Senior Theses   Student Scholarship & Creative Works

5-25-2017

Thin Film Thermal Deposition at Various Pressures

James Kela Yee Keen Grace
Linfield College

THIN FILM THERMAL DEPOSITION AT VARIOUS PRESSURES

James Kela Yee Keen Grace

A thesis submitted for the degree of Bachelor of Applied
Physics

May 2017

THESIS COPYRIGHT PERMISSIONS

Please read this document carefully before signing. If you have questions about any of these permissions, please contact the DigitalCommons Coordinator.

Title of the Thesis:

Thin Film Thermal Deposition At Various Pressures

Author's Name: (Last name, first name)

Lumay, James

Advisor's Name

Joelle Murray

DigitalCommons@Linfield is our web-based, open access-compliant institutional repository for digital content produced by Linfield faculty, students, staff, and their collaborators. It is a permanent archive. By placing your thesis in DigitalCommons@Linfield, it will be discoverable via Google Scholar and other search engines. Materials that are located in DigitalCommons@Linfield are freely accessible to the world; however, your copyright protects against unauthorized use of the content. Although you have certain rights and privileges with your copyright, there are also responsibilities. Please review the following statements and identify that you have read them by signing below. Some departments may choose to protect the work of their students because of continuing research. In these cases, the project is still posted in the repository but content will only be accessible by individuals who are part of the Linfield community.

CHOOSE THE STATEMENT BELOW THAT DEFINES HOW YOU WANT TO SHARE YOUR THESIS. THE FIRST STATEMENT PROVIDES THE MOST ACCESS TO YOUR WORK; THE LAST STATEMENT PROVIDES THE LEAST ACCESS.

✓ **I agree** to make my thesis available to the Linfield College community <u>and</u> to the larger scholarly community upon its deposit in our permanent digital archive, DigitalCommons@Linfield, or its successor technology. My thesis will also be available in print at Nicholson Library and can be shared via interlibrary loan.

OR

_____ **I agree** to make my thesis available **only** to the Linfield College community upon its deposit in our permanent digital archive, DigitalCommons@Linfield, or its successor technology. My thesis will also be available in print at Nicholson Library and can be shared via interlibrary loan.

OR

_____ **I agree** to make my thesis available in print at Nicholson Library, including access for interlibrary loan.

OR

_____ **I agree** to make my thesis available in print at Nicholson Library only.

Updated April 2, 2012

NOTICE OF ORIGINAL WORK AND USE OF COPYRIGHT-PROTECTED MATERIALS:

If your work includes images that are not original works by you, you must include permissions from original content provider or the images will not be included in the repository. If your work includes videos, music, data sets, or other accompanying material that is not original work by you, the same copyright stipulations apply. If your work includes interviews, you must include a statement that you have the permission from the interviewees to make their interviews public. For information about obtaining permissions and sample forms, see http://copyright.columbia.edu/copyright/permissions/.

NOTICE OF APPROVAL TO USE HUMAN SUBJECTS BY THE LINFIELD COLLEGE INSTITUTIONAL RESEARCH BOARD (IRB):

If your research includes human subjects, you must include a letter of approval from the Linfield IRB. For more information, see http://www.linfield.edu/irb/.

NOTICE OF SUBMITTED WORK AS POTENTIALLY CONSTITUTING AN EDUCATIONAL RECORD UNDER FERPA:

Under FERPA (20 U.S.C. § 1232g), this work may constitute an educational record. By signing below, you acknowledge this fact and expressly consent to the use of this work according to the terms of this agreement.

BY SIGNING THIS FORM, I ACKNOWLEDGE THAT ALL WORK CONTAINED IN THIS PAPER IS ORIGINAL WORK BY ME OR INCLUDES APPROPRIATE CITATIONS AND/OR PERMISSIONS WHEN CITING OR INCLUDING EXCERPTS OF WORK(S) BY OTHERS.

IF APPLICABLE, I HAVE INCLUDED AN APPROVAL LETTER FROM THE IRB TO USE HUMAN SUBJECTS.

Signature _Signature redacted_ Date 05/25/17

Printed Name James Grace

Approved by Faculty Advisor _Signature redacted_ Date 8/8/17

Updated April 2, 2012

Thesis Acceptance

Linfield College

Thin Film Thermal Deposition At Various Pressures

Submitted by: James Kela Yee Keen Grace

Date Submitted: May, 2017

Thesis Advisor: _____*Signature redacted*_____

Dr. Michael Crosser

Physics Department: _____*Signature redacted*_____

Dr. Tianbao Xie

Physics Department: _____*Signature redacted*_____

Dr. Joelle Murray

Abstract

This research was to verify the hypothesis that resistivity of metal's thin film deposited in a low pressure environment is the same as it's solid material. Thermal Evaporation is a thin film deposition technique in which metal inside a vacuum is evaporated then deposited onto a surface. Higher quality metal films are deposited when the vacuum pressure is lower. At higher pressures, more air molecules are trapped within the layers of metal, thus increasing scattering sites and increasing the resistance. However, reaching a lower pressure requires more time and effort. In this research, films were deposited at various pressures and resistivities were calculated for each film to determine an ideal pressure range that creates the least resistivity.

Contents

Chapter 1

1 Introduction

There are many ways to deposit thin films onto a substrate, which include: Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD), and Molecule Beam Epitaxy (MBE). For this research, Physical Vapor Deposition was applied using thermal evaporation through thermal induction. There are multiple other PVD techniques, such as thermal conduction and electron beam bombardment.

Evaporation is accomplished in a vacuum chamber and requires a low pressure. This thin film is usually only a few hundreds of nanometers thick. The material to be evaporated is placed in a tungsten boat and a high current is sent through the boat. The applied current heats the metal near its melting point and is evaporated onto the substrate.

These techniques have been around since the early 1900s. For example, CVD was used to coat silverware, as well as by Thomas Edison to coat his phonograph recordings [1]. Mirrors were also created using this method by applying a thin film of a shiny metal (aluminum, silver) to a large sheet of glass. This would create the reflective surface of a mirror.

There are free electrons inside conductors, so electrons move much more easily through conductors than insulators. For this reason conductive metals were used for experiments. When a current is sent through a conductor, the electrons are forced to go in one direction. The electrons to bounce off of atoms and other electrons causing inelastic collisions, transferring kinetic energy from the moving electron to the atoms and other electrons. This kinetic energy transfers to vibrations which creates higher temperature within the metal. The relationship between temperature and velocity can be explained using this equation:

$$\frac{3}{2}kT = \frac{1}{2}mv^2 \tag{1}$$

where k is Boltzmann's constant, T is temperature, m is the mass of the molecule, and v is the velocity of the molecule. Since k and mass are constant, when temperature increases velocity increases as well. This explains how the metals are evaporated. As current is sent through the metal temperature increases, causing the electrons to move through the metal faster and increasing inelastic collisions. This leads to more vibrations, breaking down the solid state of the metal into a liquid. As current increases even more, the increased vibrations change the metal from liquid to a gas, evaporating into the air.

Chapter 2

2 Background Information

2.1 Thin Film Resistivity - Drude Model

Electrons move through materials based on their placement in the Fermi energy level. The Fermi energy level is the maximum energy which electrons exist at absolute zero Kelvin. With semiconductors and insulators, there is a band gap between the valence and conduction band. For semiconductors, only a few electrons are able to pass the gap. Insulators completely block electrons moving through the gap. However, conductors surround the Fermi energy level, allowing electrons to freely pass between the valence and conduction band at 0 Kelvin. This is the reason metals are considered conductors.
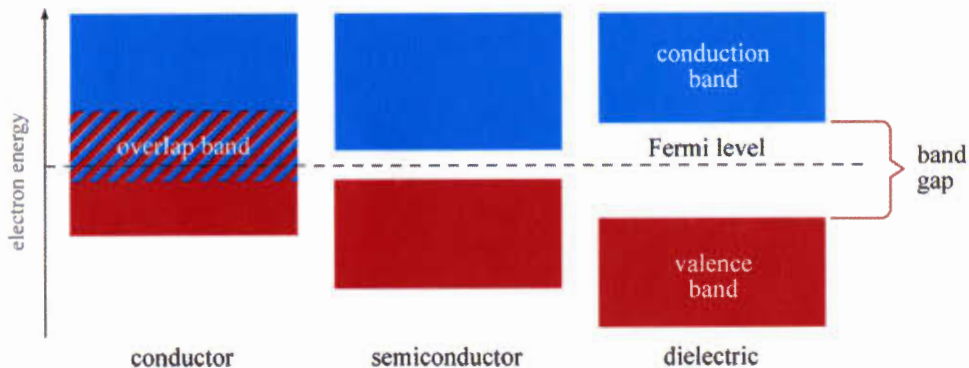
Figure 1: Energy Band Gap Graphs of Conductors, Semiconductors, and Insulators

Paul Drude and Hendrik Lorentz developed a theory of electric properties for metals based on electron gas [2]. The outer orbital electrons in metals are conductive; free to move through the metal. This free motion can be modeled as electrons, allowing us to ignore the atoms since they do not affect motion. The motion of the electrons are random and do not have a set path. For this reason electron are able to be model as a gas in conductors. Scattering changes the time it take to go from point A to point B, as seen in Figure 2.

Electrons attempt to reach their destination in a straight line, but are interrupted when they collide with atoms and other electrons, called scattering sites. The more scattering events in the material, the more the electron scatters and the longer it take for the electron to reach its endpoint [2]. As current is supplied through the material the electrons are forced to move in one direction. Constant current is needed because the scattering sites move the electrons in other directions and the electron has to be forced once again in one direction. Electrons themselves are extremely fast, but when scattering is accounted for the average speed drops significantly. For a current in the range of a few amperes, the velocity it takes for an electron to reach its destination is an average of a few millimeters per second.

This is known as drift velocity and when used in conjunction with Ohms Law, resistivity and conductivity can be used to find the scattering rate, as seen below in Figure 2. Drift velocity only occurs when electrons are under the effects of an electric field and can be analytically derived using this equation:

$$v_d = \mu E \tag{2}$$

where v_d is the drift velocity, μ is the electron mobility, and E is the magnitude of the electric field applied. The specific conductivity of a material dictates the electron mobility to be used.
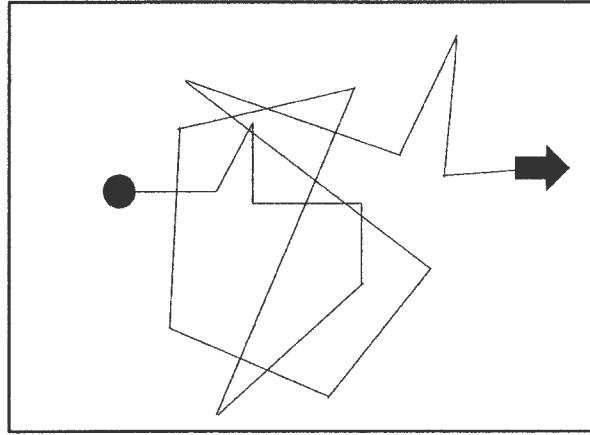

Figure 2: Model of an electron scattering through a metal. Scattering sites include atoms and electrons from the metal as well as atoms from other molecules trapped in the metal

The time between electron collisions can be expressed as τ. The time between collisions (or τ) can be expressed as the sum of the time between collisions, as seen in the equation below:

$$\frac{1}{\tau} = \frac{1}{\tau_{electron}} + \frac{1}{\tau_{photon}} + \frac{1}{\tau_{defect}} \tag{3}$$

where $\tau_{electron}$ is the time between collisions with electrons, τ_{photon} is the time between collisions with photons, and τ_{defect} is the time between collisions with defects in the metal, such as air molecules. Collisions with electrons and photons are unavoidable, since free electrons in conductors move randomly and photons constantly bombard a metal from any light source. However, collisions with defects within the metal could be avoided if the metal is completely composed of its element.

This is how the Drude Model relates resistivity to τ. The more defects in the material decrease the time between collisions, lowering electron mobility and increasing the resistivity of the material. An equation to find resistivity using the Drude Model is:

$$\sigma = \frac{1}{\rho} = \frac{n_e e^2 \tau}{m_e} \tag{4}$$

where σ is conductivity, ρ is resistivity, n_e is the density of free electrons, e is the electron charge, τ is the mean time between collisions, and m_e is the mass of an electron. Therefore, if τ_{defect} is decreased, resistivity will increase.

With the Drude Model, pressure in the deposition chamber can be related with the resistivity of the deposited films. Though the vacuum attachments pump out most of the air molecules in the chamber, unless an absolute vacuum is created there are still air molecules floating around: oxygen, nitrogen, water vapor, etc. When evaporating a metal, air molecules are trapped in the film created. Those air molecules create scattering events within the film, decreasing the electron mobility. The trapped oxygen molecules also oxidizes the metal, creating larger scattering sites within the film. The resistance of the metal will increase, thus the resistivity changes. Since the resistivity of a specific metal is already known, one can theorize that as the pressure decreases the lower levels, the closer the resistivity of the film is to the actual resistivity of the metal.

2.2 Thin Film Resistivity Measurement Method – Van der Pauw Method

The important difference between using a two point method and a four point method is the contact resistance. When measuring resistances with the two-point method, the points of contact can create additional resistance called contact resistance. The contact resistance is relatively small and does not need to be accounted for when measuring objects of large resistances. However, when dealing with samples as small as the thin films created, the contact resistance makes a measurable difference and is a large error that is need to be accounted for. When compared to the measurement found from the four-point probe, the two-point method nearly doubled that of the four-point method. Figure 3 depicts the effect of the two-point probe method.
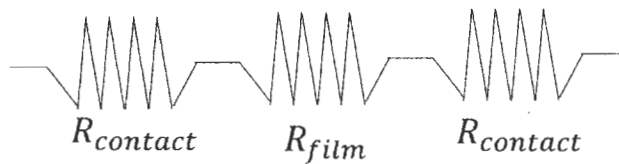

Figure 3: Effect of two-point probe method on resistance of material

Leo J. Van der Pauw created a method of measuring resistivity of an arbitrary shape using a four-point probe. With the usual method, a current is sent through the outer ends of the bar while a voltage difference is sent in the inner parts of the bar. This requires the bar to be of the same, straight shape throughout the entire bar. Van der Pauw theorized that the metal to be measured can be of any shape, so long as certain rules are followed: the contacts are at the circumference of the sample, the contacts are sufficiently small, the sample is homogeneous in thickness, and the surface of the sample is singly connected (no holes in the sample). [3] Most of these rules apply to the linear method, however the main difference is the arbitrary shape the sample may have. Resistivity can be found from the Van der Pauw Method using this equation:

$$e^{\frac{-1}{\rho} d\pi R_{12,34}} + e^{\frac{-1}{\rho} d\pi R_{23,14}} = 1 \tag{5}$$

where d is the thickness of the film, $R_{12,34}$ signifies the resistance found by the voltage difference between contact points 3 and 4 per the current through 1 and 2, and ρ is the specific resistivity of the material.
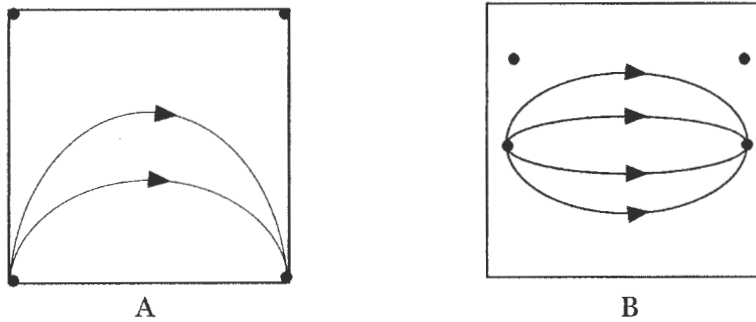

Figure 4: Model of current contact points on film. A is the ideal placement of the contact points to reduce the current from going in multiple directions. B is not ideal since current is free to go in any direction.
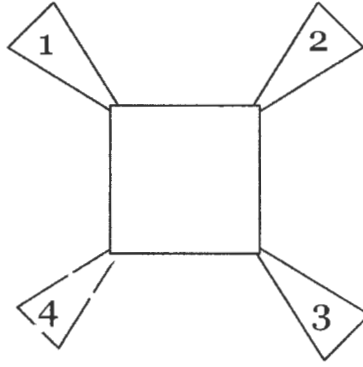
Figure 5: Model of Van der Pauw's ideal shape for a four-point probe, the Clover Method. Contact points from the inner square and the flared triangles are very small.

Van der Pauw also includes the importance of the pattern of the sample itself. Van der Pauw states that the clover method is the shape closest to ideal when measuring with the four-point probe. The four-point probe method is most successful when the probes are on the edges of the sample. As seen in Figure 4a, the current lines are only able to go in one direction if the contact points are on the edges. If the contact points are placed inside the film (like in Figure 4b), the current lines can go in any direction. It is difficult to meticulously place the contact points on the edges every time. The flared edges of the clover method are connected to the edges of the film, forcing the current to only go through the edges.

2.3 Thin Film Expected Resistance and Resistivity - Newton-Raphson Method

An expected value for each film's resistance and resistivity can be derived using equation 3. If $R_{12,34}$ and $R_{23,14}$ are have symmetry, then the two resistances can be considered of the same value and solved analytically[3].

$$R_{12,34} \approx R_{23,14} = R \tag{6}$$

where R is the average of $R_{12,34}$ and $R_{23,14}$. Applying this assumption to Van der Pauw's method changes equation 5 to:

$$2e^{\frac{-1}{\rho} d\pi R} = 1 \tag{7}$$

Equation 4 can then be rearranged to isolate resistance or resistivity:

$$R = -\rho \frac{ln\frac{1}{2}}{\pi d} \tag{8}$$

$$\rho = -R \frac{\pi d}{ln\frac{1}{2}} \tag{9}$$

Since the resistivity of specific materials are known and the thickness will be accounted for after the film is deposited, the expected resistance can be initially found. The found resistance can be plugged into equation 6 to verify if the expected resistance is indeed true.

However, equation 4 cannot be used if the resistances of the thin film are substantially different. Resistance and resistivity of the film cannot be solved analytically. In this situation, the Newton-Raphson Method can be applied. The Newton-Raphson Method is a numerical analysis based on linear approximation that uses a root-finding algorithm [9]. The root-finding algorithm finds the zero, or "root", of a function and uses iteration to produce a sequence of numbers that converge to the root as a limit.

The Newton-Raphson Method uses this equation to find the closest estimate:

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)} \tag{10}$$

where x_n is the initial estimate of x, $f(x_n)$ is the function used, and $f'(x_n)$ is the derivative of the function used [9]. Applying the Van der Pauw Method to equation 7 gives:

$$R_{12,34_{n+1}} = R_{12,34_n} - \frac{e^{\frac{-1}{\rho} d\pi R_{12,34}} + e^{\frac{-1}{\rho} d\pi R_{23,14}} - 1}{\frac{-1}{\rho}\pi d e^{\frac{-1}{\rho} R_{12,34}\pi d} - \frac{-1}{\rho}\pi d e^{\frac{-1}{\rho}\pi d(R_{12,34}+2R_{23,14})}} \tag{11}$$

$$R_{23,14_{n+1}} = R_{23,14_n} - \frac{e^{\frac{-1}{\rho} d\pi R_{12,34}} + e^{\frac{-1}{\rho} d\pi R_{23,14}} - 1}{\frac{-1}{\rho}\pi d e^{\frac{-1}{\rho}(2R_{12,34}+R_{23,14})\pi d} - \frac{-1}{\rho}\pi d e^{\frac{-1}{\rho}\pi d R_{23,14}}} \tag{12}$$

$R_{12,34_{n+1}}$ and $R_{23,14_{n+1}}$ are the estimates of the expected resistance. The estimate will be found within an error of $1 * 10^{-5}$, so the resistance found should be relatively close to the ideal resistance. Matlab code can be found in Appendix.

An ideal resistivity can be derived if the pressure of the chamber is known while the metal is being deposited. This derivation initially stems from the Ideal Gas Law:

$$PV = NkT \tag{13}$$

where P is pressure, V is volume of the container, N is the number of atoms present, k is Boltzmann's constant, and T is temperature. Moving some variables around and altering volume to surface area per unit time with average velocity is:

$$\frac{P}{kT} = \frac{N}{A <v> \Delta t} \tag{14}$$

where A is the surface area of the chip, $<v>$ is the average velocity, and Δ t is the unit time.

Average velocity ($< v >$) can be re-written as $\sqrt{\frac{2kT}{m}}$:

$$\frac{N}{A\Delta t} = \frac{P}{kT}\sqrt{\frac{3kT}{m}} \tag{15}$$

where m is the mass of the molecule, which will be modeled as N_2. To find the rate which molecules are colliding with the chip, the derivative of equation 15 is taken:

$$\frac{dN_{collision}}{dt} = \frac{PA}{\sqrt{kTm}} \tag{16}$$

The total deposition rate is found by the sum of the collision rate and the deposition rate, which will be recorded during experiments when metal is being deposited:

$$\frac{dN_{total}}{dt} = \frac{dN_{collision}}{dt} + \frac{dN_{deposited}}{dt} \tag{17}$$

The average distance an electron travels is found by the number of collisions (in this case the N_2 molecules)and deposited metal atoms. This can be expressed as a ratio:

$$\frac{N_{collision}}{N_{collision} + N_{deposited}} \tag{18}$$

This ratio is the probability of an electron colliding with an N_2 molecule in the film. λ is the length between the scattering sites an electron collides with and can be expressed using equation 18:

$$\lambda = a\left(\frac{N_{collision}}{N_{collision} + N_{deposited}}\right) \tag{19}$$

where a is the atomic spacing between atoms that are scattering sites. This can be found using the Therefore, when used concurrently with equation 4 from the Drude Model, resistivity can be found using:

$$\sigma = \frac{1}{\rho} = \frac{ne^2\lambda}{m_e v_d} = \frac{ne^2\tau}{m_e} \tag{20}$$

This equation can be used to create a curve fit of the ideal resistivity at various pressures.

Chapter 3

3 Experimental Methods

3.1 Initial Set-Up

As seen in Figure 6, evaporating the metal onto the substrate occurs in the vacuum chamber. It is important tö inspect the chamber of any leaks or tears to the O-rings, which will substantially affect the minimum pressure able to be reached in the chamber. A chip is cut from a silicon wafer and a mask in the shape of the clover method (as seen in Figure 5) is cut from UV foil. The mask covers the silicon chip and is held in place on the substrate. A metal sheet with a hole presses down on the mask to prevent any shadowing to create an even film. Gloves should be worn at all times to prevent oil from fingertips from contaminating the chamber.

Pellets of pure metals (copper, silver, aluminum) are placed in the tungsten boat. Tungsten is the preferred metal of use because of its high melting point. This prevents the boat from melting when the metal pellets are also being evaporated.
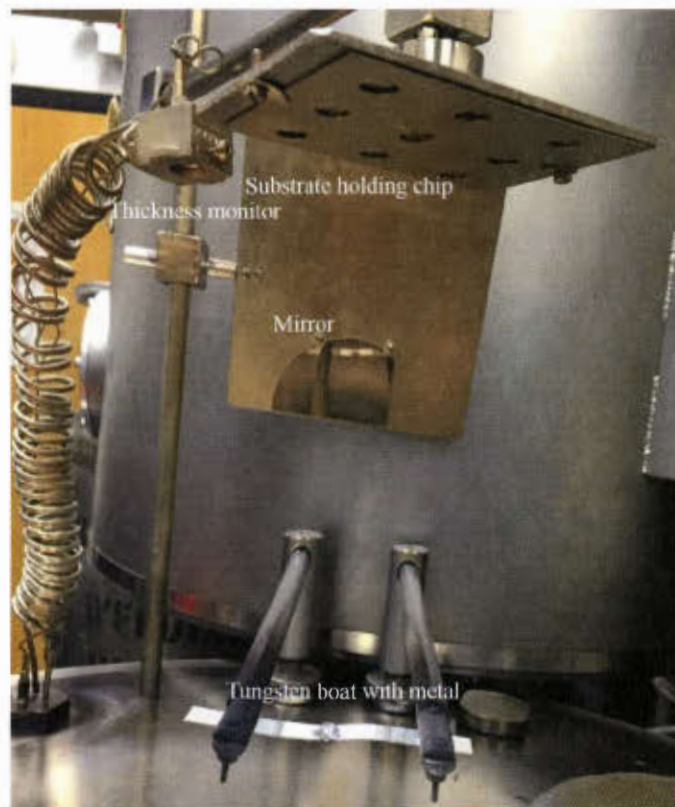

Figure 6: Photograph of internal components of the vacuum chamber. The metal plate attached to the substrate presses the mask against the chip to prevent a shadowed film. The mirror is used to view the metal in the boat during evaporation. The thickness monitor relays the thickness of the film as well as the rate of evaporation. Tungsten boat holds 99.99% pure metal to be deposited

3.2 Vacuum Attachment

The mechanical pump, or often called the forepump, initially pumps out the air from the diffusion pump. This is also called backing the diffusion pump. The chamber is then roughed by the mechanical pump and once at a low enough pressure, the hi-vac gate is opened so the mechanical pump and diffusion pump work together to pump on the chamber.

3.2.1 Mechanical Pump

The mechanical pump (also known as a forepump) is a rotary vane pump, as seen in Figure 7. Gas enters the suction chamber and is compressed by the rotor. It is then expelled in to the atmosphere through the discharge valve. The forepump is able to reach pressure levels of 10^5 Pa and is mostly used to back the diffusion pump and initially pump on the chamber [4].
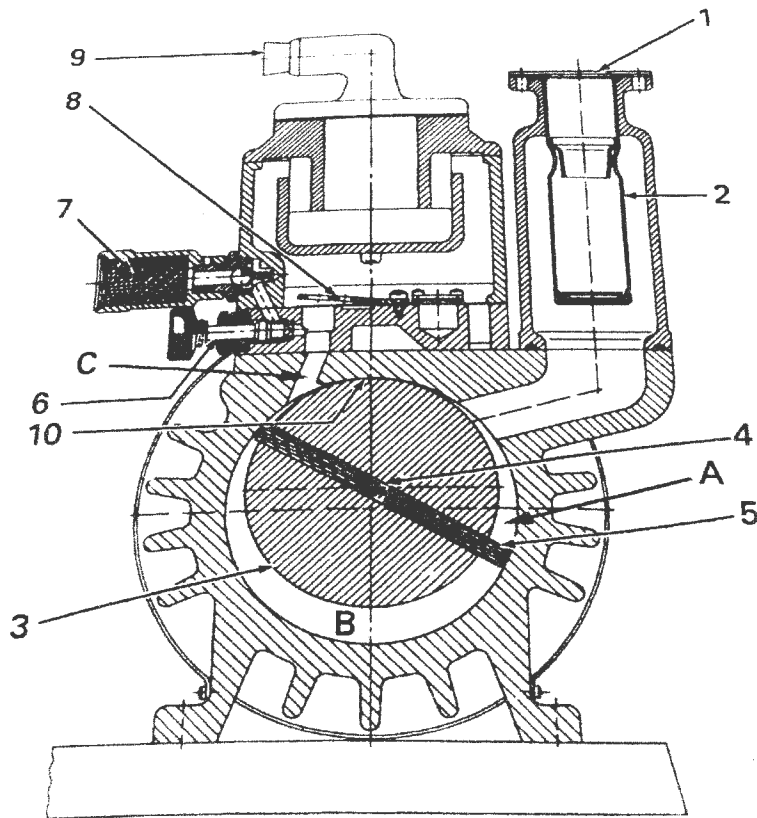
Figure 7: Model of interior of mechanical pump. Air molecules from the chamber and diffusion pump enter through the intake. They are led to the main compartment where the mechanical pump compresses, then releases to the exhaust pipe. Image from O' Hanlon [4].

3.2.2 Diffusion Pump

The diffusion pump is a vapor jet pump, as seen in Figure 8. A motive fluid (hydrocarbon oil) is heated by a broiler at the bottom of the pump until it evaporates. The vapor flows upwards through the chimney and down to the sides through a series of nozzles. [4] The outer part of the diffusion pump has a water cooling system that is required to run 50 gallons per minute so the pump does not overheat. Roughing the chamber allows the vapor to catch stray air molecules from the chamber and pulls them down to the sides. The walls of the pump are very cold, so when the vapor comes in contact it returns back to a liquid, taking the air molecules with it. The diffusion pump does have a critical fore pressure that it cannot exceed or it will completely shut down, which is why the gate to the chamber needs to be closed and the mechanical pump has to back the diffusion pump. This process is repeated until the pressure has been substantially lowered.

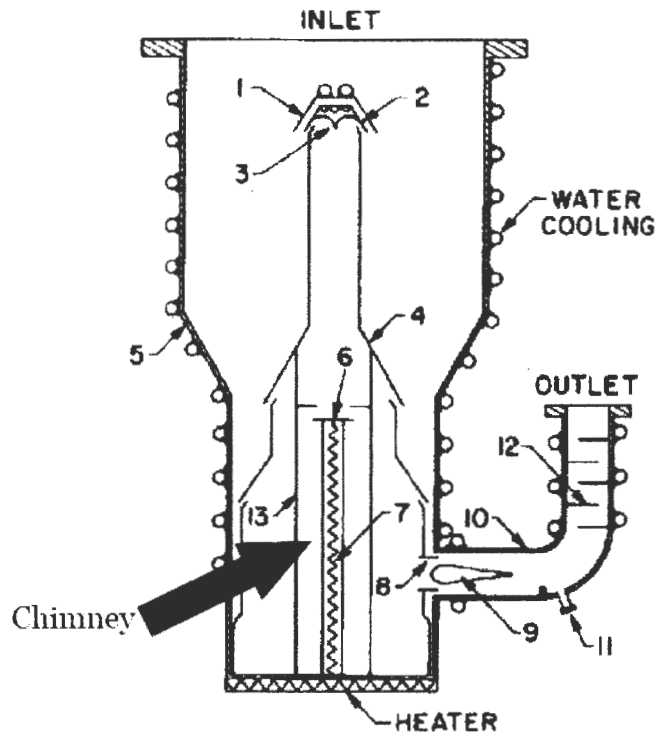Figure 8: Model of interior of the diffusion pump. The heater boils the oil, which evaporates up the chimney. The vapor latches onto the air molecules from the vacuum chamber near the inlet and are then cooled when it comes in contact with the walls. The vapor turns back into a liquid and returns to the bottom. The mechanical pumps pulls air from the outlet,"backing" the diffusion pump chamber. Image adapted from O 'Hanlon [4]

3.3 Evaporating Metals

Once the chamber is pumped down to a reasonable pressure, a current is sent through the tungsten boat. The current is raised until the metal in the boat begins to melt and then evaporate. The thickness monitor (top left of Figure 6) measures the total thickness as well as the rate the metal is evaporating. Stabilize the rate at a reasonable level (about 2 angstroms per second) and move the metal screen so the metal deposits on the chip (not shown). As the material evaporates the rate of evaporation changes, so the current will either have to increase or decrease to keep the rate constant. The mirror (as seen in Figure 6) gives a reflection of the metal being deposited. After a decent film is deposited, about one thousand Angstroms thick, replace the screen and lower the current to zero. Let the film cool for about thirty minutes and measure resistances with four-point probe.

3.4 Thickness Monitoring

Thickness monitors are used to measure the thickness of a thin film, as well as the rate which the film is being deposited. The sensor is placed equidistant from the boat as the substrate is from the boat [7]. The density, acoustic impedance (also known as z-factor), and tooling factor of the material being deposited needs to be inputted in to the monitor. The density and acoustic impedance was found using data from reference 8 and the tooling factor is always set to 100%. The tooling factor is the ratio of the rate which the material is being evaporated and the rate the material is being deposited on the substrate. However, this has not been calibrated and is a possible source of error.

The monitor uses a quartz crystal microbalance (QCM), which measures the change in frequency of a quartz crystal resonator. The resonator vibrates from the small mass of the metal depositing onto the substrate. Since the thickness monitor is placed in the vacuum chamber, the QCM is able to sense only the metal being deposited and not air molecules floating around. The thickness monitor can be found in Figure 4, inside of the vacuum chamber.

3.5 Additional Methods to Lower Pressure

In order to further reach lower chamber pressures, certain techniques can be applied. Liquid nitrogen can be added to the cold trap, pre-baking the chamber, evaporating an initial thin film, and re-applying lubrication to the o-rings.

The cold trap is a separate chamber below the vacuum chamber. Water vapor bounces around the chamber and when they collide with the walls of the chamber it sticks to the walls and freezes. Eventually the water vapor unfreezes and continues to bounce throughout the chamber, making it difficult for the vacuum attachments to pump away the vapor. By adding liquid nitrogen to the cold trap, the walls of the chamber becomes very cold. This freezes the water vapor completely so the vapor is unable to re-evaporate and move through the chamber.

Pre-baking the chamber is the opposite of using liquid nitrogen in the cold trap. Heating tape can be applied to the outside of the chamber, heating up the walls. The water vapor on the walls come off more easily. This process was not utilized since cold trap with liquid nitrogen was the technique used instead.

A film is initially deposited by heating the metal in the boat slightly. This traps air molecules and water vapor against the walls, which lowers the pressure. The initial film does not deposit onto the chip since it is covered by the screen.

If there are visible tears to the o-ring, it must be replaced before beginning experiments. A high vacuum lubricant oil is used and is reapplied every few experiments. Re-applying lubrication on the o-rings seals any cracks or tears that are not visible or not noticed. The silicon acts as a bond in the cracks of the o-rings, blocking the air from escaping and creating a solid vacuum. Since the lubrication is liquid, it fills in holes where solid blockage wouldn't fit. When the pumps turn on, the silicon is sucked away and fills the gaps.

Chapter 4

4 Results/Analysis

4.1 Resistivity

As is seen in Figure 9, after the evaporation process ends the chip produced is in the shape of the mask. Measuring the two resistances, $R_{12,34}$ and $R_{23,14}$ (as defined in section 2.2), and using the Newton-Raphson method gave the resistivity of the film. A table of the data can be found below in Table I. Copper was one of the first materials tested, so due to inexperience, the thicknesses were not uniform. This is not a problem, however, since the equation solves for films of different thickness. The thicknesses found using the thickness monitor cannot be compared to an absolute number because it was not calibrated before taking data.

Figure 9: Thin film of copper deposited onto silicon chip.

From the data found, it is clear that at lower pressures the resistance of the films are lower. This can confirm the Drude Model with the thought that at lower pressure, there are less air molecules in the chamber. With less air molecules trapped in the film, there are fewer scattering sites within the metal itself. This decreases the electron mobility, thus decreasing the drift velocity.

Table I. Data found from depositing metals onto silicon chips

Material	Pressure (Torr)	Thickness (Å)	$R_{12,34}$ (Ω)	$R_{23,14}$ (Ω)	Resistivity (Ω m)
Copper	1.3*10^-5	1.750	9.829	9.626	7.87*10^-9
Copper	5.6*10^-6	1.650	9.404	9.777	6.895*10^-9
Copper	3.3*10^-6	1.395	8.141	8.206	5.124*10^-9
Aluminum	1.8*10^-5	1.000	15.10	14.20	9.61*10^-9
Aluminum	4.8*10^-6	1.500	13.92	13.50	8.02*10^-9
Aluminum	6.8*10^-7	1.500	11.98	12.33	6.06*10^-9
Silver	1.8*10^-5	1.500	13.92	14.55	9.25*10^-9
Silver	4.5*10^-6	1.500	11.44	11.59	7.72*10^-9
Silver	6.3*10^-7	1.500	10.67	10.66	7.25*10^-9

As seen in Table I, however, the resistivities of the films made at lower pressures are smaller than the ideal resistivity. This is wrong because the additional scattering sites from the trapped air molecules should increase the resistivity, not decrease it. This is due to the fact that the thicknesses cannot be trusted because the thickness monitor was not calibrated.
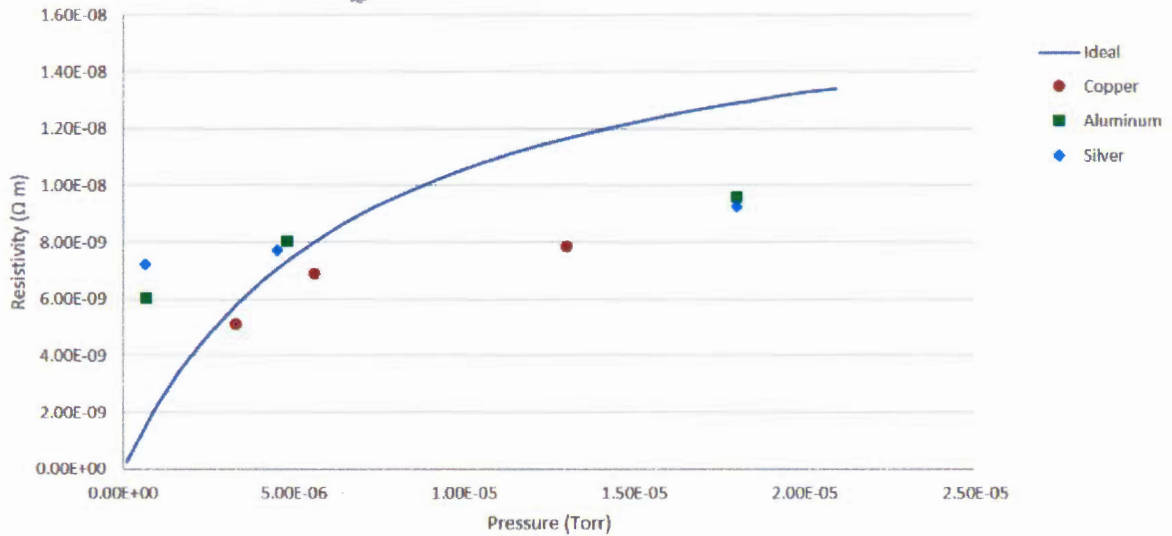

Figure 10: Graph of Pressure vs Resistivity of Films for Copper (circles), Aluminum (squares), and Silver (diamonds)

As seen in Figure 10, the ideal line was used from equation 20. Though the resistivities of the metal films do not fall on the ideal curve, it does follow the exponential pattern. As pressure increases, so too does the resistivity. The error should be from the inaccurate readings of the thickness. If the thickness could be better measured, the resistivities should be closer to the ideal line.

4.2 Expected Resistivity

From the Newton-Raphson Method, the expected resistivities of pure films were calculated. First, both $R_{12,34}$ and $R_{23,14}$ were assumed to be approximately equal so equation 5 could be utilized. The analytical and Newton-Raphson data were compared to confirm that the Newton-Raphson Method is reliable. The data found can be found in Table II.

Table II. Comparison of Analytical and Newton-Raphson data. Thickness was set at $1.5 * 10^-7m$ and the specific resistivity of each metal was used.

Material	Analytical Resistance (Ω)	Newton-Raphson Resistance (Ω)	% diff
Silver	0.0233	0.0234	0.4%
Copper	0.0241	0.0247	2.4%
Aluminum	0.0390	0.0390	0.0%

The data found from the Newton-Raphson Method is a near match to the analytical data. With such a minute difference in data, it's sufficient to say the Newton-Raphson Method is an acceptable method to use. This method can be used to find the resistivity of the film that cannot be found analytically, as seen in the table below.

Table III. Resistivity found using average resistance and Newton-Raphson Method

Material	$R_{12,34}$ (Ω)	$R_{23,14}$ (Ω)	Resistivity from Average Resistance	Resistivity from Newton-Raphson Method
Silver	9.829	9.626	7.54*10^-9	7.87*10^-9
-	9.404	9.777	6.491*10^-9	6.895*10^-9
-	8.141	8.206	4.85*10^-9	5.124*10^-9
Copper	15.10	14.20	9.42*10^-9	9.61*10^-9
-	13.92	13.50	7.89*10^-9	8.02*10^-9
-	11.98	12.33	5.91*10^-9	6.06*10^-9
Aluminum	13.92	14.55	8.98*10^-9	9.25*10^-9
-	11.44	11.59	7.52*10^-9	7.72*10^-9
-	10.67	10.66	7.09*10^-9	7.25*10^-9

Resistivity can be found analytically (using equation 5) if the average of $R_{12,34}$ and $R_{23,14}$ is taken or using the Newton-Raphson Methond with equation 12. The resistivity is within reason of each other for both methods. Using the Newton-Raphson Method should be more accurate since the actual resistances were used and not averaged. Again, the resistivity is not correct because the thickness of the films are not properly measured. Code for data can be found in Appendix.

4.3　Effect of Two-Point Probe Method

The two-point probe method was tested to verify the four-point probe method is a better choice when measuring thin films with low resistivity. To avoid the error of unknown thickness, the thickness of the films were not included. Equation 9 was altered to:

$$\frac{\rho}{d} = -R\frac{\pi}{ln\frac{1}{2}} \tag{21}$$

The analytical method was used for both the two-point method and the four-point method to ensure both quantities are derived from the same method.

Table IV. Comparison of Two-Point Probe and Four-Point Probe Method

Material	Calculated $\frac{\rho}{d}$ Four-Point Method (Ω)	Estimated $\frac{\rho}{d}$ Two-Point Method (Ω)
Silver	43.96	82.22
-	43.28	76.42
-	36.80	65.69
Copper	65.72	128.88
-	62.09	114.52
-	54.84	98.03
Aluminum	64.36	116.56
-	52.12	98.66
-	48.04	90.56

As seen in Table IV, the two-point probe method nearly doubled the resistivity found in the four-point probe method. This shows that the four-point method does work and that contact resistance does have a measurable effect on materials of low resistance.

Chapter 5

5 Conclusion

The data has shown that the resistance of the films are lower when deposited at lower pressures. The resistivity of the films were also lower at lower pressures; however, the lower resistivities were farther from the actual resistivity of the pure solid metal. The expected resistances were also much smaller than the found resistances by over two orders of magnitude. While this is not very good data, there can be more done to expect better data.

There are a few methods to further research on pressure vs resistivity of a thin film. It would be ideal if films could be made at larger ranges of pressures, especially lower ranges. The lower ranges should deposit films that are closer to the expected resistance of the metal. More data points with a larger range would reveal the curve fit of the data in better detail. A smaller chamber should be able to reach lower pressures because there is less volume for the vacuum attachments to pump on. Higher powered vacuum pumps could also be used, such as ion or turbo pumps. This should create chamber pressures in the ultra high vacuum range.

The environment which the films are being deposited could be more clean. The diffusion pump has the ability to contaminate the vacuum chamber from oil vapor. While the chamber is being "roughed" by the diffusion pump, some of the oil vapor that catches air molecules leaks into the chamber. This affects the purity of the films deposited.

Another technique for future work could be to bleed oxygen or nitrogen into the chamber while depositing metal. Nitrogen (as well as any other gas trapped in the film) would in theory create more scattering sites in the film, increasing the resistance and affecting the resistivity. The oxygen would additionaly oxidize the film, deteriorating the quality of the film. This makes the scattering sites bigger and harder for the electron to avoid, affecting the electron mobility. This would provide further insight to the Drude Model and the theory of scattering sites.

The thickness of the films can be more accurately measured during and after depositing the film. The thickness monitor is covered with layers of deposited metals after every experiment. This makes it difficult for the crystal to accurately vibrate and measure the deposition rate and thickness. This could be solved if the crystal is replaced after every deposition; however, the crystals are very expensive and it would not be cost-efficient to change the crystal each run. The thickness of the film can be more accurately verified after being deposited using Rutherford Backscattering Spectrometry (RBS). RBS is a non-destructive method of channeling ions to collide with a material. It provides depth information and is very useful when analyzing thin films.

Chapter 6

6 Acknowledgments

7   References

1. "Thin Film Deposition Technologies." Thin Film Deposition Technologies - Engineering and Technology History Wiki, 17 Apr. 2017. Web. 10 May 2017

2. "Drude Theory of Metals." (n.d.): n. pag. Web. Mar. 17.

3. Van Der Pauw. A Method of Measuring Specific Resistivity and Hall Effect of Disks of Arbitrary Shapes. Nov. 2016.

4. O'Hanlon, John F. A User's Guide to Vacuum Technology. N.p.: John Wiley and Sons, Inc, Print.

5. Schroeder, Daniel V. An Introduction to Thermal Physics. San Francisco, Calif.: Addison Wesley Longman, 2005. Print.

6. "Conductor and Insulator Diagram." N.p., n.d. Web.

7. Ohring, Milton. Materials Science of Thin Films: Deposition and Structure. San Diego: Academic. Print.

8. "Material Parameters." (2013): n. pag. Print.

9. "Newton-Raphson Method." SpringerReference (n.d.): n. pag. Web. 15 May 2017.

8 Appendix

Code used for Newton-Raphson Method

```
clear all
%dt = 0.000001;
rho = 1.59*10^-8;      %resistivity
%t = 0:dt:0.1;             %resistance
d = 1.5*10^-7;  %thickness
pi = 3.14;
%exp(-(1/rho)*t*pi*d) + exp(-(1/rho)*t*pi*d) -1 > x;
f = @(R) (exp(-(1/rho)*R*pi*d) + exp(-(1/rho)*(R)*pi*d) -1);
fp = @(R) ((-1/rho)*pi*d*exp(-(1/rho)*R*pi*d)
 - ((-1/rho)*pi*d)*exp(-(1/rho)*(3*R)*pi*d));
error = 2e-5;
p = 0.1;
i = 1;
p(i+1) = p(i) - f(p(i))/fp(p(i));
while abs(p(i+1) - p(i)) > error
    i = i + 1;
    p(i+1) = p(i) - f(p(i))/fp(p(i));
end;
p'
clear all
dt = 0.0001;
rho = 1.59*10^-8;      %resistivity
x = 0.0:dt:0.05;            %resistance
y = x*2;
d = 1.5*10^-7;  %thickness
pi = 3.14;
exp(-(1/rho)*x*pi*d) + exp(-(1/rho)*y*pi*d) -1 <0;
plot(x,y,'b');

clear all
rho = 1.8*10^-8;      %resistivity
R1 = 0.1;              %resistance
R2 = 0.5;
d = 1.5*10^-7;  %thickness
pi = 3.14;

while exp(-(1/rho)*R1*pi*d) + exp(-(1/rho)*R2*pi*d) >1;
    R1 = R1 + 0.0001;
    R2 = R2 + 0.0001;
end;
disp(R1);
disp(R2);
```