THE ELECTRIC, MAGNETIC, AND OPTICAL CHARACTERIZATION OF PERMALLOY OXIDE GROWN BY DUAL ION BEAM SPUTTERING

by

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DEDICATION

This work is dedicated to my grandfather

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I would like to thank my family and friends for their love and support though these trying times as well as Elizabeth LeBlanc and Michael Robinson for their work on this project. I would especially like to thank Dr. Geerts for his enormous commitment to his students and physics. I am a better person for having studied with him.

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1. INTRODUCTION

Transition metal oxides (TMO) are becoming more of an interest for material science and device manufacturing in the recent years. As it becomes impractical to follow Moore's law in the near future, the search for new non-volatile memory based on different principles will increase. Resistive Random Access Memory (RRAM) is an attractive candidate for a replacement. RRAM is based on a two terminal device in which a soft breakdown of a material layer occurs for a certain applied voltage and the process is reversible. The device's resistance can be switched between a low resistance state and a high resistance state. There have been extensive studies on these devices utilizing TMOs achieving switch times as low as 2 ns. [1, 2, 3]

Permalloy (Py), discovered in 1928 by H. D. Arnold and G. W. Elmen [4], is a metal alloy consisting of 80% nickel and 20% iron that has been extensively studied for its remarkable magnetic properties. Named after its high permeability, permalloy is a ferromagnetic material with a saturation magnetization of 9.30 $\times 10^5$ A/m and a very small crystal anisotropy and magnetostriction. [5] Permalloy exhibits metallic conduction with a room temperature resistivity between 20 and 60 $\mu\Omega$ cm depending on substrate temperature during growth. [6]. Because of these attractive properties, oxidation of permalloy is typically prevented. Oxidation of permalloy severely reduces its permeability and permalloy oxide itself is Anti-Ferromagnetic. [7] Therefore very little studies have been done to characterize permalloy oxide's (PyO) basic properties.

In the recent years two electronic devices have achieved significant enhancements that have been attributed to a PyO layer. In 2010, a study on lateral spin valves, fabricated using Py, was found to have an increased magnetoresistance after leaving it exposed to air. The enhancements were attributed to the oxidation of the Py layer. [8] Even more recently in 2013, the turn on voltages of Hematite based water splitting devices was lowered to record low of .61 V with the addition of an amorphous NiFeO_x layer. [9] In order to fabricate consistent devices the incorporate PyO, film thickness must be able to be monitored during or post deposition. The simplest way to monitor film thickness and roughness is to use optical measurements. This requires that the optical properties are determined prior to device manufacturing. The optical properties of PyO are thus studied in order to monitor film growth. Similarly, electrical properties of PyO need to be well understood to optimize the incorporation of PyO in electronic devices. Therefore, this thesis is dedicated to determining the optical and electrical properties of PyO. Specifically, PyO thin films made with reactive dual ion beam sputtering. The optical properties were for the first time determined by transmission and spectroscopic ellipsometry. The electric properties were measured by four point probe resistivity measurements and impedance spectroscopy.

Part of the content of this thesis was presented at the 2013 Women In Science and Engineering conference,[10, 11] the 2014 American Physics Society March meeting,[12] and the 2014 Materials Research Society Spring meeting (MRS)[13] as well as published in the on-line MRS proceedings.[14] [10]

2. PREVIOUS STUDIES

This chapter summarizes the work done on Permalloy Oxide prior to this thesis. Each section starts with the corresponding author followed by a summary of the work of that specific group.

Mihajlovic et. al [8] Py/Ag Lateral Spin Valves (LSV) were fabricated on SiN/Si substrates by e-beam lithography and shadow-mask e-beam evaporation of 25 nm thick Py and 80 nm thick Ag layers. The LSV's were then exposed to ambient air for one to two weeks. The magnetoresistance of the devices measured 17 days after fabrication was close to 7 times larger than devices tested the day of fabrication. Oxygen mapping by energy filtered transmission electron microscopy revealed an oxide layer formed at the Py/Ag interface for samples exposed to air. The observed enhancements were attributed to enhanced spin injection efficiency accross the interface. Previous studies were cited that identified the oxide as possibly α -Fe₂O₃, NiFe₂O₄, or NiO and most probably a mixture of all three.

Du et. al [9] Hematite-based water splitting cells were fabricated and the effect of a NiFeO_x layer was studied. The NiFeO_x amorphous films were prepared by a 1:1 mixtured of Iron(III) 2-ethyl-hexanoate and nickel(II) 2-ethyl-hexanoate with hexane added as a solvent. A quantity of 5 μ L of this mixture was dropped directly on a Fluorine doped Tin Oxide (FTO)-hematite electrode surface with a transfer liquid gun. The resulting structure was then annealed at 100° C for 1 hr. Device structures were verified with transmission electron spectroscopy. Photocurrent-density was measured as a function of applied voltage. With the added NiFeO_x layer, photovoltages increased from 0.24 V to 0.61 V. The turn on voltage decreased from 1.0 V to 0.6 V, a record low for water splitting cells. The effect was attributed to the minimization of the Fermi level pinning effect.

Kitada [15] Multilayered thin films were prepared by repeated sputter-deposition of permalloy, followed by oxidation of the deposited permalloy thin film surface. Oxidation was performed in dried air for 1 hour at 22-24° C. The oxide layer thickness' was found to be 2 nm. The crystal structure was evaluated by reflection high energy electron diffraction (RHEED) and the oxide NiFe₂O₄ was identified. Coercivity was measured as a function of number of layers. It was seen that the coercivity would decrease until a minimum was reached at 8 layers. The coercivity would then increase with increased number of layers at a less steep slope. The saturation magnetization decreased linearly for increased number of layers. These effects are attributed to oxidation of the permalloy surface first and then to solute oxygen in the permalloy. Magnetoresistivity was also seen to decrease with the addition of layers. Electron scattering by the oxide layer was seen as an important factor in decreasing the magnetoresistivity.

Rios et. al [7] Polycrystalline and epitaxial (Ni_{0.81}Fe_{0.19})O (PyO) and epitaxial (Bi_{0.8}Y_{2.2})·(Fe₄Ga₁)O₁₂ (Bi-YIG) were produced in the same system as used in the study of this thesis. Radical oxidation was used to tailor the exchange biasing properties of the rock-salt structured PyO structures and induce the formation of Bi-YIG layers with in-plane easy-axis properties. Atomically-smooth Si(0 0 1) substrates with a 190nm thick thermally oxidized SiO₂ layer were used to grow the PyO/Py exchange bias layers. 30nm PyO was grown on the SiO₂ layer at a temperature of 673K and then a 4nm Py was grown at 350K. The films were capped with a 5nm Ti passivation layer to protect the top Py layer from oxidation. Films were analyzed by using Bede D1 X-ray diffractometer θ -2 θ and X-ray Reflection scans. Room temperature vibrating sample magnetometer measurements were taken to study the bias layers and the effects of magnetic annealing on the films. The effectiveness of radical oxygen atom assist for reactive sputtering oxide films in an ion beam sputtering environment was demonstrated.

Salau et. al [16] Thin Py films were grown on Si (1 0 0) substrates by radio frequency diode sputtering performed with Z550 Lybold equipment. A DC magnetic field of 300 Oe was applied along the film plane during deposition. The (1 1 1) texture of fcc thins films was checked by X-ray diffractometry. Native oxide was removed with a 1 KeV ion beam. Oxidation was performed at room temperature by exposure of the sample to an O_2 partial pressure of 10^{-7} from 0 Langmuir to 5000 Langmuir. 1 Langmuir is equivalent to exposing the surface of the sample to 10^{-6} Torr for 1 second. X-ray photoelectron spectroscopy and workfunction measurements were analyzed in combination to investigate the initial factors contributing to the oxidation. It was found that the oxygen adsorption probability is related to the oxygen vacancies in the first inner layers, i.e. the Langmuir process. The NiFe oxidation process was seen to be less efficient than pure Ni or Fe due to weaker penetration of the material by oxygen. No preferential oxidation of Ni or Fe was observed. The nickel oxide was seen to be NiO while the iron oxide was first dominated by FeO and then developed into a mixture of FeO and Fe₂O₃ as oxidation continued. It was concluded that the oxidation leads to the formation of Aniferromagnetic (FeO,NiO, Fe₂O₃) and/or Ferrimagnetic (Fe₃O₄) oxide nano-layers.

Landon et. al [17] Mixed Ni-Fe oxide electrodes were tested for their oxygen evolution activity to determine the most active composition of these mixed catalysts for those created through hard-templating, dip coating, and evaporationinduced self assembly. The mixed oxides were characterized by X-ray diffraction, Raman spectroscopy, scanning electron microscopy, X-ray photoelectron Spectroscopy, Brunauer-Emmett-Teller surface analysis, X-ray absorption near edge structure, X-ray absorption fine structure, and temperature programmed reaction spectroscopy. The mixed Ni-Fe oxide catalysts showed much higher activity toward oxygen evolution and methanol oxidation than either of the pure oxides with a peak in activity occurring in 10 mol % Fe. Surface area effects were measured to ensure that the enhanced activity was due to the mixed oxides rather than increased surface area. The formation of the spinal phase NiFe₂O₄ was indicated as contributing to the enhanced activity.

3. THE DUAL ION BEAM SPUTTERING (DIBS) SYSTEM

The DIBS system currently being used is a modified 1160 Research System developed by the Commonwealth Scientific Corporation. Its original purpose was as a dual ion beam etching and deposition system. The original 3" Kaufman ion sources have since been replaced by an Oxford Applied Research Radio Frequency 50 ion source and HD 25 atom source, which will be discussed in detail in the following sections. Conventional DC or RF magnetron sputtering involves creating a plasma between the target and substrate. To enhance the sputter yield, magnets are incorporated under the target. The stray magnetic field above the target acts as an electron trap, greatly increasing the ionization probability of the argon gas. Cracked ions are then accelerated toward the target striking it with significant force to eject the target atoms. These atoms will be ejected in a cone distribution from the top surface of the target and will condense on all surfaces in the proximity, including the substrate. Because of the higher ionization efficiency of magnetron systems, the plasma will be stable at lower pressures than in non-magnetic systems, allowing deposition down to approximately 0.05 Torr. To allow for deposition at even lower pressure, one uses an ion beam sputtering system. The plasma is contained in a gun and a pressure difference exists between the gun and the chamber. Deposition can be done at pressures as low as 10^{-7} Torr. Deposition at such low pressures results in dense films with little sputter gas inclusion. For insulating targets, an atom beam rather than an ion beam can be used, avoiding charging effects of the target. The plasma is contained in the ion sources as well and does not cause any sample heating or unwanted contamination. Thus reactive dual ion beam sputtering is an attractive candidate whenever growing a magnetic oxide, as in the case of Permalloy Oxide. A simple schematic is shown in figure 3.1a.

Deposition of high quality films requires appropriate background pressure and atmosphere. The lower the pressure is during deposition, the higher the quality of the film. This is due to simply less contaminants in the system as well as a greater



Fig. 3.1: The DIBS Principle Geometry and System Picture

mean free path. A greater mean free path means the particles in the chamber travel farther before "bumping" into one another. This results in the sputter particles arriving at the substrate uniformly with high kinetic energy, yielding a denser film.

There are a variety of vacuum pumps for various pressure regimes and applications. This particular system uses a series of three pumps to obtain pressures in the low 10^{-7} Torr range: a scroll pump, a turbo-molecular pump, and a cryogenic pump. The chamber schematic can be seen in figure 3.2 and will be explained in more detail in the following sections.

3.1. The TriScroll Pump: The Low Vacuum Regime

The chamber initially starts out at atmospheric pressure, 760 Torr. A Varian Tri-Scroll pump is used to "Rough" the chamber which starts out the pumping down process. The Scroll pump is a mechanical pump in the sense that it utilizes mechanical energy to compress gas and then to expel it out from the chamber. Because of this, the scroll pump can only operate in the viscous flow regime where gas-gas collisions determine the pressure. The base pressure achieved by the scroll is in the 10 mTorr range. An advantage of these pumps is that they are "dry" and do not require oil to operate thus eliminating oil as a contaminant in the system.



Fig. 3.2: Pump Diagram

When the chamber is sufficiently pumped down, the scroll is utilized again as the backing pump for the turbomolecular pump since the turbo requires low vacuum at its outlet (< 100 mTorr) to operate. The inner chamber of the scroll pump is shown in figure 3.3.



Fig. 3.3: The Inner Chamber of the Scroll Pump

3.2. The Turbomolecular Pump: The Medium Vacuum Regime

The chamber is considered in the medium vacuum range once it has reached 1 Torr. At this point gas-gas interactions occur less and less and each particle travels farther before interacting with other particles. This length is referred to as the *mean free path* and is inversely proportional to the pressure.

$$mean free path = \frac{5 \times 10^{-3} \ Torr \cdot cm}{Pressure}$$
(3.1)

At lower pressures, gas-wall interactions determine the chamber pressure and the scroll pump can no longer compress a significant amount of gas to lower the pressure. A Varian Turbo-molecular pump is used to reach pressures of 10^{-5} Torr, or the medium vacuum range. Turbo pumps cannot evacuate directly to atmosphere so they must be backed by a roughing pump, the scroll pump in this case. Once the thermocouple gauge reads below 0.05 Torr, the roughing value is closed and the turbo foreline valve is opened. The turbo pump is already running and the line is at 0.1 Torr or below. The turbo high vacuum valve is then opened so that the turbo pump is pumping on the chamber and is backed by the scroll pump. Turbo-molecular pumps work by momentum transfer and consist of alternating rotating and stationary fan blades which can be magnetically levitated to prevent friction. When an atom and a blade come into contact, momentum is transferred to the atom in the direction of the next blade. The blades are angled so that atoms are directed toward the back of the pump and out of the chamber. Turbo-molecular pumps actually have a higher pumping speed for lower pressures since the mean free path is higher and the atoms only interact with the blades and the walls. A cutout of a turbo-molecular pump like the one on the system is shown in figure 3.4.



http://en.wikipedia.org/wiki/File:Cut_through_turbomolecular_pump.jpg Fig. 3.4: Cutout of a Tubromoleular Pump

3.3. The Cryogenic Pump: The High Vacuum Regime

The final pumping stage is carried out by a CTI-Cryo-Torr 8 with a pumping speed of 1,500 litres per second for air and operates at pressures between 10^{-4} and 10^{-10} Torr.[18] Cryogenic pumps operate by trapping or condensing gas rather than removing it. Highly pressurized, 99.9999% pure helium gas is supplied by a compressor and is released into the pump through the expander effectively cooling the cryo-arrays. This causes any gas that comes in contact with the cryo-arrays to condense and stick to the surface. The first stage is cooled down to around 80K while the second stage is held at 16 K. Most gases will condense to solid at stage 1. Gases such as hydrogen, nitrogen, and argon are much harder to trap through condensation. These gases will be trapped in the second stage which is much colder and is also made of activated charcoal. If a gas has not already condensed at this point than it will most likely be absorbed by the porous charcoal. Since the cryo pump never actually removes the gases, the pump must be regenerated from time to time in order to maintain pumping ability. This is achieved by stopping the He supply to the pump and bringing it to room temperature or slightly higher. The scroll pump is used to maintain vacuum during out gassing.



Fig. 3.5: Cut Out of a Cryogenic Pump

3.4. The Oxford Applied Research RF50 Ion Source

The primary ion source used for sputter deposition in the DIBS is an Oxford Applied Research RF 50 Ion Source. Ions are produced by dissociation and ionization in the RF discharge tube and extracted into the main chamber by an electric field held by a grid set. A 13.56 MHz AC signal, sourced by a Dressler RF power supply, is inductively coupled to the charged particles inside the discharge tube. It is important to insure that all power delivered by the power supply is transferred to the discharge tube. In order to achieve this there are variable capacitors at each end of the power line. Power can be reflected back along the line due to an impedance mismatch of the ion gun and power supply. In order to prevent any reflected power which may damage the ion source and/or power supply, the impedance of the cavity is matched to the output impedance of the power supply. This particular ion source is equipped with an ATM100 Autotune Controller by Oxford Applied Research for impedance matching. To generate a plasma in the discharge tube, ultra high purity argon is introduced into the discharge tube at 15 sccm. At first the RF signal will only effect the free electrons which begin to oscillate under the alternating fields that are applied to them. The energetic free electrons then begin to interact with the neutral argon atoms by transferring kinetic energy via collisions. At high enough power, the energy transferred to the argon atoms is great enough to ionize the Ar atoms into Ar⁺ ions. It can be seen when the plasma is generated by examining the reflected power or by the presence of a purple-pink glow in the gun. With more ions in the tube, the impedance will drastically change and the reflected power will increase significantly so the capacitors will have to be re-tuned. At 15 sccm of argon, the plasma is generated at 45 Watts. The power is increased by 15 Watts every five minutes to a maximum power of 80 Watts. Ions which make their way toward the chamber are extracted by two aperture grids held at a potential difference. The first plate, referred to as the Beam Screen, is held at a positive potential of 850 V by a high voltage supply. This screen voltage determines the energy of the beam. The second, accelerator grid, is held at potential of -185 V by a separate high voltage power supply. The potential difference between screen grid and accelerator grid is responsible for directing the ions toward the target. The accelerated ions then have to pass by the neutralizing filament carrying 5 Amps. Enough free electrons are generated so that the charged ions are then neutralized. The result is an accelerated atom beam directed toward the target.

3.5. The Oxford Applied Research HD25 Ion Source

The HD 25 Ion Source works under the same principle as the RF 50. The plasma is ignited in the same fashion but the impedance matching is performed manually. The main difference is that the ions are not accelerated toward the substrate, but rather the charged ions are deflected by a charged deflection plate. This is to ensure that only neutral oxygen atoms reach the substrate. Oxford Applied Research has been quoted claiming that the beam comprises 50-60% atomic oxygen.



Fig. 3.6: Diagram for the RF50 Ion Source



Fig. 3.7: Diagram for the HD25 Ion Source

4. **DEPOSITION**

4.1. Substrates

Substrates of SiO_2 / Si, Al / Si, and soda glass were used to grow PyO thin films. Films grown on soda glass were used for transmission and resistivity measurements. For transmission measurements, soda glass was an obvious choice since it is transparent in the visible range. SiO_2 / Si substrates were chosen to facilitate electrical and optical characterization. Linear four point probe resistivity measurements on SiO_2 / Si and glass substrates showed a resistance beyond the capability of our measurement setup (R $> 10^{14}\Omega$). Ellipsometry showed that the SiO₂ layer on the SiO₂ / Si substrates is between 5000 - 5100 Angstroms. The samples grown on SiO_2 / Si substrates were used for optical ellipsometry measurements in order to determine the thickness of the PyO films since the optical properties of SiO_2 and Si are well established. The relatively thick SiO_2 layer allows for simultaneous determination of film thickness and refraction index. [19] Impedance spectroscopy was performed on the samples grown on Al / Si. Since the Al / Si substrates are conductive, the capacitance measured was completely from the PyO as opposed to samples grown on SiO_2 / Si where the substrate effects could not be negated. All substrates were cleaned via sonication for five minutes in first acetone and then isopropyl alcohol. The substrates were then blown dry with N₂ gas and loaded into the chamber.

4.2. Film Growth

Polycrystalline PyO thin films were grown at room temperature on a sample cooled stage rotating at 40 rev / min. Background gases were determined by an RGA to ensure a clean chamber prior to deposition. H₂O and N₂ were the most prevalent gases but remained less than 1×10^{-7} Torr partial pressure each. Samples were sputtered only once the base pressure was less than 4×10^{-7} Torr. Sputter pressure was measured to be around 0.5×10^{-3} Torr but due to oxygen present in the system, pressure could not be monitored during deposition with the ion gauge. A flow rate of 15 sccm Ar was used to generate a mono-energetic Ar beam by a high energy RF ion beam source utilizing the Oxford Applied Research RF50 ion gun. The beam screen was held at a potential of 850 V while the accelerator screen was held at a potential of -185 V. A 60 mA beam current was established for sputtering. During deposition, a broad beam thermal energy (\leq 50 eV) neutral oxygen radical atom source, the Oxford Applied Research HD25, was directed at the substrates. A 50-60% atomic oxygen plasma was produced using 5-10 sccm O₂ and 200-290 W RF signal. The shutter was left closed for at least five minutes before sputtering to presputter the target. This method has been shown to produce high quality polycrystalline PyO- based exchange biased layers [7, 20]. The sputtering parameters for all samples are summarized in table 4.1.

Sample #	A£131£0	A£11001	101413	111213	814111	112613	112813	121513	nuA (ba2)	₽1914 ₽	022114	012314	021814
Target	$\mathbf{P}\mathbf{y}$	$\mathbf{P}\mathbf{y}$	Py	Py	Py	Py	Py	Py	Py	Py	Py	Ni	Не
$\begin{array}{c} {\rm BG} \ {\rm Pressure} \\ (\times \ 10^7 \ {\rm Torr}) \end{array}$	3.4	4.1	3.4		2.9	3.2	2.5	3.2	/	c,	2	2.6	2.0
${ m Working \ Pressure} \ (imes \ 10^4 \ { m Torr})$	7.2	8.2	6.4	_	4.8	8.8	2.5	8.5	~	∞	9	6	∞
Rotation (rev/min)	/	58	58	50	50	50	50	40	/	40	50	44	41
Pre Sputter time (min)	5	5	ъ	ъ	ŋ	Ŋ	IJ	ю	Ŋ	Ŋ	ю	ы	Ŋ
Sputter time (min)	20	20	20	20	20	20	40	(20)	20	20	20	20	20
		Argo	on Gu	un Pa	rameters								
Ar Flow (sccm)	15	15	15	15	15	15	15	15	15	15	10	15	14
$\operatorname{Rf}\operatorname{Power}(W)$	80	80	80	80	80	80	80	80	80	80	80	80	80
Acc. Voltage (V)	196	191	195	185	185	185	185	186	185	185	185	185	185
Acc. Current (mA)	9	9	2	9	2	2	9	9	9	2	ю	9	9
Beam Voltage(V)	870	850	850	850	850	850	850	840	850	850	850	800	860
Beam Current (mA)	54	58	56	55	55	59	60	60	63	59	56	60	58
Filament Current (A)	5	5	IJ	ъ	IJ	ы	IJ	5	S	ъ	IJ	IJ	IJ
		Oxyg	en G	un Pa	arameters								
O2 Flow (sccm)	10	10	10	10	10	10	6	10	10	ഹ	ы	ы	ъ
Rf Power (W)			278	284		297	290	287	292	225	227	214	225
Forward Power (W)	Molecular	Molecular	276	285	Molecular	300	295	290	298	224	229	219	225
O.E.D. Voltage (mV)			126	125		126	128	122	118	120	120	108	115

Tab. 4.1: Deposition Parameters

5. MAGNETIC MEASUREMENTS

In order to determine if the film was completely oxidized during growth, the magnetic moment was measured as a function of an applied, in plane, field. Since Py is ferromagnetic, a hysteresis curve would be observed for any unoxidized Py. An initial sample, 031513, was observed to have a ferromagnetic contribution at room temperature. The magnetic moment was found to be 3% of the magnetic moment of an unoxidized Py thin film of the same thickness. The oxygen partial pressure was then increased during growth to ensure complete oxidation. No ferromagnetic contribution was found for subsequent samples.

5.1. The Quantum Design Physical Property Measurement System: The Vibrating Sample Magnetometer Option

The Physical Property Measurement System (PPMS) is a liquid helium cooled environment with a superconducting magnet capable of measurements at temperatures as low at 1.9K and at magnetic fields as high as 9T. The Vibrating Sample Magnetometer (VSM) utilizes a quartz mounting stick attached to a carbon fiber rod which is inserted into the PPMS. The sample is mounted to the diamagnetic quartz mounting stick with rubber cement and centered between the two pickup coils inside the PPMS chamber. The chamber is evacuated to a pressure of less than 40 Torr. A motor is used to oscillate the sample centered between the pickup coils. The magnetic moment is measured via the electromotive force (EMF), where a current will be induced in a pickup coil whenever there is a magnetic flux change within the pickup coil. The induced current will have an associated EMF voltage which can be measured and used to calculate the magnetic moment of the sample. An in plane magnetic field is applied to the sample in order to induce a magnetic moment in the sample which will determine whether the sample is ferromagnetic, paramagnetic, or diamagnetic. The applied field does not effect the measured voltage since it is constant and thus does not change the magnetic flux in the pickup coil.

5.2. Measurement Principles

As mentioned earlier, the magnetic moment of the sample can be measured by oscillating it within a conducting coil. The voltage induced inside the coil is proportional to the magnetic flux,

$$V_{coil} = \left(\frac{d\Phi}{dt}\right) = \left(\frac{d\Phi}{dz}\right) \left(\frac{dz}{dt}\right)$$
(5.1)

where z is the vertical position of the sample with respect to the coil and t is time. Thus for a sinusoidally oscillating sample with amplitude A, the voltage of the coil is given by,

$$V_{Coil} = Cm2\pi f A \sin\left(2\pi f t\right) \tag{5.2}$$

where C is a coupling constant, m is the sample's DC magnetic moment, and f is the frequency of the oscillation. The center of oscillation is positioned at the vertical center of a gradiometer pickup coil. The voltage induced in the pickup is



Fig. 5.1: Quantum Design Physical Property Measurement System



Fig. 5.2: The VSM Pickup Coils

amplified and measured in the VSM module. [21] The dimensions of the pickup coil set can be seen in figure 5.2a. All magnetic measurements were made with an oscillation frequency of 40 Hz and an oscillation amplitude of 2 mm.

Before measurements were taken, the magnetic field would be swept from 9 T to -9T and back to 9 T. The super-conducting magnet would be set to No-overshoot mode which would make sure that the field would stop on a certain value without oscillating in the region. This was done in order to facilitate accurate hysteresis measurements to detect ferromagnetic contributions.

5.3. Measurement Results

The initial sample that was made, 031513A, was observed to have a ferromagnetic contribution as seen in figure 5.3. This is attributed to an incomplete oxidation of the permalloy during growth or a magnetic contamination of the sample between deposition and measurement. The hysteresis disappears almost completely at room temperature which implies that the hysteresis is not caused by bulk NiFe or builk Fe_3O_4 . Referring to table 4.1, this sample was grown with molecular oxidation at a flow rate of 7 sccm. Further samples were thus grown with a higher oxygen flow rate and/or atomic oxygen to ensure full oxidation of the permalloy.



Fig. 5.3: 031513A Hysteresis Curves

Sample 101413 was grown with molecular oxygen at a flow rate of 10 sccm. The magnetic measurements show no ferromagnetic contribution down to temperatures of 15K as can be seen in figure 5.4. A hysteresis eye appears to be present but it can be seen that the lines actually cross one another.



Fig. 5.4: 101413 Magnetic Moment Measurements

No magnetic moment information could be derived from the measurements. The magnetic moments measured were found to be due to the glass substrate. The same curves can be seen in figure 5.5 which was taken of the glass substrates used to grow the films. Room temperature samples are seen to be diamagnetic. Glass substrates measured at low temperature show a strong paramagnetic and maybe some ferromagnetic response. It is well known that the diamagnetic response is independent of the temperature while the paramagnetic response is inversely proportional to the temperature. A step of approximately $1 \times 10^{-8} - 4 \times 10^{-8}$ Am² was observed for all samples and substrates when changing the sign of the field. It is not clear whether the step is due to the substrate, film, or measurement system.



Fig. 5.5: Magnetic Moment Measurements of Glass Substrates

NiO is a known anti-ferromagnetic material with a Neel Temperature around 525K and PyO has been seen to create an anti-ferromagnetic pinning layer used in exchange bias layers. [20] Thus no measured magnetism is consistent with an anti-ferromagnetic layer grown on glass.

6. OPTICAL MEASUREMENTS

6.1. Ellipsometry

Ellipsometric measurements are performed by determining the phase shift difference of the component of light polarized perpendicular to the plane of incidence (*s*-polarized) and the component of light polarization parallel to the plane of incidence (*p*-polarized) upon reflection (Δ) and the ratio of the amplitude change of p and s-polarized light upon reflection ($\tan(\Psi)$). A basic diagram displaying the phase change of incident light on a material is shown in figure 6.1.



Fig. 6.1: Change in p and s-Polarization Light Incident on a Material

These ellipsometric quantities Ψ and Δ can also be calculated from the Fresnel reflection coefficients r_{pp} and r_{ss} shown in equation 6.1. The Fresnel reflection coefficients are derived by applying boundary conditions to incident transverse electric and transverse magnetic waves. This derivation follows the basic laws of reflection and refraction and is dependent on the change in refraction index between materials and the incident polarization.

$$r_{ss} = \frac{E_{rs}}{E_{is}} = \frac{n_a \cos(\theta_i) - n_s(\theta_t)}{n_a \cos(\theta_i) + n_s \cos(\theta_t)}$$

$$r_{pp} = \frac{E_{rp}}{E_{ip}} = \frac{-n_s \cos(\theta_i) + n_a(\theta_t)}{n_s \cos(\theta_i) + n_a \cos(\theta_t)}$$
(6.1)

where n_a is the refraction index of air and n_s is the refraction index of the material. The angle of incidence, θ_i , and the angle of transmission, θ_t , are related by Snell's law, $n_a \sin(\theta_i) = n_s \sin(\theta_t)$. The ellipsometric quantities, Ψ and Δ , thus describe the same phenomena as the Fresnel equations and their relationship is given by equation 6.2

$$\tan(\Psi)e^{i\Delta} = \frac{r_{pp}}{r_{ss}} \tag{6.2}$$

The refraction index in principle is a complex quantity. The real part, n, describes the speed of an electromagnetic wave in the material while the imaginary part, k, describes the absorption of the wave by the material. The extinction coefficient, k, depends on the wavelength of the incident light so it is useful to define the absorption coefficient, α , which can be seen in equation 6.3.

$$n_s = n - ki \quad where \quad k = \frac{\lambda \alpha}{4\pi}$$
 (6.3)

For an infinitely thick sample it is possible to determine the optical properties, n and k, from the measured ellipsometric quantities Δ and Ψ by solving for n and k from equation 6.1 through 6.3. Thin films do not have an infinite thickness. So light reflected from a thin film sample consists of light reflected from the top of the thin film, light reflected from the film-substrate interface, and light reflected from the bottom of the substrate. If one ignores the light reflected from the bottom of the substrate, the sample's reflection coefficient can be calculated from the Fresnel reflection coefficient of the interfaces in the sample. For a thin film on a strongly absorbing substrate the reflections for s and p-polarized light are given by equation 6.4 and are also a function of the film thickness t and the wavelength λ .

$$r_{ss} = \frac{r_{ss12} + r_{ss23}e^{-2\beta i}}{1 + r_{ss12}r_{ss23}e^{-2\beta i}}$$

$$r_{pp} = \frac{r_{pp12} + r_{pp23}e^{-2\beta i}}{1 + r_{pp12}r_{pp23}e^{-2\beta i}}$$
(6.4)

$$\beta = 2\pi \frac{t}{\lambda} n \cos(\theta_t)$$

where r_{ss12} and r_{pp12} are calculated from equation 6.1 with n_a being the index of refraction for air and $n_s = n_{(thin \ film)}$. Similarly, r_{ss23} and r_{pp23} are calculated for equation 6.1 with $n_a = n_{(thin \ film)}$ and $n_s = n_{substrate}$.

For more complex multilayer samples, the equations for the reflection coefficients become even more complex. In general the reflection coefficients for p and s-polarized light are a function of the optical properties of the materials involved, the angle of incidence, and the thickness values of the different layers. It is clear that it is not possible to unambiguously determine all those parameters from just a single ellipsometric measurement that provides a Δ - Ψ pair. More measurements need to be performed to be able to solve for all unknowns. One can measure for example at different wavelengths and at different angles of incidence. One can also do measurements on different samples. For example one could do measurements on samples that have different film thicknesses or samples that are deposited on different substrate materials. In addition not all optical properties need to be determined from the ellipsometric measurements. The optical properties of a silicon wafer or an aluminum layer are very well known and can be pulled out of a database.

While the calculation of Δ and Ψ from the optical properties and geometry of the sample is rather straight forward, the inverse problem of determining the sample parameters from ellipsometric measurements is a difficult problem. To interpret ellipsometric data, one uses the method of data fitting. Unknown sample parameters are varied within certain models to find the best fit of the generated data to the actual experimental data. Each model is derived from different effects, i.e. free carrier absorption, dipole excitation, defect states in the bandgap, etc. The most common fit parameters are thicknesses and optical constants. For the fitting algorithm, one usually uses Marquard-Levenberg. This algorithm will search for those fitting parameters that will result in the best fit. The best fit is defined as the fit for which the difference between calculated and measured ellipsometric quantities is as small as possible. This difference is referred to as mean square error and is defined in equation 6.5.

$$MSE_{CNS} = 1000 \times \sqrt{\frac{1}{3n-m} \sum_{i=1}^{n} (N_{Ei} - N_{Gi})^2 + (C_{Ei} - C_{Gi})^2 + (S_{Ei} - S_{Gi})^2}$$
(6.5)

where n is the number of wavelengths, m is the number of fit parameters, $N = \cos(2\Psi)$, $C = \sin(2\Psi)\cos(\Delta)$, $S = \sin(2\Psi)\sin(\Delta)$, and E refers to the parameters measured and G refers to the parameters calculated from the model and fit values. The M2000 which is based on the rotating compensator ellipsometer, measures data with approximately the same precision and accuracy in N, C, and S on any sample. The typical precision and accuracy of the measured ellipsometric data in terms of N, C, and S is 0.001. So an ideal model fit should have an MSE_{NCS} close to 1. Note that this definition is different from the MSE_{ρ} which is also often used in literature. MSE_{ρ} is defined in equation 6.6

$$MSE_{\rho} = \sqrt{\frac{1}{3n-m} \sum_{i=1}^{n} \left(\frac{\Psi_E - \Psi_G}{\sigma_{\Psi,i}^E}\right)^2 + \left(\frac{\Delta_E - \Delta_G}{\sigma_{\Delta,i}^E}\right)^2} \tag{6.6}$$

The MSE_{ρ} is typically much smaller than the MSE_{CNS} for the same data. To determine the thickness of PyO films by ellipsometry, the optical properties of PyO need to be determined. This results in three unknowns, i.e. the refraction

index n, the extinction coefficient k, and the film thickness. As each independent ellipsometric measurement only provides two independent measurement values, one has to measure at multiple wavelengths, multiple angles of incidence, and/or on multiple samples to determine the optical properties and the film thickness of the sample.

The optical properties measured at different wavelengths are not completely independent from each other. The physics dictates that the wavelength dependence of the refraction and extinction coefficients follow certain mathematical expressions. The spectral dependence of the optical properties is often described by the spatial dependence of real and imaginary parts of the dielectric constant, $\epsilon = \epsilon_r - i\epsilon_i$. The relation between the complex dielectric constant and the optical constant is given by the following expressions,[22]

$$n = \sqrt{\frac{\epsilon_r + \sqrt{\epsilon_r^2 + \epsilon_i^2}}{2}}$$

$$k = \sqrt{\frac{-\epsilon_r + \sqrt{\epsilon_r^2 + \epsilon_i^2}}{2}}$$
(6.7)

Without derivation, the most important dispersion models are listed in the section below:

6.2. Optical Models

The Lorentzian Model

To describe optical properties in the infrared, one often uses the Lorentzian model [Mass-Spring System]. The model describes the optical properties of solids, obtained by wave mechanics. [23]The dielectric constant is given as,

$$\epsilon_L = \frac{Amp_n Br_n En_n}{En_n^2 - E^2 - i \cdot EBrn_n} \tag{6.8}$$
where Amp_n is the amplitude of the oscillator and Br_n represents the full width half max of the transition, and En_n is the energy of the transition.

Harmonic

The Harmonic oscillator function is characteristic of quantum mechanical treatments of single electron transitions. It is useful in the description of polycrystalline and amorphous semiconductors. As the peaks of the function become narrower, Br < En, the harmonic oscillator is equivalent to the Lorentzian oscillator. The dielectric constant is given as,

$$\epsilon_H = \frac{Amp_n Br_n}{2} \left(\frac{1}{En_n - E - i\frac{Br_n}{2}} + \frac{1}{En_n + E - i\frac{Br_n}{2}} \right) \tag{6.9}$$

where Amp_n is the amplitude of the oscillator, Br_n represents the full width half max of the transition, and En_n is the energy of the transition.

The Gaussian Model

The typical use of the Gaussian oscillator model is to model amorphous and glassy films whose absorption bands have a Gaussian shape. These materials have atomic bond lengths and angles that are randomly distributed around an average value.[24] Thus absorption bands act like numerous harmonic oscillators whose resonant frequencies have a normal distribution. The primary advantage of the Gaussian is that the imaginary component of ϵ_G rapidly approaches zero beyond $E_n \pm Br$. This behavior is much different than the Lorentzian oscillator. The dielectric constant is given as,

$$\epsilon_{G} = Amp_{n} \left[\Gamma \left(\frac{E - En_{n}}{\sigma_{n}} \right) + \Gamma \left(\frac{E + En_{n}}{\sigma_{n}} \right) \right]$$

$$+ i \cdot Amp_{n} \left[\exp \left(\frac{E - En_{n}}{\sigma_{n}} \right)^{2} + \exp \left(\frac{E + En_{n}}{\sigma_{n}} \right)^{2} \right]$$

$$(6.10)$$

where Amp_n is the amplitude of the oscillator, Br_n is the full width half max, and En_n is the center energy. The function Γ is a convergence series that produces a Kramers-Kronig consistent line shape for ϵ_1 .

where
$$\sigma_n = \frac{Br_n}{2\sqrt{\ln(2)}}$$

The Tauc Lorentz Model

The Tauc-Lorentz Model is an empirical dispersion relation which uses the Tauc expression for the imaginary part of the dielectric function near the band edge:

Tauc Absorption :
$$\epsilon_2(E) \propto \frac{(E-E_g)^2}{E^2}$$
 (6.11)

This model is mainly used for amorphous materials with zero absorption below a defined bandgap energy. [25]

$$\epsilon_{T-L}(E) = \epsilon_{n1} + i\epsilon_{n2} \tag{6.12}$$

where

$$\epsilon_{n2} = \frac{Amp_n Eo_n Br_n (E - Eg_n)^2}{(E^2 - Eo_n^2)^2 + Br_n^2 E^2} \cdot \frac{1}{E} \quad Where \ E \ge Eg_n$$

$$(6.13)$$

$$\epsilon_{n2} = 0$$
 Where $E < Eg_n$

$$\epsilon_{n1} = \frac{2}{\pi} P \int_{Eg_n}^{\infty} \frac{\xi \epsilon_{n2}(\xi)}{\xi^2 - E^2} d\xi$$
(6.14)

where Amp_n is the amplitude of the oscillator, Br_n represents the full width half max of the transition, Eo_n is energy of maximum ϵ_2 , and E_{gn} is the band gap energy. The Cody Lorentz Model

The Cody Lorentz oscillator is similar to the Tauc-Lorentz in that it defines a band gap and a Lorentzian absorption peak. The Cody Lorentz differs by defining two transition energies, E_p and E_t . E_p describes transition to Cody behavior and E_t defines the transition from Cody to Urbach behavior. The Cody Lorentz model is as follows,

Cody Absorption :
$$\epsilon_2(E) \propto (E - E_g)^2$$
 (6.15)

$$\epsilon_{C-L} = \epsilon_{n1} + i\epsilon_{n2} \tag{6.16}$$

where

$$\epsilon_2 = \frac{E1}{E} \exp\left(\frac{E - E_{gn} - E_{tn}}{E_{un}}\right) \qquad \qquad Where \ 0 < E \le (E_{gn} + E_{tn})$$

$$\tag{6.17}$$

$$\epsilon_2 = \frac{(E - E_{gn})^2}{(E - E_{gn})^2 + E_{pn}^2} \cdot \frac{A_n E_{on} \Gamma_n E}{(E^2 - E_{on}^2)^2 + \Gamma_n^2 E^2} \qquad Where \ E > (E_{gn} + E_{tn})$$

$$E1 = (E_{gn} + E_{tn})G(E_{gn} + E_{tn})L(E_{gn} + E_{tn})$$
(6.18)

$$\epsilon_{n1} = \frac{2}{\pi} P \int_{Eg_n}^{\infty} \frac{\xi \epsilon_{n2}(\xi)}{\xi^2 - E^2} d\xi \tag{6.19}$$

In this equation we have $G(E) = \frac{(E-E_{gn})^2}{(E-E_{gn})^2+E_{pn}^2}$ as the near-bandgap function that defines the Cody absorption behavior. The function transisitions to Lorentzian absorption at the energy $E_g + E_p$. The transition between Urbach absorption and Cody absorption is marked by $E_g + E_t$.

Fitting Techniques

Determining optical constants as well as film thickness from the same ellipsometric measurement is often convoluted and not straight forward due to the optical properties having a dependence on the film thickness. A possible technique to over come this is to grow samples of varying thickness on the same substrate. In this study, the PyO films are partly absorbing and partly transparent. This leads to a significant fraction of the illuminating beam to transmit the absorbing layer, pass through the transparent layer, be reflected from the substrate, and pass back out through the absorbing layer. This allows for the optical properties and the thickness to be fit without strong correlations.[19]

6.3. Measurement Results

Figure 6.2 shows the MSE values for the different ellipsometry models for sample 121513 grown on Al / Si. Better fits were obtained for the Cody Lorentz model, the Tauc-Lorentz Model, and the Gaussian Model which are known to describe semiconductor materials. There is a tendency to obtain a lower MSE value for models with more fit parameters. The Cody-Lorentz fits often result with $E_g = 0$ eV which suggests there is no physical meaning for values obtained by the Cody-Lorentz model for our PyO samples.



Fig. 6.2: Effect of the Number of Fitting Parameters vs Goodness of Fit

The transmission spectra of PyO, NiO, and FeO thin films of as well as the microscope glass substrate are shown in figure 6.3. Above 650 nm the optical properties of all three oxides are very similar. The 65% transmission is not caused

by absorption in the oxide, but reflection caused by a refraction index significantly higher than 2. For wavelengths shorter than 650 nm, absorption becomes significant. All three oxides become opaque for wavelengths of 300 nm and under. Absorption takes place at longer wavelengths for PyO compared to FeO and NiO.



Fig. 6.3: Transmission

The calculated spectra of the optical constants found by the Cody-Lorentz model of samples grown on glass are shown in figures 6.4 and 6.5. The extinction spectrum was used to calculate PyO's absorption spectra from equation 6.3.

The calculated spectra of the index of refraction determined by the Cody-Lorentz model of samples grown on glass are shown in figure 6.4a. The index of refraction of NiO and FeO are plotted as well for comparison. A weighted medium approach was attempted to derive PyO's optical properties from a mix of NiO and FeO using an effective medium approach but was unsuccessful. The black bars represent the standard deviation from the set of all measured samples.

Figure 6.5a shows the measured extinction coefficients for all PyO samples. Figure 6.5b compares the average k of PyO with the k spectra for NiO and FeO. It can be seen for high wavelengths that PyO's extinction coefficient converges to zero more gradually than NiO and FeO determining that PyO absorbs a much broader range of wavelengths.

The absorption coefficient α was calculated by the familiar equation $\alpha = \frac{4\pi k}{\lambda}$. The gradual onset of absorption is displayed in figure 6.6. This data is in agreement



Fig. 6.4: Index of Refraction, n, Measured on Samples Grown on Glass



Fig. 6.5: Extinction Coefficient, k, Measured on Samples Grown on Glass

with the transmission data and shows that PyO has very little absorption under 2 eV. The data suggests that the bandgap of PyO is smaller than that of NiO (4-4.3 eV) and closer to that of FeO (2.4 eV) [26]



Absorbtion Coefficient

Fig. 6.6: Absorption Coefficient

Typically the energy of the bandgap can be extrapolated from the absorption data. In order to make this calculation it must be certain whether the semiconductor is a direct or indirect semiconductor. Indirect bandgap semiconductors imply that either a release or absorption of a phonon must occur whenever a photon is absorbed or emitted. This is determined by examining if $\alpha \hbar \omega \propto (\hbar \omega)^{1/2}$, i.e. direct, or $\alpha \hbar \omega \propto (\hbar \omega)^2$, i.e. indirect, in the regions of strong absorption ($\hbar \omega$ is the energy of the incident photon). These models are given by,

$$\alpha = \frac{(\hbar\omega - E_g)^{1/2}}{\hbar\omega} \tag{6.20}$$

for direct transitions, and

$$\alpha = \frac{(\hbar\omega - E_g \pm E_{phonon})^2}{\hbar\omega}$$
(6.21)

for indirect transitions with the absorption/emission of a phonon. One method to determine whether a material has a direct or indirect band gap is to plot $\alpha \hbar \omega^n$ vs $\hbar \omega$ for $n = \frac{1}{2}$ and n = 2 and see whether the plot is linear in the strong absorption regime. The average absorption coefficient data was analyzed in order to make statements on the nature of the bandgap. The two plots of the measured data can be seen in figure 6.7. The direct bandgap model implies a bandgap of 4.5 eV, fairly close to NiO (4.3 eV) while the indirect model implies a band gap in the vicinity of 2 eV depending on phonon energy. Neither of the energies can be correlated with further analysis of electrical properties. Similar studies would have to be performed on crystalline samples and extrapolated to the amorphous case in this study. If one just assumes $\alpha \propto (\hbar \omega)^n$, n is found to be 3-4 depending on the photon energy range modeled. This is evidence that there are forbidden states in transitions involving a multiphonon process. [27]



Fig. 6.7: Typical Tauc Plots to Determine Direct or Indirect Transitions

7. IMPEDANCE SPECTROSCOPY

A MDC 811-150 mercury probe with a HP 4192A LF impedance analyzer were used to measure the dielectric properties of PyO in a frequency range of 10 Hz - 13 MHz. Similarly to optical excitation measurements, impedance spectroscopy involves analyzing the excitation effects of different frequencies in order to separate properties of the material. Figure 7.1 represents the basics of impedance spectroscopy. An AC current with known frequency and amplitude is sourced to the device under test (DUT) and the resulting AC voltage is measured. AC voltage and current are normally not in phase. The ratio of the voltage amplitude and current amplitude can be considered to be the AC resistance of the DUT. Using complex notation for voltage and the current,

$$I = I_o e^{i\omega t} \tag{7.1}$$

$$V = V_o e^{i\omega t} e^{i\theta} \tag{7.2}$$

One defines the complex impedance as:

$$Z = \frac{V_o e^{i\omega t} e^{i\theta}}{I_o e^{i\omega t}} = \frac{V_o}{I_o} e^{i\theta}$$

$$Z = Z' + iZ'' = R + i\frac{1}{\omega C}$$
(7.3)

where Z is the complex impedance.

Analysis of impedance measurements involves treating the test device as an analog circuit and performing circuit analysis. Thus an accurate circuit model needs to be employed to obtain meaningful data. Figure 7.2 shows the typical



Fig. 7.1: Measurement Characteristics of Impedance Spectroscopy

circuit models. The series model, shown in figure 7.2a, is representative of a highly resistive device where current leakage through the device is minimal. The parallel model, shown in figure 7.2b, is used when there is significant current passing through the film. The parallel model was used in this study to measure the capacitance of PyO thin films grown on Al / Si substrates. Figure 7.2c is more accurate to the physical situation, where the resistance of the substrate is taken into account. As the frequency changes, the resistance of the device will often change as well. Even though PyO is highly resistive, the resistance measured through a 245 nm thick PyO film is low enough that it must be considered. That being said, the conductance measured was just above the limits of the HP 4129A.



Fig. 7.2: Device Models for Impedance Analysis

7.1. The MDC 811-150 Mercury Probe

The MDC 811-150 Mercury Probe incorporates three contacts to the sample.

A circular Hg dot with a diameter of 775 μ m is in the center of a 0.5 inch diameter Hg ring, which has an area 48.5 times larger than the dot. A stainless steel plate can be used as a back contact but was not utilized for measurements on the PyO samples sputtered on Al / Si. The capacitance was measured between the dot and the ring contacts. PyO grown on Al / Si substrates were used for capacitance measurements since the aluminum layer would not contribute to the capacitance and resistance of the device. The series resistance of the aluminum layer was calculated from the size of the contacts and the measured sheet resistance (0.05 Ω square) and was estimated to be smaller than 0.02 Ω . The influence of the series resistance of the Al layer is dependent on the frequency of the oscillation and was found to be negligible over the measurement range.[28] The offset of the cables and the test fixture was corrected for by measuring the capacitance and conductance with the sample in place while the mercury probe was in the purge position (not connected).



(a) Hg Probe (b) Device Diagram

Fig. 7.3: The 811-150 Mercury Probe

7.2. The HP4192A LF Impedance Analyzer

Before sample measurements, the calibration of the HP 4192A was checked with the Keithley 5906 calibration sources at 1 kHz, 100 kHz, and 1 MHz. The measured values differed less than 0.6% with the face value for all capacitance sources of the 5906 set except for the two lowest capacitance sources measured at 1 kHz: 5% for the 0.381 pF capacitor and 2% for the 1.3708 pF capacitor. Capacitance measurements were taken at room temperature, with the HP 4192A set to parallel mode.

Due to the much larger surface area of the Hg ring, the dielectric constant was calculated from the capacitance of the Hg dot alone. This estimates the total capacitance of the system within 98% of the actual value. The capacitance from the Hg ring and the capacitance from the Hg dot act like two capacitors in series. This calculation can be seen in equation 7.4.

$$C_{Total} = \left[\frac{1}{C_{dot}} + \frac{1}{C_{ring}}\right]^{-1} = \left[\frac{t}{\kappa\epsilon_o A_{dot}} + \frac{t}{\kappa\epsilon_o A_{ring}}\right]^{-1}$$
$$= \left[\frac{t}{\kappa\epsilon_o A_{dot}} + \frac{t}{\kappa\epsilon_o 48.5A_{dot}}\right]^{-1} = \left[\frac{t}{\kappa\epsilon_o A_{dot}}\frac{49.5}{48.5}\right]^{-1}$$
(7.4)
$$= .98C_{dot}$$

7.3. Measurement Results

The dielectric constant was calculated by $\kappa = \frac{C_{dot}t_{PyO}}{\epsilon_o A_{dot}}$ after the offset capacitance of the system was subtracted from the measured capacitance. The measured offset of the system can be seen in figure 7.4 and the results of the measurements are shown in figure 7.5. With a driving oscillation amplitude of 1 V, an electrochemical reaction was noted. The capacitance appeared to be time dependent and the film appeared to be etched in the spots that made contact to the mercury. The time dependence was smaller than 0.03% per minute when measured at 100 kHz. Prolonged exposure to mercury in the Hg probe (longer than 12 hours) resulted in the creation of pin holes through a 245 nm PyO layer. For lower oscillation voltages, i.e. 0.1 V, the time dependence decreased with a factor 5. Electrochemical activity was also observed by others on FeO nanoparticles. [29] This effect can be seen in figure 7.5 where the measurements were taken 12 minutes apart. The dielectric constant was determined to be 510 at 320 Hz and 16.7 at 8 MHz. This is seen to be much larger than the dielectric constant for NiO. A similar dependence of the dielectric constant on frequency was noted for CoO \cdot NiO mixed crystals where a dielectric constant of 200 at 100 Hz and 42 for 1 MHz were reported. [30] At these frequency ranges, excitations due to mobile ions, dipole orientation, and space-charge polarization can all contribute to the dielectric constant at low frequencies.



Fig. 7.4: Capcitance Offset of the System



Fig. 7.5: Dielectric Constant

8. RESISTIVITY MEASUREMENTS

8.1. Modification of the Janis Cryostat

A Janis Research Model ST-100 Supertran cryostat system was used as an environment for temperature dependent resistivity measurements. Initially the cryostat was wired with very thin copper wires. This caused current to be leaked through the wire's insulation before traveling through the sample. The wires inside the cryostat that are connected to the sample probes were replaced with stainless steel coaxial cables to prevent as much leakage as possible. Brass, spring driven probes were used to make contact to the sample. A thermocouple probe was mounted to the copper plate to measure temperature at the sample and a heating coil was wrapped around the stalk to control the temperature via a Lakeshore 331 temperature controller. Liquid N_2 was used to cool the cryostat to a minimum temperature of 77K. Samples grown on glass substrates were attached to the copper mounting plate with low temperature vacuum grease to ensure thermal contact.

8.2. The Keithley 7001 Switching Matrix with a 7065 Hall Effect Card

Due to the high resistivity of the sample, extra precautions must be taken when measuring the resistivity of the samples. Voltmeters rely on having an input resistance that is substantially higher than the device under test so they will draw as little current as possible. Once the measured resistance is of the same order of magnitude as the input resistance of the voltmeter, the voltmeter will act like a shunt resistor and a portion of the current no longer goes through the sample. The Keithley 7001 switching matrix with a 7065 Hall effect card not only includes a high resistance mode that switches unity buffer amplifiers between the sample and the voltmeter but also contains a switching matrix that allows for automatically swapping of the current and voltage electrodes. The 7065 hall effect card in high restance mode uses unity buffer amplifiers which have a minimum value of 100 T Ω .[31] These amplifiers allow the samples with resistances of 10¹⁴ Ω to be measured. The difference between high resistance and low resistance modes is shown in figure 8.2. The unity amplifier effectively holds the input voltage and output equal. The input voltage is guarded with the output voltage as well which nullifies capacitance effects in the triax cable. In low resistance mode, the buffer amplifier is used to hold the guard at nearly the same potential as the input voltage which is directly connected to the voltmeter. In the high resistance mode, the input capacitance of the buffer amplifier is not negligible and together with the sample resistance, produces a high RC time constant. The 2182A nanovoltmeter itself has an input impedance greater than 10 G Ω for the 10 mV-10V range.[32] Sufficient delay time must be used between sourcing the current and actually measuring the voltage. Delay times were measured by sourcing a current and waiting for the voltage to stabilize and recording the time.

For highly resistive samples, the current that makes its way through the sample is much less than the current sourced. Thus, it is important to measure the current





(a) Assembled Cryo- (b) Cryostat Insert stat



Fig. 8.1: Modified Janis Cryostat



Fig. 8.2: Unity Buffer Amplifer Schematic



Courtesy of Keithley Instruments Inc. [31]

 $Fig.\ 8.3:\ 7065$ Hall Effect Card Schematic

going through the sample. In the setup, this is performed with a 6514 electrometer. Using guarded triaxial cables further reduces leakage current and increases the accuracy of the measurements. The cables have a shield surrounding the inner cable that is held at the output potential of the buffer amplifiers. The cryostat only has BNC connectors so the triax cables were connected to BNC cables just before the Cryostat. Due to the buffer amplifier guarding the wire connecting the current source, the buffer amplifier introduces a current offset less than 150 fA.[31] This is accounted for by measuring the resistivity with both positive and then negative current for the same electrode configurations and averaging the results.

8.3. Room Temperature Linear Four Point Probe Resistivity Measurements

A linear four point probe setup based on a Jandel universal probe stand and Keithley electrical characterization equipment including a 7065 Hall effect card in a 7001 switching matrix, a 6221 current source, a 6514 electrometer, and a 2182A nanovoltmeter were used to measure the room temperature resistivity. (See figure 8.4 The Jandel probe was set to an electrode descent rate of 1mm per second and an electrode force of 80 N. The Jandel has Tungsten carbide electrodes separated by 1 mm. The current was sourced through two electrodes, while the electric potential was measured across the other two electrodes. Resistivity was calculated by equation 8.1. [28]

$$\rho = \frac{\pi t}{\ln(2)} R_{avg} \tag{8.1}$$

where $R_{avg} = \frac{R_{14,23} - R_{14,32} - (R_{41,23} - R_{41,23}) + R_{23,14} - R_{23,41} - (R_{32,14} - R_{32,41})}{8}$. $R_{ab,cd}$ refers to the voltage measured accross contacts c and d when the current is sourced through contacts a and b, $R_{ab,cd} = \frac{V_{34}}{I_{12}}$. For the numbering of the contacts see figure 8.5.



Fig. 8.4: Jandel Linear Four Point Probe



Note: The 1234 labels are interchangeable

 $Fig.\ 8.5:$ Electrical Transport Measurement Setup

Sample #	Oxygen Flow Rate	Substrate	ρ (Ω cm)
031513A	7	Glass	2.00 E5
100113	10	Glass	1.30E4
		$\rm SiO_2/Si$	5.63E3
101413	10	Glass	3.60E3
111413	10	Glass	5.00E3
121513	10	$\rm SiO_2/Si$	6.62 E3
021914	5	Glass	5.06E4
		$\rm SiO_2/Si$	$3.32\mathrm{E4}$
099119	E	Glass	$6.14\mathrm{E4}$
022113	G	SiO_2	$3.04\mathrm{E4}$

Tab. 8.1: Measured Resistivity with the Linear Four Point Probe

8.4. Measurement Results

It is seen that the resistivity decreases with increased oxygen flow rate and the use of atomic oxygen. This phenomena can also be seen in ITO thin films. [33] Films grown on SiO_2/Si substrates were consistently found to have a lower resistivity. Care was taken to make sure that there was no chance that the PyO film could be shorted to the Si substrate. It is possible that the interface between PyO and SiO₂ is significantly different from PyO and glass yielding different properties.

8.5. The Semi Infinite Plane: Derivation of the van der Pauw Equation

Van der Pauw measurements are an industry standard for resistivity measurements. The sample can be any shape and the spacing between contacts is not important. The only requirement is that the contacts must be placed on the sample's edges, the contacts are assumed to be infinitely small, the surface of the sample is simply connected (no holes exist in the sample), and the thickness is uniform. The following derivation follows L. J. Van der Pauw's derivation in his famous 1958 paper. [34] The van der Pauw equation, shown in equation 8.10, will first be derived for a specific case and then extrapolated for general cases. The situation first considered is shown in figure 8.6. Current is passed through point 1 and extracted through point 2. In this case, with the contacts on the edges of a sufficiently thin sample ($t \ll probe spacing$), the current will travel radially outward in a cylindrical distribution with surface area πtr where t is the thickness and r is the distance away from a specific probe. The current will never flow through the surface of the sample so the distribution is given by $\mathbf{J} = \frac{I}{\pi tr}$.

$$\mathbf{E} = \rho \mathbf{J} = \frac{\rho I}{\pi t r} \hat{\mathbf{r}}$$
(8.2)

The electric fields of the two probes, written in Cartesian coordinates with the origin on point one, are given by



Fig. 8.6: Contacts of Arbitrary Spacing on a Semi-Infinite Sample

$$\mathbf{E}_{1} = \frac{\rho I(x\hat{\mathbf{x}} + y\hat{\mathbf{y}})}{\pi t(x^{2} + y^{2})}$$

$$\mathbf{E}_{2} = -\frac{\rho I((x - a)\hat{\mathbf{x}} + y\hat{\mathbf{y}})}{\pi t((x - a)^{2} + y^{2})}$$
(8.3)

The voltage between probes 3 and 4 is found by the negative line integral of the electric field between the two points.

$$V_{34} = V_3 - V_4 = -\int_3^4 (\mathbf{E}_1 + \mathbf{E}_2) \cdot d\mathbf{\hat{x}}$$
 (8.4)

$$V_{34} = \frac{\rho}{\pi t} \int_{a+b}^{a+b+c} \left(\frac{I}{x} - \frac{I}{x-a}\right) dx \tag{8.5}$$

$$V_{34} = \frac{\rho I}{\pi t} \left[\ln \left(\frac{a+b}{b} \right) - \ln \left(\frac{a+b+c}{b+c} \right) \right]$$
(8.6)

$$V_{34} = \frac{\rho I}{\pi t} \ln \left(\frac{(a+b)(b+c)}{b(a+b+c)} \right)$$
(8.7)

$$R_{12,34} = \frac{V_{34}}{I_{12}} = \frac{\rho}{\pi t} \ln\left(\frac{(a+b)(b+c)}{b(a+b+c)}\right)$$

or (8.8)
$$\exp\left(\frac{-\pi t R_{12,34}}{\rho}\right) = \frac{b(a+b+c)}{(a+b)(b+c)}$$

In the same fashion it can be shown that,

$$R_{23,14} = \frac{V_1 - V_4}{I_{23}} = \frac{\rho}{\pi t} \ln\left(\frac{(a+b)(b+c)}{ca}\right)$$

or (8.9)
$$\exp\left(\frac{-\pi t R_{23,14}}{\rho}\right) = \frac{ba}{(a+b)(b+c)}$$

Adding equations 8.9 and 8.10 given that b(a+b+c)+ca = (a+b)(b+c) yield the desired van der Pauw equation,

$$\exp\left(-\frac{\pi R_{12,34}d}{\rho}\right) + \exp\left(-\frac{\pi R_{23,14}d}{\rho}\right) = 1$$
(8.10)

In order to negate the effect of the current offset of the switching matrix and any offset voltages present, $R_{12,34}$ is replaced by an average of the horizontal measurements and $R_{23,14}$ is replaced with an average of the vertical measurements. For contact numbering see figure 8.3.

$$R_a = \frac{R_{12,43} - R_{12,34} + R_{43,12} - R_{34,12}}{4} \tag{8.11}$$

$$R_b = \frac{R_{14,23} - R_{41,23} + R_{23,14} - R_{32,14}}{4} \tag{8.12}$$

Note: equations 8.10, 8.11, and 8.12 are valid as long as the contacts are placed on the edge of the sample. This specific case of the semi-infinite plane can be generalized toward the general case of an aribtrarily shaped sample by the theory of conformal mapping. The edge of the semi-infinite plane can be mapped onto the edge of the arbitrarily shaped sample. This is the reason why contacts must be placed on the edge of the sample for van der Pauw measurements to be valid.

8.6. The Infinite Plane: Rectangular Geometry

Given a rectangular probe configuration on a sample with resistivity ρ and thickness t, it is possible to model the sample as an infinite plane. This particular method is an attractive measurement technique for isotropic samples that have a large enough surface area to negate edge effects. Figure 8.7 details the measurement configuration. Ideally the probes would be in a square geometry but is derived for a rectangle for generality.



Fig. 8.7: Measurement Configuration for an Infinite Plane

In the first case, a current I will be passed through probe 1 and be extracted through probe two. The voltage is then measured between probes 3 and 4 in the same fashion as the van der Pauw derivation. The major difference between the contacts on the edge of the sample and in the middle is the electric field derived from Ohm's law. In this case the current will travel in all directions and thus penetrate the surface area of a complete cylinder.

$$\mathbf{E} = \rho \mathbf{J} = \frac{\rho I}{2\pi t r} \hat{\mathbf{r}}$$
(8.13)

In Cartesian coordinates with probe 4 as the origin, the electric field from the probes is given by,

$$\mathbf{E}_{1} = \frac{\rho I(x\hat{\mathbf{x}} + (y-b)\hat{\mathbf{y}})}{2\pi t(x^{2} + (y-b)^{2})}$$

$$\mathbf{E}_{2} = -\frac{\rho I((x-a)\hat{\mathbf{x}} + (y-b)\hat{\mathbf{y}})}{2\pi t((x-a)^{2} + (y-b)^{2})}$$
(8.14)

The voltage that would be measured between points 3 and 4 is found by,

$$V_{43} = V_4 - V_3 = -\int_3^4 (\mathbf{E}_1 - \mathbf{E}_2) \cdot d\mathbf{\hat{x}}$$
 (8.15)

$$V_{43} = \frac{\rho I}{2\pi t} \int_{0,y=0}^{a} \left(\frac{x}{x^2 + b^2} - \frac{x - a}{(x - a)^2 + b^2}\right) dx \quad (8.16)$$

$$V_{43} = \frac{\rho I}{2\pi t} \ln\left(\frac{a^2 + b^2}{b^2}\right)$$
or
$$exp\left(\frac{-2\pi t R_{12,43}}{\rho}\right) = \frac{b^2}{a^2 + b^2}$$
(8.17)

A similar calculation can be done for the voltage between probes 1 and 4 with current sourced through probe 2 and extracted through probe 3.

$$V_{14} = \frac{\rho I}{2\pi t} \ln\left(\frac{a^2 + b^2}{b^2}\right)$$

or (8.18)
$$\exp\left(\frac{-2\pi t R_{23,14}}{\rho}\right) = \frac{a^2}{a^2 + b^2}$$

Addition of the equations 8.17 and 8.18 yields the infinite plane van der Pauw equation,

$$\exp\left(\frac{-2\pi t R_{12,43}}{\rho}\right) + \exp\left(\frac{-2\pi t R_{23,14}}{\rho}\right) = 1 \tag{8.19}$$

Thus there is a factor 2 difference between the two equations. Note: equation 8.19 is valid when the sample is much larger than the distance between the probes. For a rectangular arrangement, $R_{12,43}$ and $R_{23,14}$ are replaced with R_a and R_b of equations 8.11 and 8.12.

8.7. Correction Factors

Often times edge effects, sample thickness, probe spacing, and/or probe orientation effect the measurement results so that neither equations 8.10 or 8.19 yield an accurate result of the resistivity. Thus equation 8.10 is worked into a more general form,

$$\rho = CF \cdot t \frac{(R_a + R_b)}{2} \tag{8.20}$$

Where CF is a correction factor determined by geometrical calculations of the specific orientation. It has been shown that CF varies from 1, for contacts on the edges, to 2 for sufficiently large samples. Correction factors for various geometries and spacings have been extensively calculated and studied.[35, 36, 37] Yamashita et. al calculated how the CF depends on the sample size for a rectangular arrangement of the probes. The results are shown in figure 8.8.[36] The correction factor was determined to be approximately 6.2 from this curves and the sample's edges were about a probe spacing away from the probes.

8.8. Edge Effects

Before actual measurements were taken, the effect of edges was taken into consideration. At an abrupt edge, image charge effects are present and the current density is not so easily defined. In this case, the measured voltage will be greater and the measured resistivity will be larger near the edge of the sample. This effect



Fig. 8.8: Correction Factor Calculated by Yamashita for probe spacing of 0.12 cm and film thickness 0.01 cm

can be seen in figure 8.9 for a PyO sample on glass. The resistivity was measured as a function of the probe distance from an edge and was found to be independent of the probe distance from the edge. Edge effects only showed up for samples whose edges were cut. (See figure 8.9) It was found that PyO deposited on the 1 mm edges of the glass sample masked the edge effects described above.



Cut Edges vs Non-Cut Edges

Fig. 8.9: Edge Effects of Resistivity

8.9. Measurement Results

Table 8.2 lists the resistivity values to the samples measured at varying temperatures. It is seen that the resistivity follows the familiar semiconductor temperature dependence, $\ln(\rho) \propto T^{-1}$. Semiconductor theory derives the relationship by electron hole pairs generated through thermal energy excitations dictated by an activation energy, E_a . For most semiconductors this activation energy is just the bandgap. This relationship is given as $\rho = \rho_o e^{\frac{E_a}{2k_b T}}$, where k_b is Boltzmann's constant. The energy value can be calculated from the slope of plotting $\ln(\rho)$ vs T^{-1} where the slope= $\frac{E_a}{2k_b}$. The values measured vary from 0.55 eV to 0.60 eV, which is significantly less than the bandgap range suggested from optical transmission measurements. This is discussed in the band diagram section.



Ln(Rho) vs 1/T

Fig. 8.10: Temperature Dependent Resistivity Measurements

Tomporature (K)	$ ho \ (\Omega \cdot cm)$		
Temperature (K)	100113	101413	111413
200	2.73E + 06	4.30E + 05	8.91E + 05
225	4.97E + 05	9.88E + 04	2.21E + 05
260	6.45E + 04	1.46E + 04	$3.19E{+}04$
296	1.11E + 04	2.86E + 03	6.04E + 03
320	4.03E + 03	1.13E + 03	2.37E + 03
Slope of $Ln(\rho)$ vs $1/T$	3479	3189	3183
$\mathbf{Ea} \ (\mathbf{eV})$.60	.55	.55

Tab. 8.2: Resistivity vs Temperature Measurements

8.10. Comments on the Band Diagram

In typical semiconductors, the valence and conduction band is comprised of overlapping s and p orbitals. The situation becomes much more complicated whenever conduction is effected by the d orbitals. Electron-electron interactions are no longer negligible and spins are not necessarily anti-aligned. The covalent bonding between atom's d-d orbitals and d-p orbitals can take many forms as well as many different bonding energies. A simplified result is shown for the 3d transition metal oxides in figure 8.11.[38] The 2p orbital band makes up the valence band and the conduction band is of the 4s orbitals. The 3d band, which is expected to have a higher energy than the 4s band, acts as a mid band gap state due to the d-p bonds made between the metals and oxygen. Shown in figure 8.11a, is the band diagram for an early transition metal such as scandium or titanium. Figure 8.11b displays how the 3d band level begins to overlap the 2p band for late transition metals such as zinc. In our case we have iron, n = 6, and nickel, n = 8. So it is expected that permalloy oxide will have a band diagram similar to figure 8.11b. The electric and optical measurements indicating inter bandgap states could be explained by this model. The d band orbitals act as inner bandgap states which result in absorption of a wider range of energies. The obtical data agrees with this since absorption was measured over a wider range than pure NiO and FeO. The electrical excitation energy measured is lower than expectation which also suggests these inner bandgap states. Since there are two transition metals in PyO, the situation becomes more complicated with more orbital bands contributing the electric and optical properties.





9. CONCLUSION

Permalloy oxide thin films were successfully grown using reactive dual ion beam sputtering using a $Ni_{80}Fe_{20}$ target. Films were deposited on substrates of glass microscope slides, SiO_2 / Si, and Al / Si at a deposition rate of approximately 1.01 Angstroms/second. The oxygen assist beam was used to expose the substrate to a beam of molecular or atomic oxygen during deposition.

Magnetic moment measurements were carried out to reveal no ferromagnetic component in the films with a saturation magnetization $< 10^{-9}$ Am². This was satisfactory since it was not expected that PyO would be ferromagnetic. It was concluded from these results that there was no metallic ferromagnetic permalloy in the PyO films.

The optical properties of PyO were determined from ellipsometric measurements. Transmission data revealed that PyO absorbs a wide range of light in the visible range, more so than NiO and FeO. The determined index of refraction can now be used in simpler optical equipment to measure film thickness without having to perform ellipsometry for every sample. It is still unclear from the ellipsometric data whether PyO is a direct or indirect semiconductor and there is evidence to suggest forbidden states in the bandgap.

Impedance spectroscopy was performed and the dielectric constant was calculated over a wide range of frequencies. The dielectric constant, κ , was found to have a maximum of 522 at 320 Hz and a minimum of 16.6 at 8 MHz for the measured frequency range. The frequency dependence is consistent with previous studies carried out on CoO · NiO mixed crystals and could be due to the presence of mobile ions, dipole orientation, and/or space charge effects.

The electrical resistivity was measured for different samples at room temperature and at different temperatures for select samples. The resistivity was found to be dependent on the oxygen flow rate and would increase for decrease of oxygen flow during deposition. This phenomena occurs in other conducting oxides prepared by reactive dual ion beam sputtering, such as indium tin oxide.[39] The temperature dependent measurements showed the familiar semiconductor resistivity dependence on temperature, $\ln \rho \propto T^{-1}$. At this point it is not clear whether conduction occurs in the *d* band, *s* band, or is a result of hopping. Further studies must be taken in order to determine the conduction mechanism.

10. FUTURE STUDIES

The questions one asks about mixed transition metal oxides such as PyO are questions about the effect of orbital mixing on the film's properties. Seebeck measurements would be a strong next step in determining the the effect of the *d* band on the conduction mechanism. The temperature dependent resistivity measurements were held back by the apparatus and measurements need to be taken at lower temperatures. This can be achieved by guarding the wires all the way up to the sample and incorporating further high resistance measurement techniques. Now that some novel properties have been measured, incorporation into devices should be studied. It would be worth while to do a study on various RRAM devices with PyO with either varying Ni Fe content or the inclusion of another transition metal layer.

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