in photolithography [Izumi 06]. See Hexamethyldisilazane(HMDS) figure 4.1 and quartz crystal figure 4.2.

4.2.1 Safety and Precautions

It has an adour like Ammonia [for Biotechnology Information]. One must be careful while using this compound as it may be toxic if you inhale and may irritate your skin as well as your eyes. Due to its bad smell toxic nature, one must use Face mask and gloves too It can also decompose when it comes to contact with water and moisture or if heated [Anderson 01, for Biotechnology Information].

4.3 Experimental setup

To make a system that is capable of detecting mass within the range microgram to nanograms. One can use the vacuum tiffin box or a desiccator depending on the interest and for suitable system preparation. I took a desiccator, including a valve that helps in maintaining a vacuum. In the subsection, I mention the required materials and electronic components.

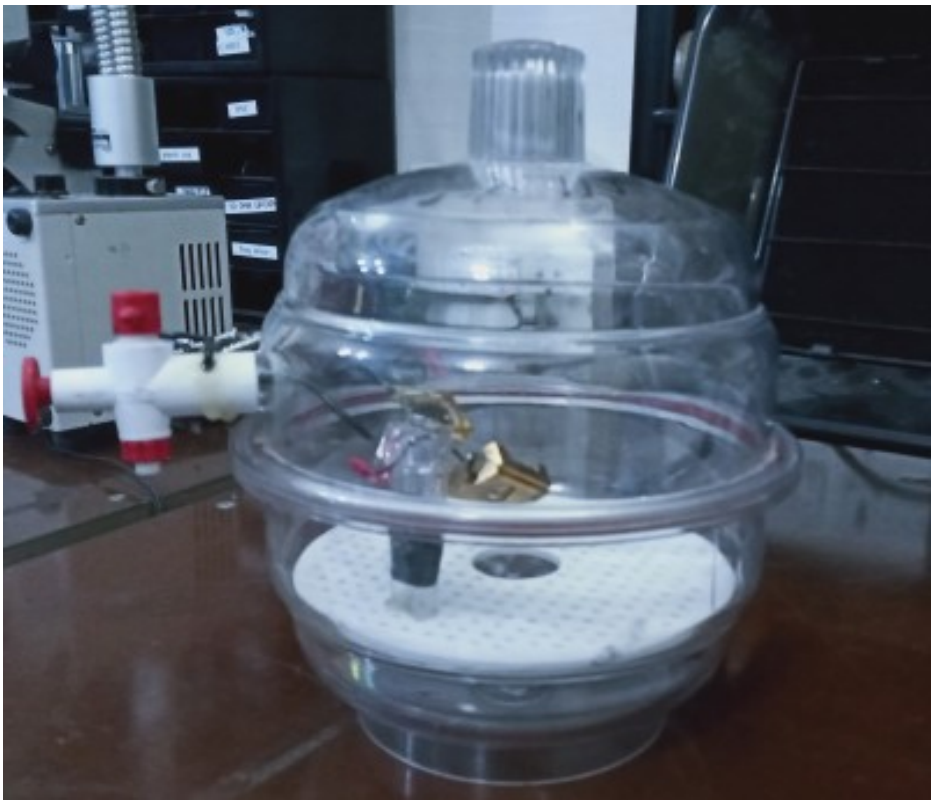

Figure 4.3: The mass measurement setup

4.3.1 Material and electronic components required

- USB cable and Wires: This is used to connect the system with the openQCM software.
- Desiccator: It is used to create a rough vacuum if needed.
- Small plastic box cylindrical shape to put compound of interest: This is used to put a sample of interest.
- Drill machine: It is used to drill hole to take wire inside the system.
- openQCM micro-controller
- Quartz crystals(6 and 10 MHz)

- Araldite adhesive

4.4 openQCM device software

openQCM is easily available free software, which is very easy to use. It is an open hardware technique that incorporates micro-controller, and in which, open-source quartz crystal is considered the heart of the openQCM device. The active surface of quartz crystal, together with micro-controller, opens many possibilities in the research in the fields of physics, chemistry, and biology. In this technique, Quartz crystals of the frequencies from 1 MHz to 10 MHz can be used. Moreover, one can modify the sensitivity of specific purposes of the study.

4.4.1 Active Surface of Quartz Crystal as a Sensing Lab

Quartz crystal micro-weighing technique has paved a way to realize that molecular phenomena on the surface of quartz crystal as this is an ultra-sensitive surface technique. Therefore, it is utilized a wide variety of research in various fields due to its friendly nature and easy to handle.

4.4.2 Open quartz crystal micro-balance's sensing principle

The principle of sensing of openQCM is based on the fantastic property of "Piezoelectricity", which I discussed in chapter 1. When we apply that voltage across electrodes, it causes mechanical vibration in the quartz crystal, and the vibration range is in MHz. This technique measures the change in the frequency upon mass application and thus calculates mass change caused by frequency shift. It can measure the change in mass due to mass load down to 0.1 nanograms. This most flexible technique is not restricted to vacuum and air but also can be used in a liquid environment.

4.4.3 The factors that significantly affect quality(Q) factor of quartz

From the observation during my experiments, I come across several factors affect the quality factor of QC or quality of sensing in liquid media which are the following:

- Viscosity of liquid
- Mass load of the liquid drop
- Ionic or polar nature of liquid materials

4.5 Results

I took the compound the HMDS initially to check how this software works, and then I started my experiments. I have detected the mass of this compound in the micrograms and

nanograms range. The value of the detected mass is 1.59 $\times 10^{-8}$ grams using the Suerbrey equation and calculation for 5 MHz quartz crystal oscillator.

4.5.1 Calculation of mass deposited of HMDS

Since Diameter of quartz active surface is 6.5mm and so r is 0.325cm. Now the active area of 6 MHz quartz crystal oscillator by the formula $A = \pi r^2 = 3.1416 \times (0.325)^2 \approx 0.332$ cm^2. $\sqrt{\rho_{qc}\mu_{qc}} = (2.947 \times 10^{11} \times 2.648)^{1/2} = 883383.04 \ \frac{g}{cm^2.sec}$ and A$\times\sqrt{\rho_{qc}\mu_{qc}} = 293106.49 \ \frac{g}{sec}$, and then $\frac{A \times \sqrt{\rho_{qc}\mu_{qc}}}{2}$ becomes 146553.24 $\frac{g}{sec}$, which is nothing but the constant C_{qc} used in the Sauerbrey equation 3.14. Ultimately the m_{HMDS}=$-\frac{\Delta f}{f_{qc}^2} \times 293283.16$ = -1.59 $\times 10^{-8}$ grams

4.5.2 Plots for deposited mass of HMDS and resonant frequency of QCO in rough vacuum

Below, the figures are of the base frequency and frequency of deposited HMDS.

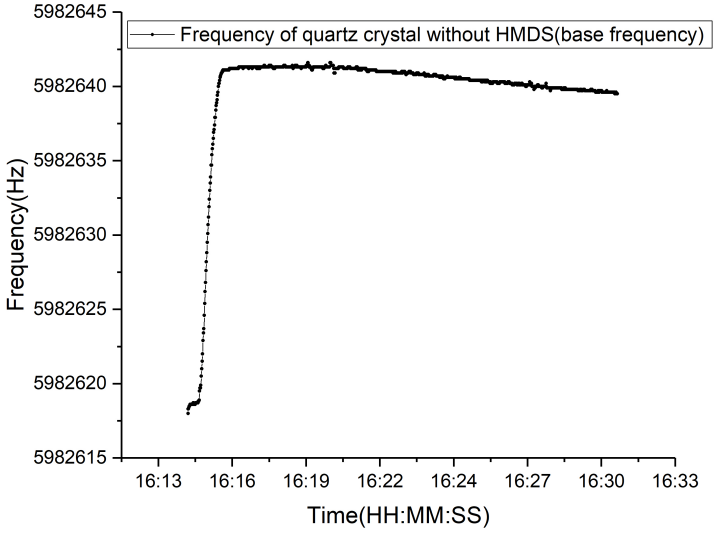

Figure 4.4: Frequency Versus Time plot without HMDS

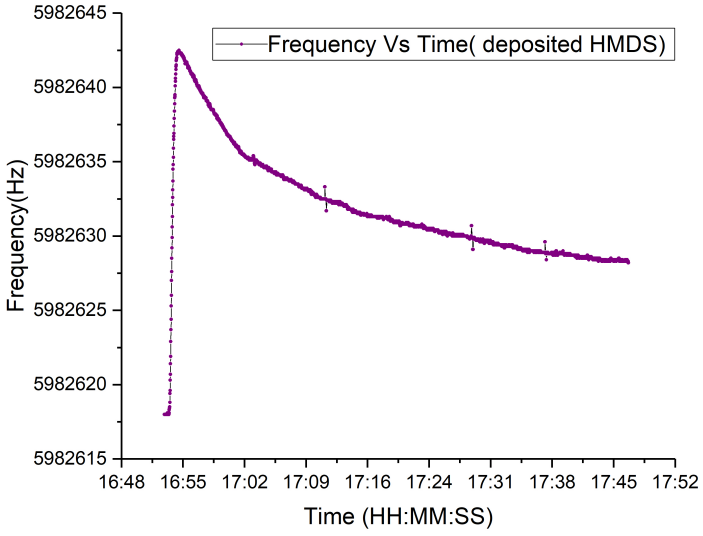

Figure 4.5: Frequency Versus Time plot for deposited HMDS

Chapter 5

Study of Physical Properties of Liquid Crystal

Abstract

In this chapter, study of the physical properties such as phase transition of one phase to another, of a liquid crystal 4-Cyano-4'-pentylbiphenyl(5CB) is done. I use of quartz crystal(QC) of 10 MHz, including LabVIEW, Signal generator, Lock-in Amplifier. It has chemical formula C18H19N and goes to isotropic phase from nematic phase at 35° [Lebovka 13].

5.1 Introduction

Micro-weighing through piezoelectric quartz crystal(PQC) also plays an important role in the study of many thermal physical properties, especially phase transition temperatures of Liquid Crystals(LCs) and lipid multilayers films [Okahata 89]apart from wide application in making mass sensors. Micro-weighing through piezoelectric quartz crystal has become a powerful tool to examine the structural changes at solid-liquid interface [Ishida 07] because of its high sensitivity on the surface of quartz crystal. The basic principle is the same as I showed the change in mass due to frequency shift, but there I was looking changes with time, in this obviously with temperature.

5.2 Material and electronics required

- Lock-in amplifier and signal generator
- SMA cables and BNC cables
- 5CB liquid crystal
- Injection with a syringe

5.3 Setup for experiments

I have described the main materials and electronics required to make setup for measurement in section 5.2.

Figure 5.1: 5CB liquid Crystal phase transition measurement setup

5.4 4-Cyano-4'-pentylbiphenyl liquid crystal

The liquid crystal 4-Cyano-4'-pentylbiphenyl whose short name is 5CB. See figure 5.2

It goes crystalline phase to nematic phase at 24 ° and nematic to isotropic phase 35°. See figure 5.3. It is commonly used in the nematic phase, and its molecular formula is C18H19N. During its alteration in the phase nematic(the milky color) it becomes colorless

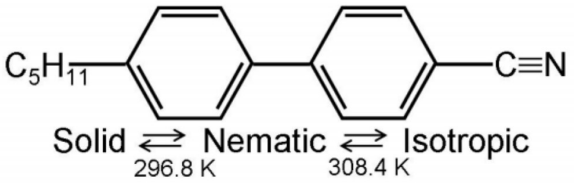

Figure 5.2: Chemical structure of 5CB with its phase transitions
Figure Courtesy: https://arxiv.org/pdf/1303.0569

in the isotropic phase that I observed during the experiment. William Gray, Ken Harrison, and J.A. Nash at the University of Hull in 1972 are those who first synthesized it.

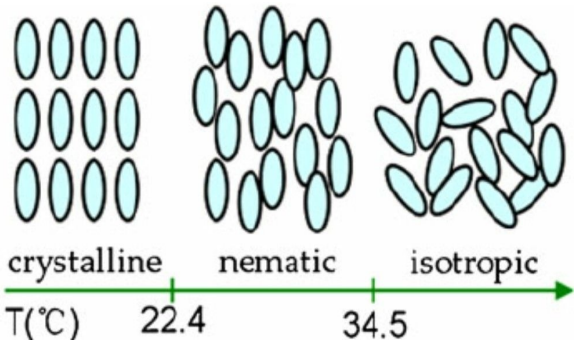

Figure 5.3: Molecular arrangement of 5CB liquid crystal at transition temperatures
Figure Courtesy: https://link.springer.com/article/10.1007/s00397-013-0732-4

5.5 Methodology

One needs a mini circuit splitter through which three SubMiniature version A (SMA) comes out and in which one goes reference of the signal generator, and the second one goes to reference in of lock-in amplifier that goes to another electrode of quartz, and the third one goes one of the electrodes of quartz crystal. For the data collection, what one needs is to write a program in LabVIEW. In the figure on the table, we have a quartz crystal resonator connected with the thermocouple and heated via irradiation from an artificial lamp.

5.6 Results

I have got a signature of phase transition of 5CB liquid crystal in the vicinity of its transition temperature. This deviation from its exact transition temperature is due to not having excellent control of the heating system. I have obtained a sharp change in frequency at temperature 34.2 °C. Moreover, to confirm, I used the openQCM system to take more data points and to observe a sharp change in frequency to heat 5CB liquid crystal. But this data of frequency is with respect time not with temperature. I have also measured the Q factor,

which also sharply changes during the transition. The ultimate concept in such change from the nematic phase to the isotropic phase entirely depends on the mass variation due to the change in its molecular arrangement while heating via irradiation of light, which heats the crystal. One can see the phase transition of 5CB liquid crystal in these figures 5.4, 5.4, 5.6, and 5.7 respectively.

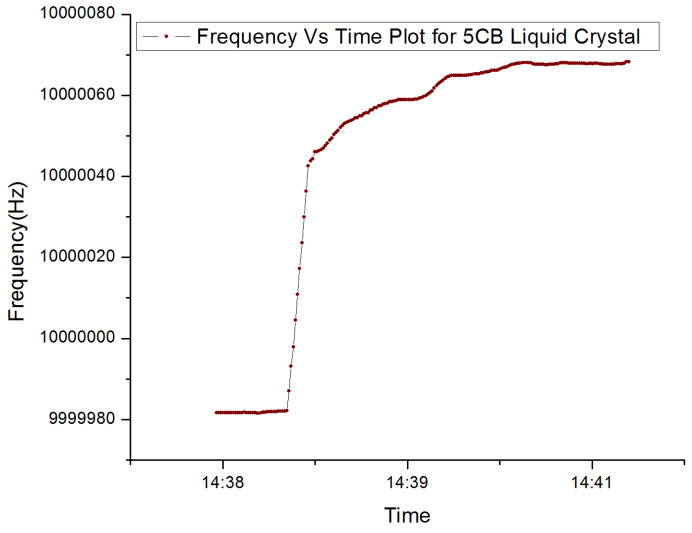

Figure 5.4: Frequency versus Time plot for 5CB liquid crystal(run 1)

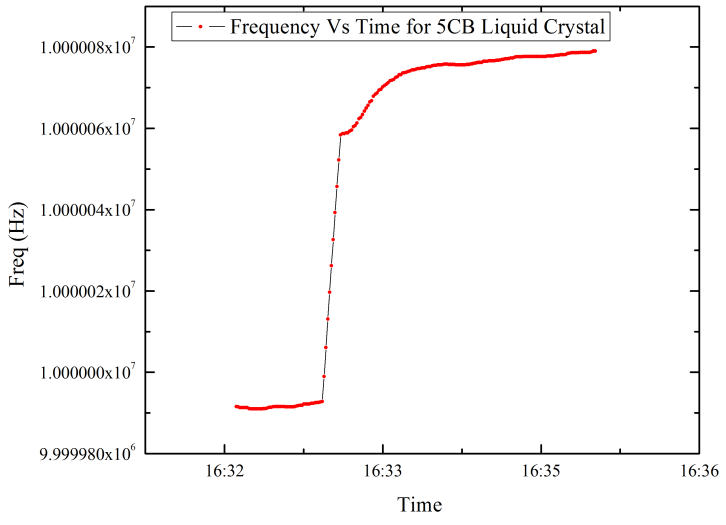

Figure 5.5: Frequency versus Time plot for 5CB liquid crystal(run 2)

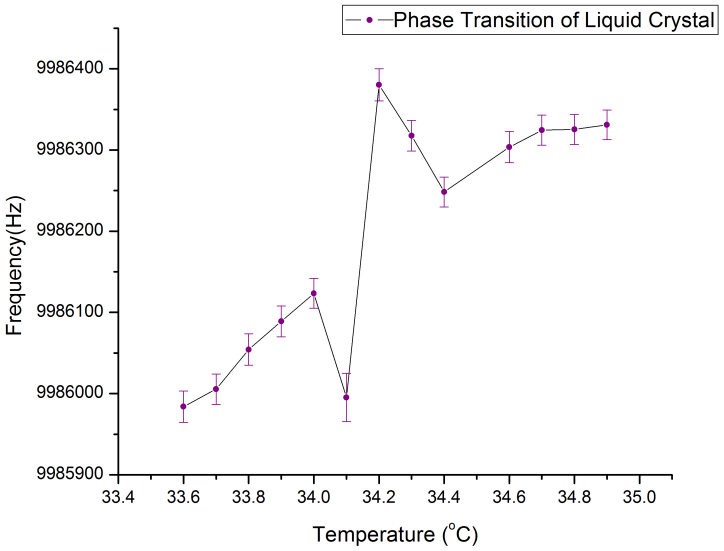

Figure 5.6: Frequency Versus Temperatute plot for 5CB liquid Crystal

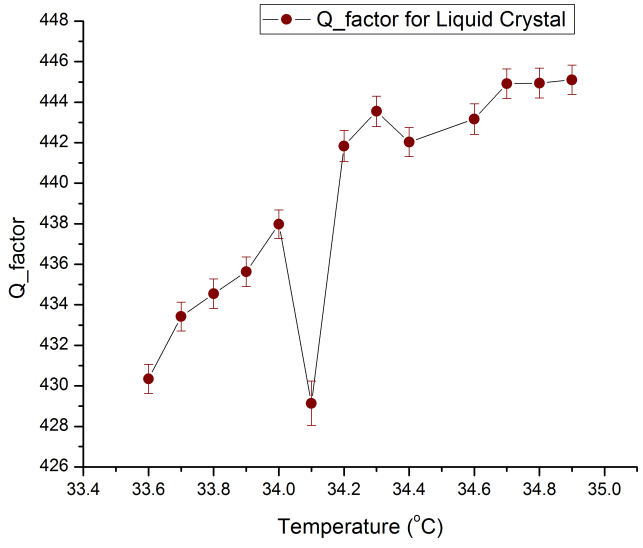

Figure 5.7: Q factor of quartz for 5CB liquid crystal phase transition

Chapter 6

Future Plans

6.1 Plans in the future

In my master thesis, the scientific work that I did is limited to mass detection and phase transition study. I have not touched the probing bio-molecular interaction in this thesis and have not directly involved in the application of quartz crystal resonator from the physics point of view. For example, since the articles have reported that magnetic properties be studied [Janata 10] and noise measurement [Sedlak 12] can be done using quartz crystal microbalance. I am excited and curious to develop the system for such studies very compatibly. My plans in the future are the following-

- With the slight, the modification in the developed system, to precisely observe phase transition of those liquid crystals which have more than one phases
- Developing a system that utilizes quartz crystal oscillator with the inclusion of other electronics such as oscilloscope, lock-in amplifier, and signal generator
- Study magnetic properties of different materials by developing a more suitable system described in article [Janata 10]
- Study of bio-molecular interaction of using quartz crystal microbalance

Appendix A

Gold Etchant: Potassium Iodide Solution Preparation

A.1 Purpose

Gold etchants are those chemical solutions that purposely are used to etch thin film of gold in micro/nanoelectronic devices fabrication.

A.2 Time required to etch gold

The thickness of the film is a crucial factor on which time to etch gold in this process depends, and The rate to etch gold at room temperature for the KI solution is 0.5 – 1 μm/min.

A.3 Material required

Potassium Iodide
Iodine
DI water
Glass container (Beaker)

A.4 Personal safety equipment(PSE)

The following equipment are essential for this process:

1. Safety glasses for eyes protection (optional with face shield).
2. Use Nitrile safety gloves and check gloves for leaks before use.
3. Wear cleanroom suit for protective clothing

A.5 Preparation recipe

To complete this process, it takes approximately five minutes. The preparation recipe for KI solution with Iodine is given below:
4 g KI (solid)
1 g I_2 (solid)
40 ml distilled water

A.6 Preparation procedures

The solution is prepared in the following ways:

1. Before entering the cleanroom, wear a cleanroom suit. To measure KI(4 grams) and I_2(1 gram), use the digital balance.

2. Then pour 40 ml distilled water in the container and dissolve these solid materials by shaking. Dissolve both solids using mild shaking.

3. Put the solution in a bottle (glass) and label "Gold etchant 1:4:40 I_2/KI/H2O" and level it with the date and your name. After the preparation solution looks as in the figure A.1

Figure A.1: KI + I_2 solution prepared for gold etch

A.7 Operational procedures

For the operational procedure, one must follow these steps:

1. Take two clean glass beakers in the operated fumehood, and pour distilled water in one of them for rinsing the sample and another one for the gold etchant.

2. Estimate the time for etching your sample, and for that, you need to know the thickness of your gold layer.Recommended operating temperature by Transene Company is 20 – 80 ^{o}C (30 – 40 ^{o}C most common). See A.2 for the etch rate as function of the temperature.

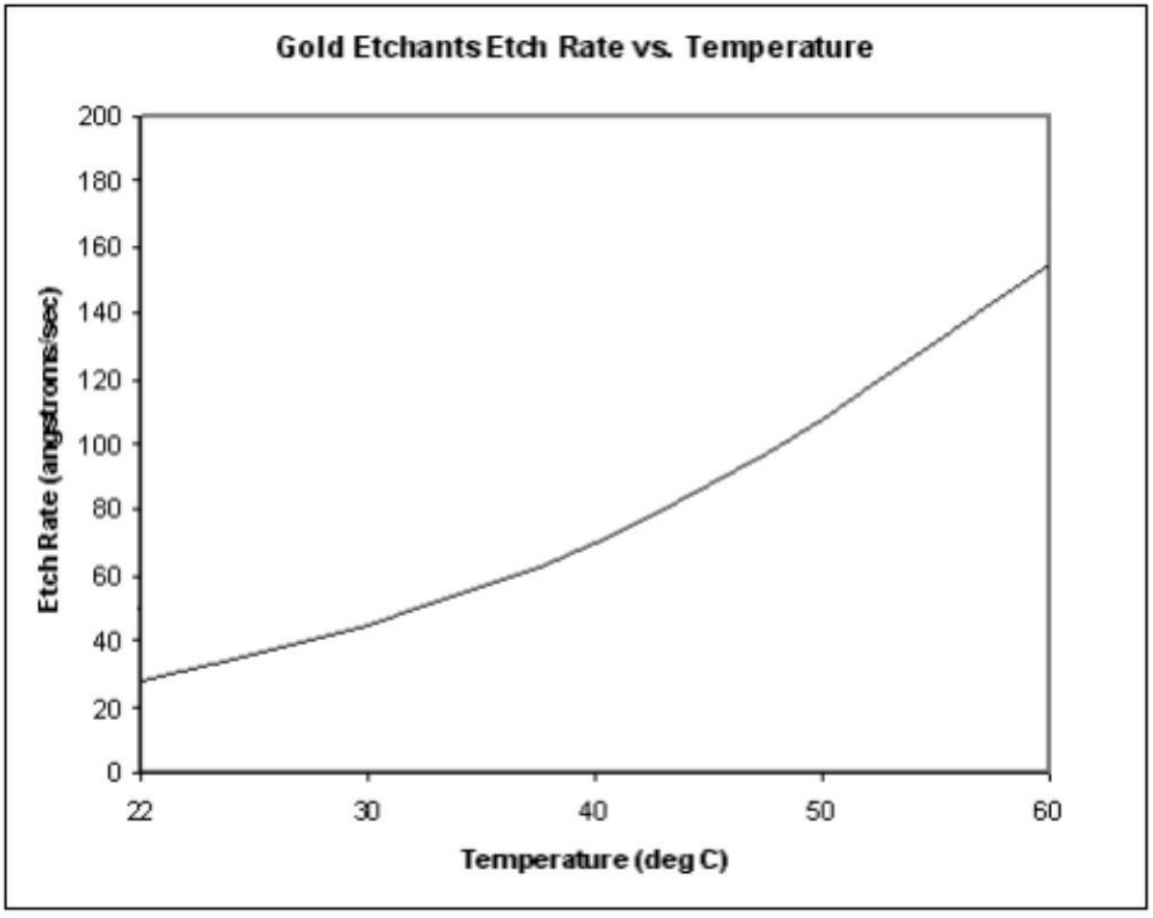

Figure A.2: Etching rate versus temperature graph
Figure Courtesy:https://engineering.tufts.edu/microfab/documents/SOPGoldEtch.pdf

3. To etch gold etch, Put your substrate into the etchant (use a Teflon tweezer if you have), for the appropriate amount of time calculated in the previous step. Near the expected etch-time, check the substrate rinsing it by distilled water every 30 seconds until the gold color is gone.

4. If etchant at the surface becomes saturated and fresh etchant cannot reach the surface, then etching will slow down. Mild shaking can be used to bring etchant to the surface and promote etching. In this case, it will be useful to use a magnetic stirrer and carefully swirl your etchant to accelerate the etch and improve uniformity [6].

5. The etchant can also be re-used if it is clean. Put recycled etchant back in the proper location (in an assigned position under a fume hood).

A.8 Rinsing with distilled water

For rinsing, one must follow these steps:

1. When you see the etch process is complete, move the substrate with care to rinse first with distilled water for 5 minutes.

2. If you used Teflon tweezers in this process, then you should also rinse your tweezers.

3. Bring your substrate in another glass beaker with new DI water and rinse again for another 5 minutes.

A.9 Blow dry of the substrate

For this process, one must follow these steps:

1. When the rinsing process is finished, remove your sample and blow-dry with the N_2 gun.

2. If the sufficient amount of water has gone, it is your choice to dry the samples on a hotplate at 150^{o}C or at 120 ^{o}C in the oven.

3. Check whether some un-etched gold features are remaining, and if features are visible, use an optical microscope. If more etch time is required, transfer the substrate back into the glass beaker with the etchant for another 30 seconds while swirling. Repeat the processes for rinse and drying the substrate.

4. It is suggested but optional by the supplier Transene that if some dark residues are remaining on the substrate, one can do rinse them with alcohol followed with another alcohol rinse.

A.10 Cleanup

First, let the etchant cool down to room temperature. The cold etchant can be reused again following the supplier specifications. The etch capacity is 17.2 g/L. If the etch capacity is achieved, you can follow the following steps.

1. When the used etchant is at room temperature, pour it in over the other two beakers filled with DI water.
2. Fill the glass beaker where you put the etchant with DI water. To take out the waste from all the beakers, one can use venturi.
3. Rinse all the beakers with DI water three times, turn all the beakers upside down, wash the outside with DI water, and blow-dry them with the N_2 gun.
4. Put all used equipment at their place in the fume hood and cleanroom suit to its proper location.
5. Throw gloves in the waste container

A.11 Safety and Emergency

The most important point is this for personal safety among all the above points. One must follow safety and emergency procedural regulations suggested by INRF. It is suggested to perform this work in the fume hood with nitrile gloves and eye protection.

The toxic nature of Iodine may be dangerous in case of inhalation or swallowing. It is corrosive and causes burn by breath and through skin absorption. It is readily absorbed through the skin, very destructive for the lungs, eyes, and skin, a severe irritant. Sublimation of Iodine takes place at room temperature to yield dangerous levels of vapor. Inhalation of KI dust can also cause in the respiratory system. It is also an eye irritant; therefore, it may cause sensitization or allergic reaction.

1. In the situation of exposure to eyes, immediately flush with diphoterine and also lift upper and lower eyelids occasionally after diphoterine, flush with water for at least 15 minutes. To minimize burn, seek immediate medical attention. Press the evacuation button.
2. In the situation of exposure to skin, take off clothes that are contaminated. Wash your skin with diphoterine, flush your face then with water for 15 minutes. For any irritative sensitization, seek immediate medical attention. Press the evacuation button.
3. In the situation of Inhalation, come to take fresh air. Revivification if it is necessary. Be careful not to inhale any fumes that come out from the victim's lungs. Press the evacuation button.
4. In the situation of Ingestion, do not bring about vomiting. Get immediate medical attention. Press the evacuation button.

Appendix B

Hanging/Suspended PMMA for Facile Electon Beam Lithography

B.1 Purpose

Facile spin-free dry transfer of method based on electron beam lithography is beneficial for the substrates that are fragile, non-planar, and irregular. For example, Si substrate, cylindrical shape wire., etc. In this technique, PMMA of uniform thickness is done by dry transfer including electron beam lithography, lift-off process, and thermal metal deposition [Chang 14].

B.2 Introduction

Miniaturization and performance improvements are two important key points that have been very attentive in the fabrication of microscale and nanoscale electronic devices [Tseng 03], and thus for the advancement of nanotechnology; hence, driving the electric industry to make the size smaller and smaller the electronic components. Electron Beam Lithography(EBL) is an inevitable technique for patterning submicrometer features [Rius Suñé 08] on a chip/substrate; therefore, this technique has a significant advantage in the characterization of materials, commercial applications and for fundamental research in the field such as bio-engineering, nanomechanics.
For high-resolution electron beam lithography, it is essential to get a uniform coverage of electron to resist on the substrate/sample, so for that such uniform coverage, Polymethyl methacrylate (PMMA) is most commonly used. One demerit of PMMA is that it is incapable of providing such uniform coverage on the irregular shapes due to edge bead effects. Moreover, there is a big problem with EBL on the samples that have highly curved surfaces. Several alternative methods have been provoked to overcome such challenges, including photo-resistant evaporation, use of dry-film photoresist, or even films of ice, spray coating.

In the electron beam lithography, spray coating of PMMA, which acts as an electron beam resist, is a decent technique to deposit uniform electron beam resists layers on the non-planner surfaces or the surface with high topography with a controllable thickness. Spray coating method [Linden 11] requires special kind optimized mixture of ketone, acetate, and PMMA to realize vaporization during the process of spray coating. Ice resist has been invoked to non-planner and fragile substrate, for example, carbon nanotubes. For ice lithography, A special kind of system is required in which the field emission scanning electron microscope (SEM) modified, and the sample must be kept below 120 ^{o}C [Han 12]. Evaporation of Polystyrene (PR) thermally has been applied in e beam lithography to get 15 nm resolution, but due to weak exposure sensitivity of PR compared to PMMA and Evaporation(thermally), equipment makes complicated and accounts for the cost to the process. Furthermore, Focused Ion beam [Tao 91] provides similar benefits but the problems are very high cost and limitation of deposition materials.
Ultimately, technique with low cost for pattern transfer on fragile and non-planar substrate would be more beneficial. Such a technique is facile electron beam lithography. [Chang 14].

B.3 Preparation of hanging/suspended PMMA

We will learn in this section how to make suspended PMMA. To achieve hanging/suspended PMMA, In the cleanroom, take a clean glass slide. See B.1(a). Attach a scotch tape on the clean glass plate and then in the spin coating machine, Lift of Resist PMMA is coated, it is baked at 150^{o}C. Please wait for it to come to room temperature. Then Again, spun PMMA A4 on a glass plate in a spin coating machine and Bake at 150^{o}C. See B.1(b). After this, take Kapton tape and make a hole using a razor blade, as shown in B.1(c) and attach it carefully on the glass slide and press the opposites sides whose space are much smaller than the size of the hole in the square. See B.1(b & c). At last, peel the Kapton tape off, but be careful while doing so lesser space sides of Kapton tape may tear. After doing this, one must be able to achieve hanging/suspended PMMA highlighted with a red square. See B.1(e)

B.4 Application of hanging/suspended PMMA

Facile spin-free dry transfer of method based on electron beam lithography has many applications in the fields of NEMs/MEMS, nanoscience, and material physics.

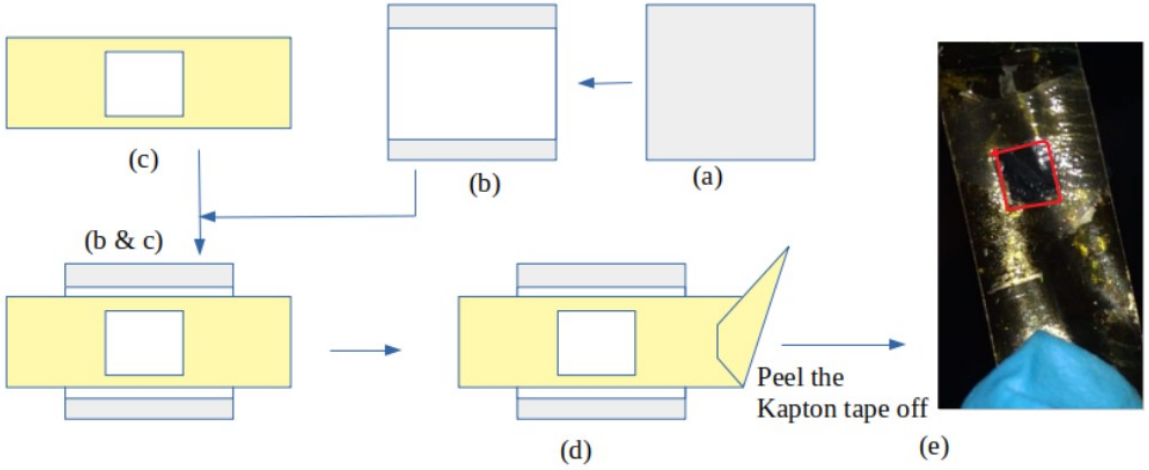

Figure B.1: Hanging/Suspended PMMA steps through figures (a,b,c,(b&c),d),e)

Appendix C

Substrate Cleaning, Coating and Metal Deposition in the Cleanroom

C.1 Purpose

In the nanofabrication, it is very important to know about substrate cleaning in the cleanroom. This is the primary and first and foremost process that is very important for nanoscale device fabrication. Moreover, it is a compulsory process which is adopted by scientific research and manufacturing.

C.2 Material required

Isopropyl Alcohol/Ethanol
Methanol
Acetone
Si-substrate.
Diomond cutter
N_2 gun
Ethyl lectate
Nitrile Safety Gloves and Mask

C.3 Procedure of cleaning Si substrate

The following steps are very important for cleaning. To follow the procedures below, Wear the first cleanroom suit and gloves then after entering the cleanroom.

Cutting

1. Coat PMMA on the substrate before cutting using diamond cutter it into small pieces(Cut more than three in a single time.

Simple cleaning

2. Remove PMMA with acetone and heat it at 50^o C.
3. Dip the chips in Isopropyl alcohol or methanol and blow dry them with N_2 gun.

Proper cleaning

4. Dip the chips in ethyl lactate and sonicate for 5 minutes in a sonicator. Then flow dry chips with N_2 gun.
5. Dip the chips in acetone and sonicate for 5 minutes in a sonicator. Do not blow-dry chips taken out from acetone, with N_2 gun as it will make the surface of chips rough.
6. Dip the chips in Isopropyl alcohol or methanol and sonicate for 5 minutes in a sonicator. Then blow-dry chips with N_2 gun.
7. Take a clean glass and wrap it with aluminum foil.
8. Put the chips on top of this glass slide wrapped with aluminum, then on a hot plate at 180^o C for 5 minutes.
9. Leave the chips for cooling for 5 minutes.

Coating

For coating, there are two types of resist. One for lift-off process(sensitive to electron beam) and the second one to make pattern or mask (sensitive to PMMA)

10. Spin coat the resist (firstly LOR 1A and then PMMA) setting the following parameters in a spin coating machine.
    (i) 500 rpm for 5 seconds
    (ii) 4000 rpm for 30 seconds
11. Bake the chips on a hot plate at 180^o C for 5 minutes.
12. Scratch edge for focusing electron beam.
13. For the good focus using spot focusing.

C.4 Deposition of the Au-Pd in thermal evaporator and results from SEM characterization

I attempted to make a thin film metallic glass of Au-Pd in a cold environment, I mean in the presence of liquid nitrogen that affects the kinetics of molecule, which results in changes in the uniformity of deposited substrate.

- Rate : 10 $\mathring{A}$ per second
- Current : 167 Amp
- Vacuum : 1.2 $\times 10^{-6}$
- Thickness: 90nm

Results from the SEM characterization I got were the ratio of Pd to Au was 30% : 70%. Grain size after deposition varies from 10 to 15 nm. So it becomes clear that Au-Pd does not make a thin film in the cold environment and the rate, current, vacuum mentioned above.

Appendix D

EagleCAD For Wilkinson Power Devider

D.1 Purpose

Wilkinson power divider is used to divide power into two arms. EagleCAD software is used to make it.

D.2 About EagleCAD software

EagleCAD stands for Easily applicable graphical layout editor Computer-Aided Design. It is PCB design software which is widely made schematic of electronic circuit and layout of a board, designing PCB and adding features such as schematic editor, a printed circuit board (PCB) layout, and an Auto Router Module, computer-aided manufacturing (CAM). It is beneficial for students and professional researchers in electronic circuits design.

D.3 How to start EagleCAD ?

To get start EagleCAD, look at the following steps.

1. Choose first your operating system.
2. Click on the link:https://www.autodesk.in/products/eagle/free-download and see also features of EagleCAD if you wish.
3. After downloading, install your system and create your in Autodesk to start EagleCAD or if you already have then log in.

D.4 How to make Wilkinson power divider

Follow the following steps to make it.

1. Open the EagleCAD by clicking. Go the Projects and make a folder and name it.
2. Go to the new project just by right-clicking.
3. Go to New and choose the library. Choose footprint and at below click it and write the name of your wish.
4. Choose layer one and click on the polygon.
5. Choose wire bend accordingly and spacing as well.
6. Write down the coordinates using the parameters listed in table D.1 below for 4GHz, D.2 for 6GHz, and D.3 for 8GHz respectively.

4 GHz Wilkinson Power Devider					
$\epsilon_r = 10$ & h = 0.6mm & t = $35\mu m$ & $f = 4$ GHz					
Impedance(Z)	Width(w)	$\frac{\lambda}{4}$	Impedance(Z)	Width(w)	$\frac{\lambda}{4}$
50 Ohm	0.5374005 mm	7.3992031 mm	70.7 ohm	0.2165527 mm	7.69007988 mm

Table D.1: Parameters value for 4 GHz Wilkinson Power Devider in EagleCAD

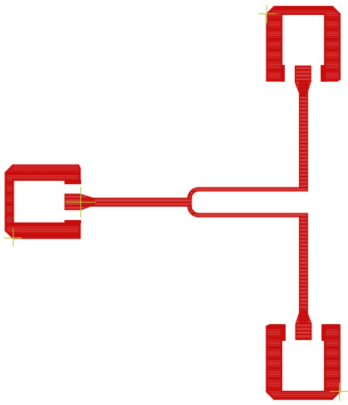

Figure D.1: 4 GHz Wilkinson power devider in EagleCAD

6 GHz Wilkinson power devider					
$\epsilon_r = 10$ & h = 0.6mm & t = $35\mu m$ & $f =$ 6 GHz					
Impedance(Z)	Width(w)	$\frac{\lambda}{4}$	Impedance(Z)	Width(w)	$\frac{\lambda}{4}$
50 Ohm	0.5312 mm	4.9106 mm	70.7 ohm	0.2140029mm	5.10998 mm

Table D.2: Parameters values for 6 GHz Wilkinson power devider in EagleCAD

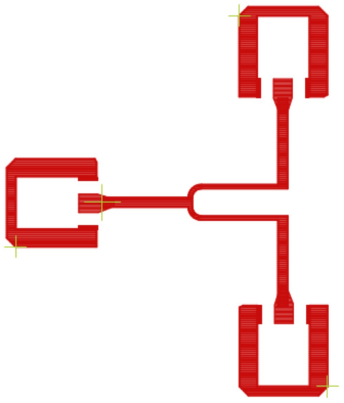

Figure D.2: 6 GHz Wilkinson power devider in EagleCAD

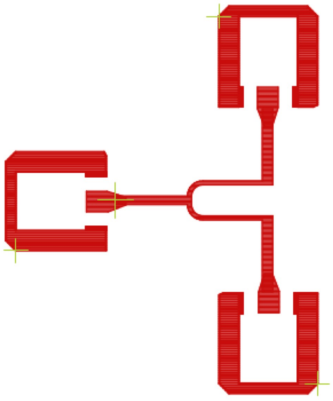

Figure D.3: 8 GHz Wilkinson power devider in EagleCAD

8 GHz Wilkinson power devider					
$\epsilon_r = 10$ & h = 0.6mm & t = $35\mu m$ & $f =$ 8 GHz					
Impedance(Z)	Width(w)	$\frac{\lambda}{4}$	Impedance(Z)	Width(w)	$\frac{\lambda}{4}$
50 Ohm	0.0.5237121 mm	3.6661118 mm	70.7 ohm	0.2106 mm	0.3815689 mm

Table D.3: Parameters values for 8 GHz Wilkinson power devider in EagleCAD

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