

ELECTRICAL TRANSPORT PROPERTIES OF ILMENITE-MANGANESE
CERAMIC SERIES AND PSEUDOBROOKITE-MANGANESE BULK AND THIN
FILMS

THESIS

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by

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	iv
LIST OF TABLES	viii
LIST OF FIGURES	x
 CHAPTERS	
1 INTRODUCTION	1
2 SAMPLE PREPARATION	4
2.1 Synthesis of Manganese doped Ilmenite and Hematite doped Ilmenite Ceramics	4
2.2 Synthesis of Ilmenite-Hematite Thin Film	7
2.2 Synthesis of Pseudobrookite Single Crystal and Manganese doped Pseudobrookite Single Crystal, ceramics and thin films	10
2.3.1 Pseudobrookite-Manganese Ceramics	10
2.3.2 Pseudobrookite-Manganese Thin Films	11
2.3.3 Pseudobrookite Single Crystal and PsB-Mn Single Crystal	11
3 PROPERTIES OF MATERIALS-PREVIOUS STUDIES.....	13
3.1 Ilmenite-Hematite Ceramics and Thin Films.....	13
3.1.1 Electrical Properties	13
3.1.2 Magnetic Properties	27

3.2	Ilmenite-Manganese.....	30
3.3	Pseudobrookite-Manganese	35
4	MEASUREMENT TECHNIQUES	38
4.1	Electrical Characterization.....	38
4.1.1	Two-Point Probe Method.....	38
4.1.2	Four-Point Probe Method	39
4.1.3	van der Pauw Method	45
5	SET UPS AND EQUIPMENT	50
5.1	Electrical Characterization Set ups and Equipment.....	51
5.1.1	Pulse mode versus Lock-in Amplifier	52
5.1.2	Keithley 7001 Switch System.....	58
5.1.3	Model 22 CTI Cryogenics Cryostat and Model 8200 CTI Cryogenics Helium compressor	59
5.1.4	Lakeshore 331 Temperature Controller	60
5.1.5	Electromagnet, Power Supply and Switch Unit.....	61
5.1.6	Delta Model 6400 Temperature Chamber	62
5.2	Optical Characterization Set ups and Equipment	63
6	MEASUREMENT RESULTS.....	69
6.1	Electrical Characterization.....	69
6.1.1	Ilmenite Ceramic Sample.....	69
6.1.1.1	Determination of I-V Relation of Contacts.....	70
6.1.1.2	Model Contacts	81
6.1.1.3	Resistivity Measurements	90

	6.2.1 Ilminite-Manganese Thin Film	133
	6.2.2 Ilmenite-Hematite Thin Film	138
7	DISCUSSION AND CONCLUSION.....	143
	APPENDICES	
	Appendix A.....	145
	Appendix B	154
	Appendix C	155
	BIBLIOGRAPHY	157

LIST OF TABLES

Table 2.1	Material List.....	4
Table 2.2	Material Weight.....	6
Table 3.1	Switching voltage for IH Ceramics ¹¹	21
Table 3.2	Comparison of Resistivity for Film and Ceramic ¹⁸	26
Table 3.3	Magnetic Properties of Spicimens ¹⁴	30
Table 3.4	Nominal and Actual Compositions of Manganese	31
Table 3.5	Resistivity versus Manganese Concentration	32
Table 3.6	Activation Energy versus Manganese Concentration	34
Table 5.1	Alpha-Numeric Contact Codes.....	59
Table 5.2	Wavelength Cut offs	64
Table 6.1	Ilmenite Ceramic Data.....	76
Table 6.2	Contact 1 and 2 Data.....	77
Table 6.3	Ideality Constants at Varying Temperatures	95
Table 6.4	Leakage Currents at Varying Temperatures	95
Table 6.5	Ilmenite-Mn(15%) Data.....	101
Table 6.6	Ideality Constants at Varying Temperatures	107
Table 6.7	Leakage Currents at Varying Temperatures	107
Table 6.8	Ilmenite-Mn(40%) Data.....	112
Table 6.9	Ideality Constants for Varying Temperatures.....	117
Table 6.10	Leakage Currents for Varying Temperatures	117

LIST OF FIGURES

Figure 2.1 Flow Chart.....	6
Figure 2.2 Ceramic Flow Chart	7
Figure 2.3 XRD IH Films	8
Figure 2.4 Ceramic Flow Chart	10
Figure 2.5 Protocol for Single x'tal Growth.....	12
Figure 2.6 TEM micrograph of PsB x'tal	12
Figure 3.1 Resistivity vs Temperature for IH Ceramic ¹⁴	15
Figure 3.2 Resistivity versus Hematite Composition ¹⁴	16
Figure 3.3 Resistivity vs Temperature of Specimen #5 ¹⁴	17
Figure 3.4 Seebeck voltage vs Temp ¹⁴	18
Figure 3.5 Seebeck Voltage vs Hematite Composition ¹⁴	18
Figure 3.6 Seebeck voltage vs Temperature #5 ¹⁴	18
Figure 3.7 Resistivity vs Temperature for IH series Ceramics ¹¹	20
Figure 3.8 2pp I-V Characteristics of p-type and n-type Ilmenite-Hematite ¹¹	21
Figure 3.9 SEM of a)x=0.1 and b)x=0.27 grain sizes ²¹	22
Figure 3.10 Varistor Schematic	23
Figure 3.11 Resistivity vs Temperature IH Films ¹⁸	25
Figure 3.12 Crystal and Magnetic Structure of Ilmenite ¹⁵	27
Figure 3.13 Various Spin Arrangements for Ilmenite ¹³	28
Figure 3.14 Temperature dependence of Susceptibilities at 13.8 kOe ¹⁵	29

Figure 3.15 SEM Ilmenite-Mn(15%) ²¹	31
Figure 3.16 SEM Ilmenite-Mn(40%) ²¹	32
Figure 3.17 Resistivity vs Temperature for Ilmenite-Manganese Series ²¹	33
Figure 3.18 Transition from p- to n-type in I-Mn ²¹	34
Figure 3.19 Transition from p- to n-type in IH ²¹	35
Figure 3.20 Resistivity versus Temperature for PsB-Mn(40%) Film ²⁴	36
Figure 3.21 4pp I-V Non-Linear with Field Effects for PsB-Mn(40%) Thin Film at 300K and 441K ²⁴	37
Figure 4.1 2pp I-V Set up	38
Figure 4.2 4pp Set up	40
Figure 4.3 4pp Arrangement and Set up	41
Figure 4.4 Bridge Sample ⁹	45
Figure 4.5 Lorentz Force ¹⁰	46
Figure 4.6 Contact Configurations for van der Pauw Technique ⁹	47
Figure 4.7 I-V Configurations for van der Pauw Technique ¹⁰	48
Figure 4.8 VDP Ratio Correction Factor ⁹	49
Figure 5.1 Schematic for a Lock-in Amplifier ²⁸	54
Figure 5.2 Pulsed I-V Curve vs DC Curve ²⁸	56
Figure 5.3 Schematic of DUT with parallel capacitor	57
Figure 5.4 Sample Contact Numbers	59
Figure 5.5 SMU Schematic ³⁰	62
Figure 5.6 Efficiency vs Wavelength ³³	64
Figure 5.7 Higher Order Diffraction Beams ³³	64

Figure 5.8 Shunt ammeter (left) and feedback ammeter (right)	65
Figure 5.9 Picoammeter	65
Figure 5.10 Light over right Contact	67
Figure 5.11 Light over left Contact.....	67
Figure 5.12 Flooded Sample	67
Figure 6.1 Series Resistance	69
Figure 6.2 2-Dimensional Current Distribution.....	71
Figure 6.3 3-Dimensional Current Distribution.....	71
Figure 6.4 Photo of Ilmenite Sample with Contact Areas and Positions.....	73
Figure 6.5 I-V for 2pp Configurations Ilmenite Ceramic	74
Figure 6.6 I-V for Independant Probes	74
Figure 6.7 I-V 1342 4pp Ilmenite Ceramic.....	75
Figure 6.8 I-V Relation for Contacts 1 and 2.....	78
Figure 6.9 I-V Relation for Contacts 1 and 2 Corrected.....	78
Figure 6.10 PSpice Schematic and Simulation	79
Figure 6.11 Asymmetric I-V Relation of Contacts 1 and 2	80
Figure 6.12 PSpice Simulation of Rectifying Behavior.....	82
Figure 6.13 PSpice Schematic	82
Figure 6.14 I-V Relation of Contacts from Eq (6-5)	83
Figure 6.15 Average I-V Relation of Contacts	83
Figure 6.16 Metal to p-type Band Diagrams and Contact ³	84
Figure 6.17 High/Low Bias Slopes of Contact #1	86
Figure 6.18 Diode Profile for Contacts at 300K	87

Figure 6.19 MathCad Simulation.....	87
Figure 6.20 I-V Average Contact #1.....	89
Figure 6.21 Contact #1 I-V Forward Bias Comparison.....	90
Figure 6.22 Resistivity vs $1/T$	91
Figure 6.23 Resistivity vs $1/T$	91
Figure 6.24 Diode Profile for Contacts at 40K	94
Figure 6.25 Diode Profile for Contacts at 373K	94
Figure 6.26 $F1$ versus V for contact #4.....	96
Figure 6.27 Modified Norde Plot for Contacts #3 and #4	97
Figure 6.28 I-V Relation 2pp.....	100
Figure 6.29 I-V Relation 4pp 3421	101
Figure 6.30 IV Relation for Contacts.....	102
Figure 6.31 Diode Profile of Contacts	103
Figure 6.32 Diode Profiles for Contacts at 300K	104
Figure 6.33 Forward Bias IV Profile Contact #4.....	105
Figure 6.34 Resistivity vs $1/T$	106
Figure 6.35 $F1$ versus V for contact #4.....	108
Figure 6.36 Modified Norde Plot for Contacts #1 and #2	109
Figure 6.37 I-V Configuration 1234	111
Figure 6.38 Diode Profile of Contacts	113
Figure 6.39 Diode Profiles for Contacts at 300K	114
Figure 6.40 Forward Bias I-V Profile Contact #4.....	115
Figure 6.41 Resistivity vs $1/T$	116

Figure 6.42 F1 versus V for contact #4.....	118
Figure 6.43 Modified Norde Plot for Contacts	118
Figure 6.44 SEM mage of Ilmenite Ceramic	120
Figure 6.45 SEM Image of Ilmenite-Mn(15%)	121
Figure 6.46 SEM Image of Ilmenite-Mn(40%)	121
Figure 6.47 I-V Configuration 1234	124
Figure 6.48 I-V Configuration 1234	125
Figure 6.49 I-V Configuration 1234	125
Figure 6.50 Resistivity vs $1000/T$	126
Figure 6.51 I-V Configuration 1234 at 100K	127
Figure 6.52 Non-Linear I-V Configuration 1234 at 100K.....	127
Figure 6.53 Non-Linear I-V Configuration 1234 at 300K.....	128
Figure 6.54 Resistivity vs $1000/T$	129
Figure 6.55 I-V Configuration 1234 at 300K	129
Figure 6.56 Non-Linear I-V Configuration 1234 at 300K.....	130
Figure 6.57 Non-Linear I-V Configuration 1234 at 100K.....	130
Figure 6.58 SEM Image of PsB-Mn(40%) Ceramic.....	132
Figure 6.59 SEM Image of PsB-Mn(40%) Thin Film	132
Figure 6.60 SEM Image of PsB-Mn(40%) x'tal	133
Figure 6.61 Intensity vs Wavelength	135
Figure 6.62 Intensity vs Wavelength from Factory ³²	135
Figure 6.63 Radiant Intensity vs Time from Factory ³²	136
Figure 6.64 Radiant Intensity vs Time.....	137

Figure 6.65 Open Terminal Voltage vs Wavelength

CHAPTER 1

INTRODUCTION

Ilmenite-Hematite ($(1-x)\text{Fe}_2\text{TiO}_3 - x\text{Fe}_2\text{O}_3$) is a multi-functional material with interesting semiconducting, dielectric, and magnetic properties. The material is radiation hard and has a bandgap of 2.6 to 3 eV and is thus potentially interesting for application in high power components, military devices, and space electronics. Pure Ilmenite is p-type and non magnetic. As the concentration of Hematite is increased in the compound, the material makes the transition to n-type and becomes ferrimagnetic.

Manganese doped Ilmenite and Manganese doped Pseudobrookite also have promising potential for applications due to their multifunctional nature (i.e. electrical and magnetic properties as well as a wide bandgap semiconductor). Similar to the Ilmenite-Hematite— $(1-x)\text{Fe}_2\text{TiO}_3 - x\text{Fe}_2\text{O}_3$, the oxide series Ilmenite-Manganese— $(1-x)\text{Fe}_2\text{TiO}_3 - x\text{Mn}_2\text{O}_3$ has a p-type to n-type transition with increasing manganese concentration around $x=20$. Since these are relatively new materials, there is little literature available on their properties.

Although several groups have measured the electric properties of these materials, up to date no systematic study of the electric transport properties over a large temperature range has been performed. The high resistivity of these materials and there magnetic properties make electrical characterization less from trivial.

I performed a systematic study of the electric transport properties of Ilmenite-Manganese ceramic series with varying concentrations of Manganese and Psuedobrookite-Manganese series: ceramic, thin film and single crystal with 40% Manganese. I determined the resistivity, activation energies and contact-resistance of the Ilmenite-Manganese series. The temperature dependence of the contact resistivity could provide information on the material such as the effective mass of the electrons and work functions of the samples. Measurements were made of the electrical properties and magnetic field effects of the Manganese doped Psuedobrookite samples as a function of the temperature (10-400Kelvin) and as a function of the applied magnetic field. Third, I studied the electrical transport properties under exposure of the sample to UV-light of the IH thin film and the Ilmenite-Manganese thin film.

The thesis begins with a literature discussion of the oxide series Ilmenite-Hematite— $(1-x)\text{Fe}_2\text{TiO}_3 - x\text{Fe}_2\text{O}_3$, the oxide series Ilmenite-Manganese— $(1-x)\text{Fe}_2\text{TiO}_3 - x\text{Mn}_2\text{O}_3$, Psuedobrookite (PsB) and Psuedobrookite-Manganese— $\text{Fe}_3\text{TiO}_5 - 40\% \text{Mn}_2\text{O}_3$ including sample preparations and previous studies of electrical and magnetic properties. The thesis also includes the discussion of the Van der Pauw technique of characterizing materials and the equipment used for data collection. In the equipment section I discuss the benefits of the DC pulse mode using the Keithley 2812A nanovoltmeter for determining IV characteristics with low signals versus a DC mode or a lock-in amplifier. The thesis will discusses the equipment preparations, equipment designs, and LabView VIs used in the experiments. The thesis concludes with results of the experiments, data analysis, and recommendations for future work.

The experiments performed on samples made available through collaboration with the University of Alabama at Tuscalusa. Thin film samples as well as ceramic bulk samples of various hematite concentrations and various manganese concentrations were available. Using four point VDP technique, a derived 4pp correction factor tailored to each sample (both bulk and thin film) and two point probe I-V measurements I characterized the electrical properties of the samples. A large electromagnet was available to apply a magnetic field to the samples under study and a helium closed cycle refrigerator system was employed to vary the temperature of the sample. The influence of UV light on the electric transport properties were investigated using the Xenon-lamp and monochromator of the ellipsometer.

CHAPTER 2

SAMPLE PREPARATION

The samples were prepared at the University of Alabama by Dr. Kumar Pandey. This chapter gives an overview of how the samples were prepared. Table 2.1 shows the samples of interest for this thesis.

Table 2.1 Material List

Materials List from University of Alabama					
Material	Type	Contacts	Thickness	Resistivity	Area
FeTiO ₃	ceramic intrinsic	Ag	2.2 mm	0.13 ohm cm	6.1 ± 5.7 mm ²
Ilmenite-Mn(40%)	ceramic n-type	Ag	2.0 mm	4.05 ohm cm	6.9 ± 5.8 mm ²
Ilmenite-Mn(15%)	ceramic p-type	Ag	1.75 mm	16.5 ohm cm	5.9 ± 6.0 mm ²
PsB-Mn(40%)	Film on MgO	Ag	500 nm	3 ohm cm	
PsB-Mn(40%)	ceramic	Ag	1.5 mm		4.6 ± 5.0 mm ²
PsB-Mn(40%)	single crystal	Ag			
Ilmenite-Mn(40%)	Film on AlO ₃				
Ilmenite-Hematite(33%)	Film on AlO ₃		92 nm		

2.1 Synthesis of Manganese doped Ilmenite and Hematite doped Ilmenite

Ceramics

The Ilmenite-Manganese series samples (Ilmenite ceramic, Ilmenite-Mn(15%) ceramic and Ilmenite-Mn(40%) ceramic) and the Ilmenite-Hematite series (Ilmenite-Hematite(15%) and Ilmenite-Hematite(45%)) were fabricated using the standard

technique of ceramics as shown in figures 2.1 and 2.2 respectively. The fabrication method can be found in references [21] and [22]. For the Ilmenite-Mn samples, Ilmenite (FeTiO_3) was doped with high purity Mn_2O_3 . The ceramics were fabricated with varying concentrations of Mn_2O_3 . The appropriate weights of the two powders used to generate each sample can be found in table 2.2. Note that in reference [21] there are more compositions. For this thesis only three are studied (Ilmenite ceramic, Ilmenite-Mn(15%) and Ilmenite-Mn(40%)). The ball milling process used for easier pressing was approximately four hours. For the pressing process, ceramic targets of 1 inch diameter were prepared at room temperature by a CARVER automatic press²¹. For the Ilmenite ceramic, an organic binding agent was used to prevent cracking during the anneal process. The automatic press applied 8000 lbs at a slow decompression rate for 5 minutes.

After the pressing process the samples were then sintered in a quartz tube furnace in an Argon atmosphere at 1200°C for 12 hours at a rate of 1.5°C/minute ²¹. The long sintering process assured a homogeneous and dense sample²¹. The final samples were cut using a diamond blade. The dimensions of each sample are available in Chapter 6.

For the Ilmenite-Hematite samples, Ilmenite (FeTiO_3) was doped with high purity hematite (Fe_2O_3). The ceramics were fabricated with varying concentrations of Fe_2O_3 . For every composition of IH (Ilmenite-Hematite) ceramic the appropriate concentrations of high purity powders are mixed by ball milling for 10 hours and passed through a sieve of 400 mesh. Samples of 0.5 inch diameter and a thickness of 3 mm were produced. The same conditions were employed for the IH ceramics as in the Ilmenite-Mn ceramics with the CARVER automatic press: applied force of 8000lbs; dwell time of 90 seconds and an

ject force of 2000lbs. Since the Ilmenite is oxygen sensitive, the annealing process was completed under vacuum. The samples were sintered in an evacuated quartz tube at 1100°C for 48 hours at a rate of 1.5°C/minute²².

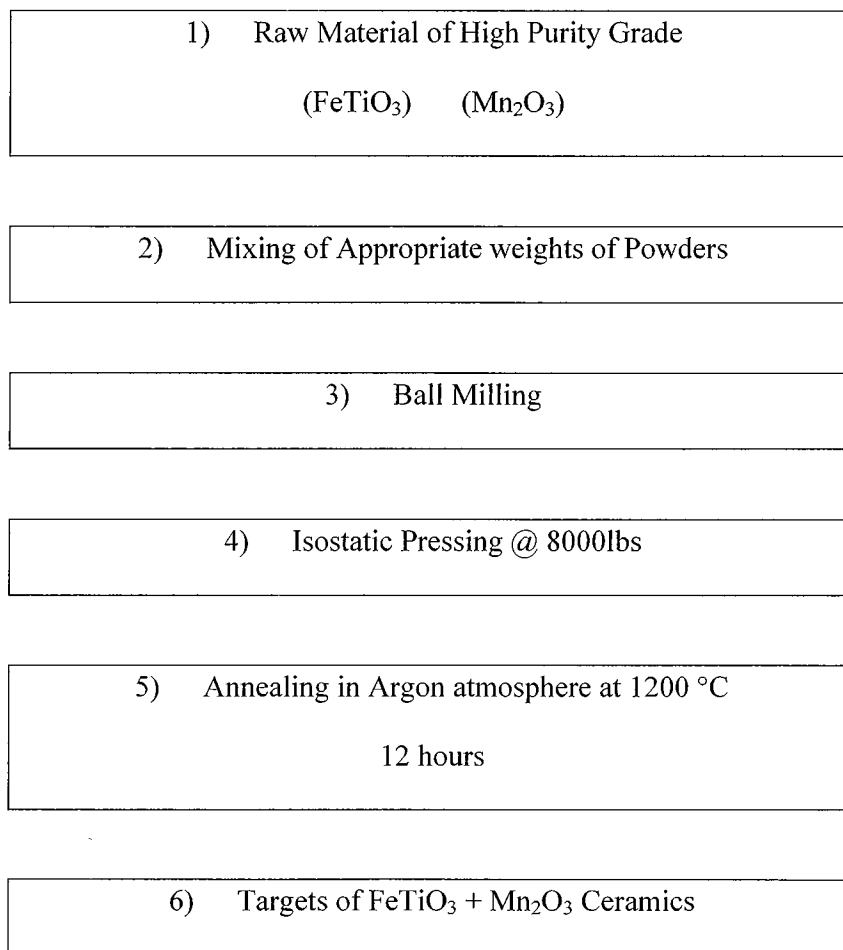


Figure 2 1 Flow Chart

Table 2 2 Material Weight

<u>Mn mole %</u>	<u>Wt. of FeTiO₃</u>	<u>Wt. of Mn₂O₃</u>
0%	9 grams	0 grams
15%	9 grams	1.40448 grams
40%	9 grams	3.74528 grams

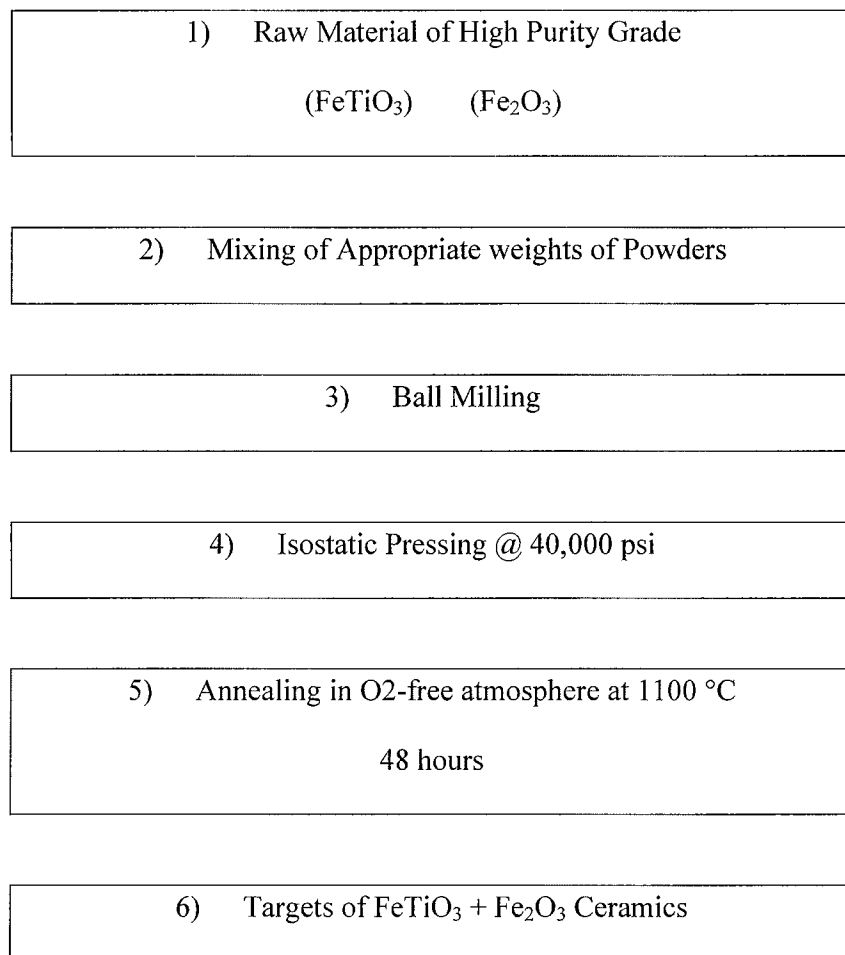


Figure 2 2 Ceramic Flow Chart

2.2 Synthesis of Ilmenite-Hematite Thin Films

The IH films were prepared using the Pulsed Laser Deposition technique—PLD. The targets for the PDL were fabricated under standard ceramic techniques. High purity Ilmenite and Hematite powders were pressed into 1 inch diameter pellets with a thickness of 4 mm at room temperature under the protocol mentioned in section 2.1. PLD under vacuum focuses a high-powered pulsed laser at the ceramic target generating a plume of highly energized atoms, ions, particulates, electrons, etc. Temperature and pressure are

critical for uniform deposition. Previous work by Dai *et al.* has been published with success in depositing IH thin films on sapphire (0001) substrates with PLD. The IH45 thin film studied in this thesis was grown by PLD on sapphire (0001) substrate. Sapphire was chosen not only by the 7% mismatch, which is large but still suitable for lattice matching, but because IH does not react with sapphire either during deposition or annealing which ensures chemical and structural integrity of the film¹⁸. This process of PLD used a 248 nm KrF excimer laser from Lambda Physique with a maximum power rating of 0.5 Joules per pulse with a pulse duration of 5-50 ns. To insure conformity, the target and the substrate were both rotated. However the distance between the target and substrate was constant 10 cm. A laser density of approximately 1-2 Joules/cm² per pulse with a frequency of 10 Hz was used for the film depositions and carried out under vacuum. Even though this thesis only used the IH45 film a range of $(1-x)\text{Fe}_2\text{TiO}_3 - x\text{Fe}_2\text{O}_3$ films were grown with $x=0, 0.10, 0.20, 0.27, 0.35$ and 0.45 . A large number of films were grown over a range of parameters. Some of the parameters used were; substrate temperature from 600 to 825°C, a growth time from 15 to 60 minutes and an annealing time from 30 to 60 minutes. XRD in figure 2.3 and SEM confirmed the film growth.

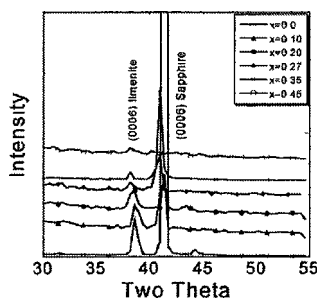


Figure 2.3 XRD IH Films

The films were c-axis oriented and exhibited excellent epitaxy. Since the samples were oxygen sensitive, it was imperative to grow the films under vacuum. The film thicknesses of the series varied between 50 and 150 nm. Zhou et al. stated that the best parameters leading to high quality films were: substrate temperature of 825°C, a growth time of 30 minutes and an annealing time of 60 minutes with a laser power density of 1-2 Joules/cm² per pulse with a frequency of 10 Hz.

PLD has proven advantageous in high quality film growth. Some of the advantages of PLD are as follows²¹:

1. The deposition of multi-element oxide materials from homogeneous targets.
2. The background chamber pressure, the distance between the target and substrate and other parameters are independent such that altering one parameter does not interfere with the others in the film deposition.
3. Possible multi-layer deposition.

However PDL is not without shortcomings²¹:

1. Particulate formation due to the particle interaction in the plume which could cause defects in the film.
2. The plume is typically of narrow distribution causing large area scale-up very difficult.

Although not available in literature, targets of Ilmenite-Mn have been used to generate, under similar protocol, Ilmenite-Mn thin films. This thesis contains a section in Chapter 6.2 on optical characterizes of an Ilmenite-Mn thin film.

2.3 Synthesis of Pseudobrookite Single Crystal and Manganese doped

Pseudobrookite Single Crystal, Ceramics and thin films

2.3.1 Pseudobrookite-Manganese Ceramics

Of the iron titanates, Pseudobrookite (PsB) is the most stable and at equilibrium with atmospheric oxygen. Ceramics of PsB-Mn were fabricated using the standard techniques of ceramics. High purity Pseudobrookite and Manganese oxide powders were used with an automated press at 10,000 psi. The initial press was carried out at room temperature in air then sintered multiple times and finally annealed in an Argon atmosphere²⁴.

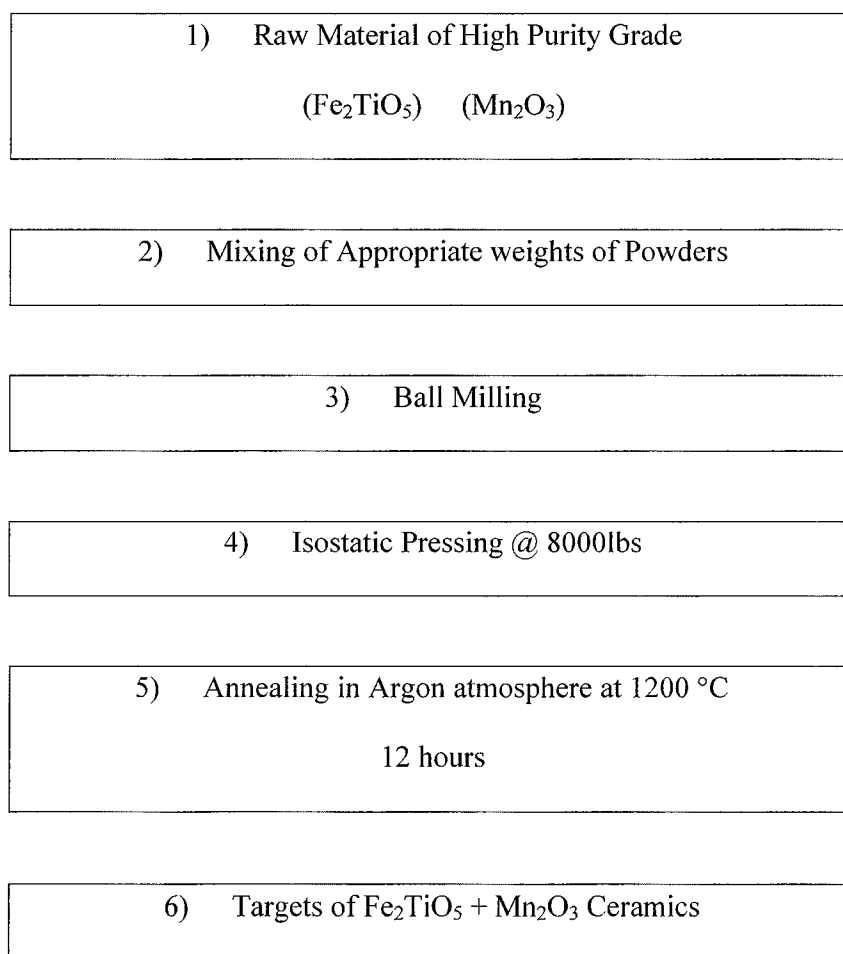


Figure 2 4 Ceramic Flow Chart

This method of fabricating high quality ceramic samples insured dense, chemically homogeneous ceramic samples suitable for film growth. The PsB-Mn ceramics followed the same protocol for the ceramic Ilmenite-Hematite samples in section 6.1.

2.3.2 Pseudobrookite-Manganese Thin Films

The PsB-Mn films were grown by PLD using the PsB-Mn ceramic sample as a target. The films were grown on a MgO substrate using a 248 nm wavelength Lambda Physique Excimer Laser with a power rating of 500 mJoules per pulse. The substrate temperature was between 625 and 675°C with a chamber pressure of 10^{-5} Torr²⁴.

2.3.3 Pseudobrookite Single Crystal and PsB-Mn Single Crystal

PsB and PsB-Mn single crystal were fabricated using the Czochralski single crystal growth method. PsB crystallizes in orthorhombic structure with lattice constants a , b and c of 9.81, 9.95 and 3.73 Angstroms respectively. A monoclinic phase converts to the orthorhombic phase at about 927°C which allows a fast cooling phase of 10°C/hour. For single crystal PsB, high temperature solution growth method was used for initial crystal growth using PbO.V₂O₅ flux with a constant charge to flux ratio of 7.5:92.5 by weight²⁴. This produced small high-quality crystals. Seeding the melt produced larger high quality crystal—8-12 mm x 2-3 mm x 3-5 mm—according to the protocol in figure 2.5. A platinum crucible was employed during the crystal growth due to the aggressive nature of molten flux and the high temperature in air²⁴. TEM confirmed single crystal growth as shown by the electron diffraction pattern in figure 2.6. Using the

same protocol as the PsB crystals, PsB-Mn single crystals were produced by adding 40% Mn to the charge.

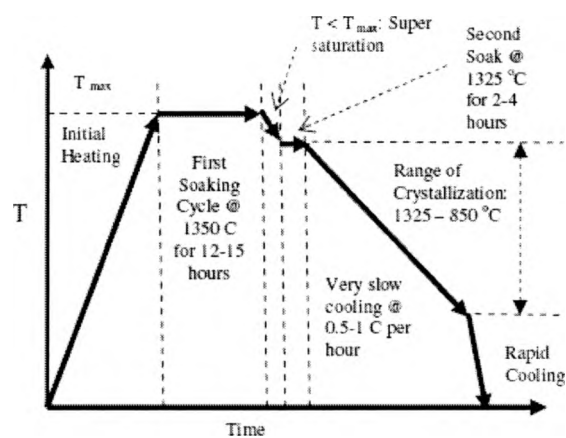


Figure 2.5 Protocol for Single x' tal Growth

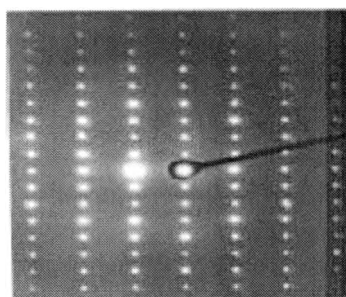


Figure 2.6 TEM micrograph of PsB x' tal

CHAPTER 3

PROPERTIES OF MATERIALS-PREVIOUS STUDIES

3.1 Ilmenite-Hematite Ceramics and Thin Films

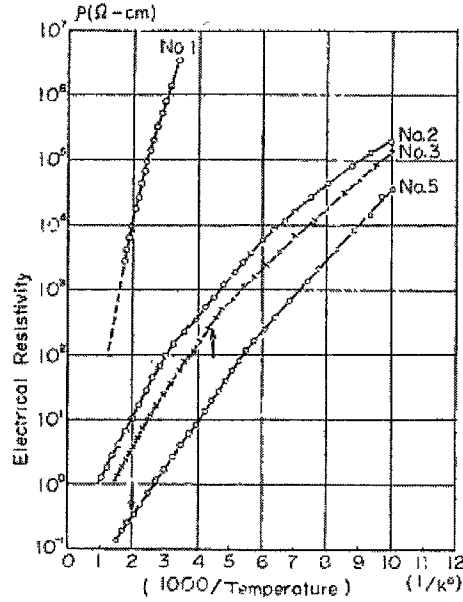
Electrical characterization of materials has evolved over the years. In the early 1800's, the resistance and conductance of materials—R and G respectively—were considered measurable physical quantities derived from the I-V characteristic of the material in a standard two-point or direct measurement. Later, it became obvious that the resistance was merely a component of another property since the same material could yield different R values for different geometries from the direct method. This led to the understanding of resistivity and conductivity. Therefore the resistivity of a material can be determined regardless of the material's geometry. However with the introduction of semi-conductors and the technology to alter materials, it was evident that more than one material can have the same resistivity. Therefore, resistivity is not necessarily a fundamental parameter. To resolve this, employing parameters such as carrier concentrations and mobility are useful in characterizing materials.

3.1.1 Electrical Properties

Ilmenite and Hematite are both wide band gap semiconductors. For electrical characterization it is difficult to evaluate pure ilmenite. Not only due to difficulty in

fabricating single crystalline ilmenite but also to the materials extremely high resistivity. Therefore it is typical to characterize solid solutions of IH or as denoted as a varying concentrations of Hematite— $(1-x)\text{Fe}_2\text{TiO}_3 - x\text{Fe}_2\text{O}_3$. There are two possible valence states for Ilmenite, the 2/4 state or the 3/3 state or better noted as the $\text{Fe}^{2+}/\text{Ti}^{4+}$ state or the $\text{Fe}^{3+}/\text{Ti}^{3+}$ state. Although not thoroughly examined in the magnetic characterization, the valence states are important in electrical properties. According to Ishikawa it is assumed that in the 2/4 state the Fe^{3+} ions in Hematite are substituted with the Fe^{2+} ions in Ilmenite with the IH solid solution increase in ilmenite. This increase in Fe^{3+} and Fe^{2+} pairs in the solution increases the conductivity. Therefore the solution is *n* type with high concentrations of hematite and *p* type with increasing concentrations of ilmenite¹⁴. Therefore in the 3/3 state the Fe^{3+} ions are always trivalent so when prepared stoichiometrically are poor conductors.

In Ishikawa's article¹⁴, the IH ceramic specimens were prepared into parallelepipeds of 4 x 4 x 20 mm samples under $5 \frac{\text{ton}}{\text{cm}^2}$ and sintered for over 12 hours at 1200 °C and quenched (cooled rapidly) to room temperature. Next the electrical resistivity was measured as a function of temperature using the potential probe method and a DC signal. For this measurement only the results for samples 1, 2, 3 and 5 were recorded. An anomaly was mentioned with respect to sample #2— $x=0.05$ —or ~95% ilmenite. All samples were stable below 800 K except for sample #2 which the measurement was up to 1100 K.



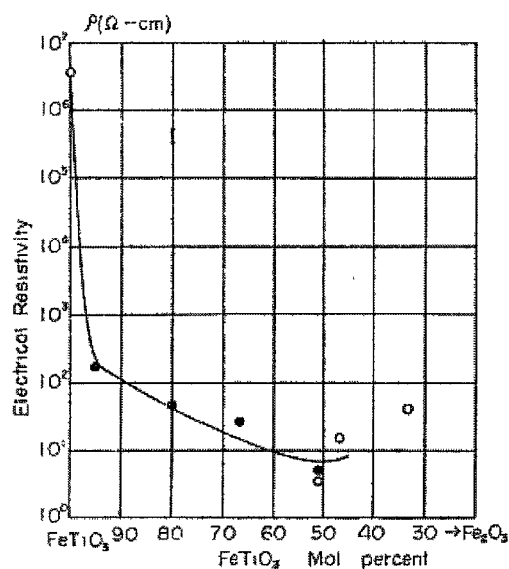
D.C. resistivity vs. the reciprocal of temperature. Arrows indicate the Curie points of the specimens.

Figure 3.1 Resistivity vs Temperature for IH Ceramic¹⁴

Figure 3.1 shows that the resistivity of $(1-x)\text{Fe}_2\text{TiO}_3 - x\text{Fe}_2\text{O}_3$ follows the Wilson's formula

$$\rho = \rho_0 \exp\left(\frac{E}{2kT}\right) \quad (3.1)$$

where T is the absolute temperature, E is the activation energy, k is the Boltzmann constant, ρ_0 is the resistivity at room temperature and ρ is the resistivity. From the same data at room temperature, Ishikawa plotted the resistivity as a function of Ilmenite concentration. Although the plot is non-linear nor logarithmic, it is safe to conclude that the resistivity decreases continuously as the concentration of Ilmenite in the IH samples decrease (or with the increase in hematite).



D.C. resistivity at room temperature vs. the composition.

●.....ferrimagnetic specimens.

○.....antiferromagnetic specimens.

Figure 3.2 Resistivity versus Hematite Composition¹⁴

Another possible variable that controls the resistivity is the heat treatment or a secondary heating and cooling process. It is noted that similar concentration of IH can yield different magnetic and electrical properties simply by varying the appropriate heat treatment. Figure 3.3 shows the resistivity of sample #5 as a function of heat treatment. Note that sample #5 was ~50% Ilmenite yet had ambiguous results. For the chart below (figure 3.3), sample #5 was once again sealed in a quartz tube, heated and this time cooled very slowly thus establishing order between Fe and Ti ions and as a result became ferrimagnetic.

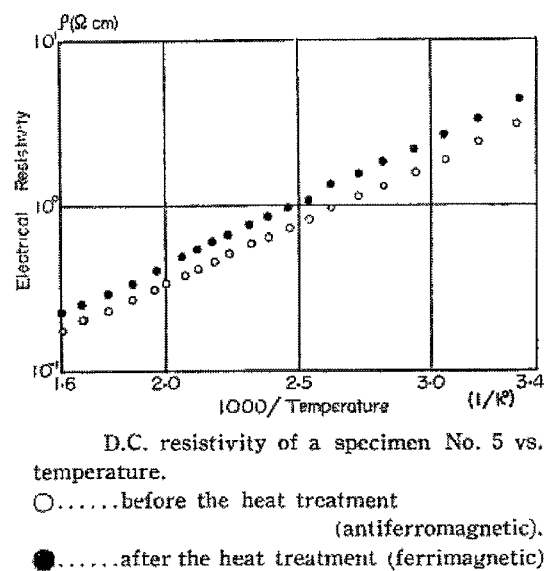


Figure 3.3 Resistivity vs Temperature of Specimen #5¹⁴

After the treatment, the resistivity showed little change. In addition to electrical resistivity, Ishikawa also measured the Seebeck voltage. The Seebeck voltage is a consequence of the Seebeck effect which is a conversion of heat differences to electricity. First discovered by physicist Thomas Seebeck in 1821 by accident—as do many discoveries—when he found that a potential difference existed between two ends of a metal bar when a temperature gradient existed across the bar. In this case the temperature gradient is across the sample and the contact. Therefore the voltage, or thermoelectric EMF, is created at the interface of the two materials. Typically this causes a continuous current with a measurable voltage on the order of a microvolt per K up to a millivolt per K. Also the voltage produced is proportional to the temperature difference between the two materials. The proportionality constant is coined the Seebeck coefficient as is denoted as α such that

$$V = \alpha \nabla T \quad (3.2)$$

where ∇T is the temperature gradient. The Seebeck voltage of Ishikawa's samples were measured with respect to PtRh wire. Below are figure 3.4 and 3.5 of the Seebeck voltage as a function of temperature and as a function of concentration respectively.

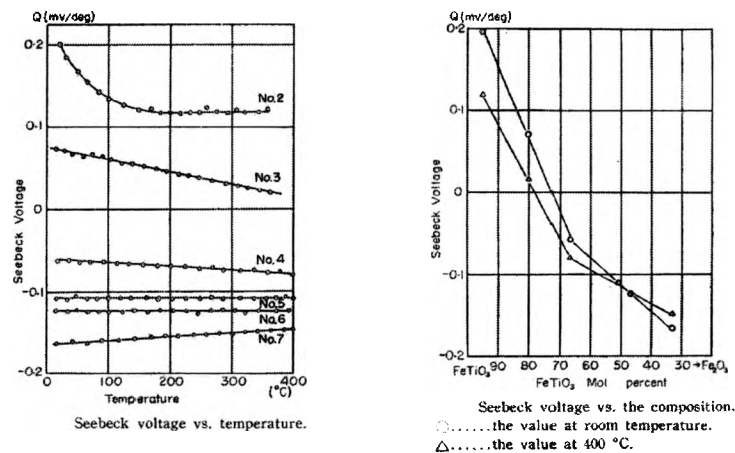


Figure 3.4-5 Seebeck voltage vs Temp¹⁴ Seebeck Voltage vs Hematite Composition¹⁴

Finally the Seebeck voltage, $\frac{mV}{^{\circ}C}$, is measured again on sample #5 before and after the heat treatment to determine if the Seebeck voltage is greatly affected by the treatment.

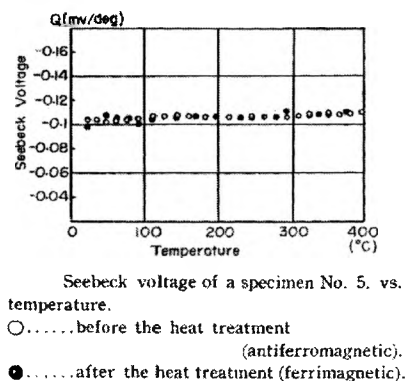
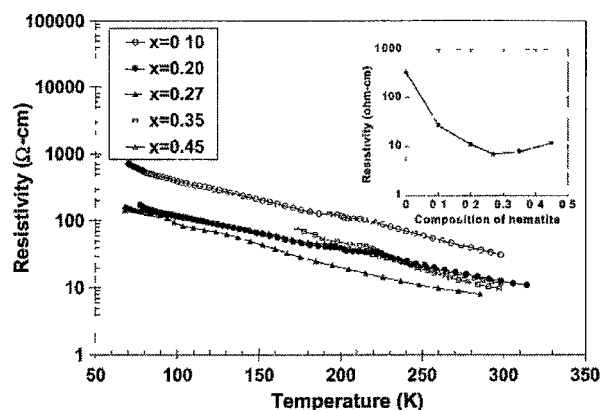


Figure 3.6 Seebeck voltage vs Temperature #5¹⁴

Although the magnetic properties are clearly dependent on the heat treatment of the IH sample, the resistivity (and inversely the conductivity) and the Seebeck voltage are relatively unchanged by the secondary heat treatment. However future study will show that the resistivity in IH is directly related to the preparation temperature

Other studies of Ilmenite-Hematite ceramics show the I-V characteristics reported on the resistivity and Seebeck coefficients. As discussed earlier 2/4 to 3/3 exchange as a result of the Fe concentration partitioned IH into *p*-type and *n*-type. Zhou *et al*¹¹ defined the partition at $x=0.2$ as opposed to Ishikawa at $x=0.27$. Zhou *et al* stated that samples of the IH series were prepared using standard ceramic techniques. Six samples of $(1-x)\text{Fe}_2\text{TiO}_3 - x\text{Fe}_2\text{O}_3$ were prepared from high-purity powders of (99.999%) Fe_2O_3 and (99.8%) FeTiO_3 with $x=0, 0.10, 0.20, 0.27, 0.30$ and 0.45 . The material were pressed into round pellet ceramics of 1 inch diameter by 4 mm thickness under a pressure of 268 MPa at room temperature then sintered under vacuum for 48 hours at 1100 °C. XRD confirmed the sample compositions. Resistivity measurements were taken using the van der Pauw technique with two part silver epoxy and silver wire contacts. The same contacts were used for the I-V and Seebeck voltage measurements. From the XRD Zhou *et al* confirmed earlier study that the cell parameters of IH increase linearly with the increase in Fe_2O_3 . Since Fe_2TiO_3 and Fe_2O_3 both have hexagonal cell structures, when combined the cell structure remained the same. The resistivity measurements as a function of temperature of Zhou *et al* had a similar profile to earlier studies by Ishikawa. The resistivity as a function hematite composition also showed the same continuous function as the earlier study as shown in figure 3.7.



Resistivity as a function of temperature in the $(1-x)\text{FeTiO}_3\text{Fe}_2\text{O}_3$ ceramics with x ranging from 0 to 0.45. The inset shows how resistivity changes with the composition of hematite in the IH series.

Figure 3.7 Resistivity vs Temperature for IH series Ceramics¹¹

A final section on resistivity showed the resistivity as a function of preparation temperature. These results come from samples made at the University of Alabama under the following conditions: the mixing of high-purity powders of (99.999%) Fe_2O_3 and (99.8%) FeTiO_3 followed by ball milling, isostatic pressing at 40 kpsi and annealing at two different temperatures, 650 °C and 850 °C. However, similar to the secondary heat treatments from the earlier samples, the differences in the primary heating yielded negligible results. Yet the material displayed semiconducting electrical properties. Another important electrical property of the samples prepared by Zhou *et al* was the I-V characteristics and the nonlinear coefficients α calculated from the reciprocal of the slopes of the I-V curves—not to be confused with Seebeck coefficient mentioned earlier. Figure 3.8 shows the non-linear 2pp I-V characteristics of the *p*-type and *n*-type IH ceramic samples.

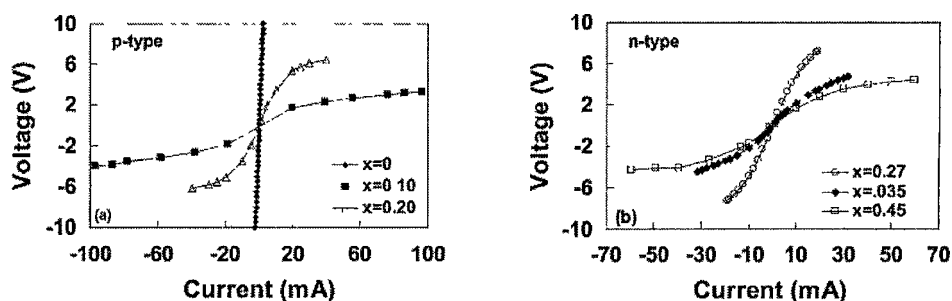


Figure 3.8 2pp I-V Characteristics of p-type and n-type Ilmenite-Hematite¹¹

Zhou *et al* stated that the I-V relation is linear at small voltages and non-linear after that. This characteristic is consistent with the behavior of a low-voltage varistor (an electronic device that senses and limits transient voltages in a circuit and can quickly switch from resistive to conductive). At the point where the I-V relation is no longer linear is referred to as the switching voltage of the device. For the *n*-type ceramics and *p*-type ceramics, table 3.1 shows the non-linear coefficients, the current range and the switching voltages from the I-V measurements.

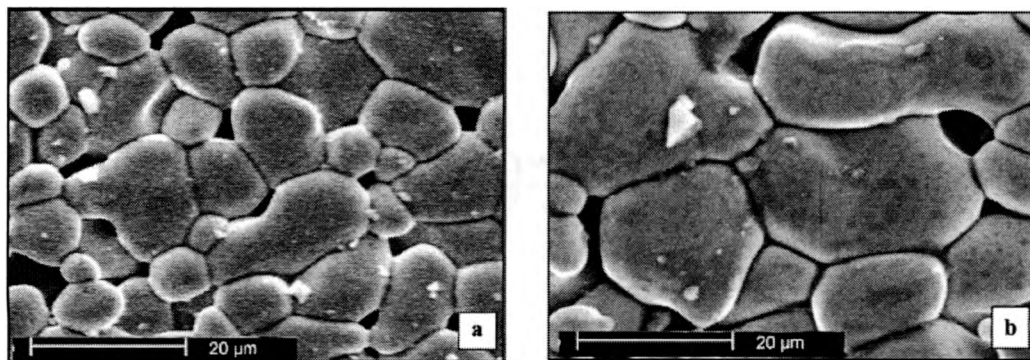
Table 3.1 Switching voltage for IH Ceramics¹¹

Non-linearity coefficient (α), current range and switching voltage for various compositions of hematite in the $(1-x)\text{FeTiO}_3\text{-}x\text{Fe}_2\text{O}_3$ ceramic series

Composition (x)	α	Current range (mA)	Switching voltage (V)
0	1		
0.10	2.4	60–100	2
0.20	3.7	20–40	5
0.27	1.8	10–20	6
0.35	1.75	20–30	3.6
0.45	2.9	40–60	3.5

Zhou *et al.* used a SEM to show the relation between Hematite compositions and grain size and connectivity. For pure ilmenite, the grain boundaries were not well defined. However, with the Hematite doped ceramics, the grain boundaries became more defined. The grain sizes are directly related to the I-V characteristics. For the $x=0.10$ and 0.45 ceramics the grain sizes were between $6-8\ \mu\text{m}$ and for the $x=0.20$, 0.27 and 0.34 the grain sizes were between $10-16\ \mu\text{m}$. As mentioned earlier, the doped ceramic sample have varistor like behaviors. It is proposed that this is a consequence of the grains or moreover the grain boundaries¹¹.

A varistor is commonly composed of a metal oxide grain matrix with intergranular layers separating the grains. The grain matrix is sandwiched between two metal plates that act as electrodes. At low voltages, two adjacent grains are equivalent to two Schottky diodes facing back to back at the intergranular layer. For the IH case, the random assortment of grains, as shown below in figure 3.9, effectively act as diodes.



Scanning electron micrographs of $(1-x)\text{FeTiO}_3\cdot x\text{Fe}_2\text{O}_3$ ceramic, with (a) $x=0.1$ and (b) $x=0.27$ showing the effect of composition x on grain size and connectivity.

Figure 3.9 SEM of a) $x=0.1$ and b) $x=0.27$ grain sizes²¹

From the diode characteristic, low voltages allow only small currents to pass. Current passes through the varistor as electrons cross the intergranular layer, or barrier, by tunneling. At low voltages, the barrier may be low enough so that electrons can travel thermally across. However this process occurs slowly at room temperatures, therefore, at low voltages, the varistor has a high resistance and conversely the device has low resistance at high voltages due to the avalanche effect. At high voltages, the diodes break down due the avalanche effect—similar to a Zener diode. So, once breakdown has occurred, a large current can flow, giving the varistor low resistance. Also varistors have non-linear I-V relations characterized by their non-linear coefficient α . If an MOV (metal oxide varistor) is exposed to voltages higher than its breakdown potential, the varistor may be permanently damaged. MOVs can be used to protect communications equipment such as phone lines and modems from interfering low-voltage transient signals, in which case, the capacitance of the device is of importance and operates as a filter. Below is a schematic of a varistor parallel to the device that needs protecting.

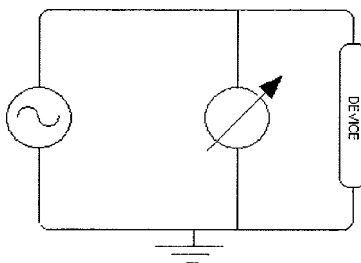


Figure 3.10 Varistor Schematic

From figure 3.10 one can see that by changing the voltage, the I-V characteristic of the varistor varies the current through the varistor and consequently through the protected

device or in the case where the capacitance is important, by limited or filtering frequencies allowed through the device. The I-V relation of a varistor can be expressed as

$$I = CV^\alpha \quad (3.3)$$

where C is a constant that is related to the geometry of the varistor and α once again is the non-linear coefficient. Recently there has been interest in TiO₂-based varistors¹¹. Low voltage varistors using doped TiO₂ have been reported with α values between 7 and 12. However, α values for ZnO have been reported with values from 35 – 100. Note that in general, the higher the coefficient α , the better the device. However for low-voltage circuits this may not be the case.

Other than ceramic samples, Zhou *et al.* submitted results on the study of IH films (2002). The film growth of IH was motivated by their success in IH ceramic studies. Therefore the targets used in the pulsed-laser deposition were samples from the ceramic studies of (1-x)Fe₂TiO₃ – xFe₂O₃ with x=0, 0.10, 0.20, 0.27, 0.30 and 0.45. Prior to this (1998) Z. Dai *et al* attempted to deposit FeTiO₃ epitaxial thin films onto a sapphire substrate by pulsed-laser deposition (PLD). Their successful results yielded good quality films with superior epitaxy at the surface and fair epitaxy at the interface likely related to a high density of misfit dislocations arising from a large lattice mismatch of about 7-8%¹⁷. Dai *et al* states that their best results were from samples deposited at 450°C for 30 minutes under a mixed ambient of oxygen and argon. Although Ilmenite and sapphire have lattice mismatch of 7-8%, sapphire is a good candidate for growing epitaxial films since Ilmenite and IH do not react with sapphire during the growth process or anneal process¹⁸. Contrary to Dai *et al*, Zhou *et al* grew their films under high vacuum since

the IH samples are sensitive to oxygen. From the six ceramic samples, thin films were fabricated under these parameters: a substrate temperature from 600 to 800°C, a growth time from 15 to 60 minutes and an anneal time from 30 to 60 minutes. From these parameters, the ones that yielded epitaxial films with good semiconducting and material properties were from an 825°C substrate temperature, a growth time of 30 minutes and an anneal time of 60 minutes at 825°C¹⁸. Since the LPD yields amorphous crystals it is imparetive to anneal to increase the crystal order. The film thicknesses varied between 50-150 nm. Resistivity measurements were performed over a temperature range from room temperature down to 100 K. The contacts for the samples were the same as for the bulk ceramics—silver epoxy and silver wire. Figure 3.11 shows the thin film resistivity for varying concentrations IH as a function of 1/Temperature¹⁸.

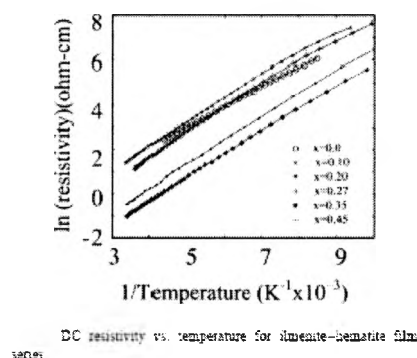


Figure 3 11 Resistivity vs Temperature IH Films¹⁸

At room temperature Zhou *et al* plotted the resistivity as a function hematite concentration, x . Table 3.2 below shows the comparison of the thin film and bulk ceramic resistivities with respect to their concentrations of hematite at room temperature.

Table 3 2 Comparison of Resistivity for Film and Ceramic¹⁸

Resistivity at room temperature for film and ceramic of FeTiO_3 - Fe_2O_3

Composition (wt)	Resistivity ($\Omega \text{ cm}$)		
	Film	Ceramic	Single crystal
0	4.12	33.40	0.001-0.002
0.10	3.93	26.77	—
0.20	0.65	10.94	—
0.37	2.51	7.97	—
0.53	0.60	7.92	—
0.45	0.35	11.34	—

x

The resistivity function in the thin films show a decrease in resistivity as the hematite concentration increases. This is consistent with ceramic measurements however the $\frac{d\rho}{dx}$, where dx is the change in Hematite concentration, for the films is considerably different than that of the ceramics. The lower resistivity measurements in the films can be contributed to the epitaxial nature, the well-defined crystal orientation and the absence of defects and grain boundaries¹⁸. Possibly future work on the films (i.e. Seebeck voltage measurements) can better explain the behavior of the sample.

Ilmenite and Hematite are wide-bandgap semiconductors with a bandgap of 2.54 and 2.0 eV respectively. There is a large demand for wide-bandgap materials with range of potential applications including radiation-immune solar cells, high-temperature integrated circuits, high-powered electronic devices, solid state lasers and short-wavelength LEDs¹⁸. Ilmenite, Hematite and possibly IH can be candidates for some of these applications. Further study could yield promising results for the industry.

3.1.2 Magnetic Properties

Early studies of Ilmenite and IH have shown unique electrical and magnetic properties. A majority of these studies were published in the *Journal of the Physical Society of Japan*. Ishikawa and Kato, independently, were the main contributors. The dependence of Ilmenite's structure on temperature, pressure and composition is strongly coupled to its electronic and magnetic properties¹⁶. For pure Ilmenite there is little known. However, one unique property of Ilmenite is the magnetic phase transition. From a grown single crystal of Ilmenite using the zone floating method, Kato *et al* state that below the T_N —Néel temperature, or in other articles referenced as the Curie temperature—of approximately 60 K, Ilmenite is antiferromagnetic and since Ilmenite is an anisotropic (directionally dependent) material its moment lies along the c direction.

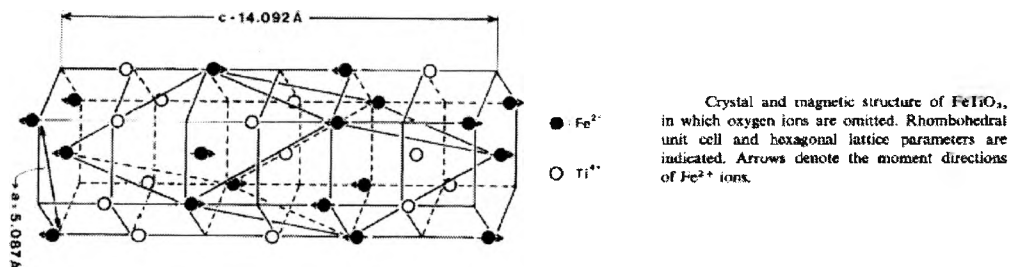


Figure 3 12 Crystal and Magnetic Structure of Ilmenite¹⁵

From figure 12, the Fe^{2+} moments are ferromagnetically coupled within a c plane and antiparallel between adjacent planes. A phase transition occurs when an external field is applied along the c -axis. Ilmenite undergoes an abrupt metamagnetic phase transition or a superlinear increase of magnetization from antiferromagnetic to ferromagnetic¹⁵. Note

from the above figure that Ti^{4+} ions do not contribute to the magnetization. There is also an $\text{Fe}^{3+}/\text{Ti}^{3+}$ state not discussed in this article where the titanium ions do contribute from their spin arrangement.

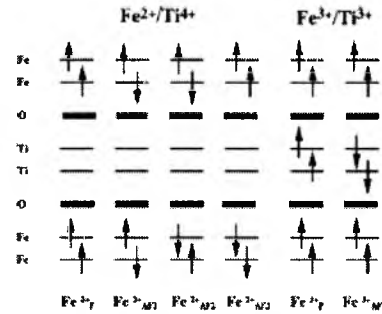


FIG. 3. The various spin arrangements considered for the $\text{Fe}^{2+}/\text{Ti}^{4+}$ and $\text{Fe}^{3+}/\text{Ti}^{3+}$ states.

Figure 3 13 Various Spin Arrangements for Ilmenite¹³

Since ilmenite has an anisotropic behavior, its measured susceptibility is dependent on orientation. Kato *et al* reports two cases of susceptibility, $\chi_{\perp}$ and $\chi_{\parallel}$ both with respect to the c -axis as functions of temperature with an applied field of 13.8 kOe with close attention to the T_N . $\chi_{\parallel}$ has a very sharp maximum at the T_N of 58.0 ± 0.3 K. Note that the earlier discussion mentioned a T_N of ~ 60 K. Other documentations stated a transition temperature as high as 68 K. At the sharp maximum, $\chi_{\parallel}$ has approximately twice the susceptibility as $\chi_{\perp}$. It is important to note that the structural and therefore the magnetic properties of natural ilmenite and grown ilmenite can be somewhat different. This could also be contributed to the natural formation hematite in the natural ilmenite crystal.

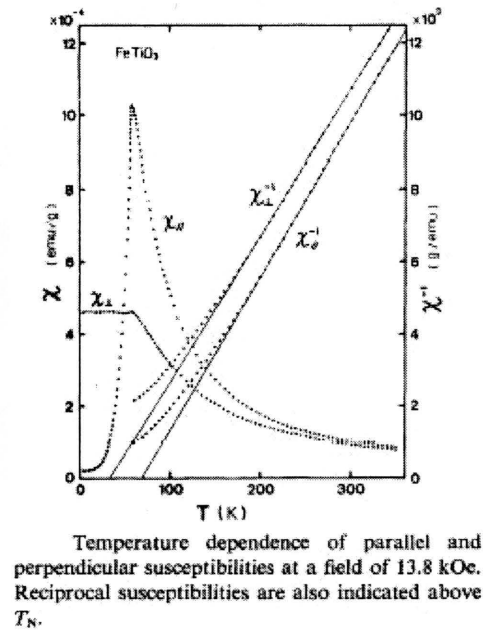


Figure 3 14 Temperature dependence of Susceptibilities at 13.8 kOe¹⁵

As mentioned earlier, the T_N of pure Ilmenite varies in early publications. Yet an early study of IH combinations $((1-x)\text{Fe}_2\text{TiO}_3 - x\text{Fe}_2\text{O}_3)$ show that the T_N increases almost linearly from 68 K for $x=0$ to 950 K for $x=1$ ¹². Although the T_N is notably continuous as x varies in the solid solutions it would be intuitive to assume that magnetic properties would as well follow suit. However according to Ishikawa *et al* this is not the case. For $x > 0.6$ the solution is very ferromagnetic at ~ 80 K and feeble ferromagnetic for $x < 0.55$. The chart below (table 3.3) shows the result of seven ceramic IH samples prepared and analyzed by Ishikawa.

Table 3 3 Magnetic Properties of Specimens¹⁴

No.	FeTiO ₃ mol %	Curie point	Magnetic property
1	100	55 (°K)	antiferromagnetic
2	95	63	ferrimagnetic
3	80	224	ferrimagnetic
4	67	394	ferrimagnetic
5	51	483	antiferromagnetic
5	(51)	530	ferrimagnetic
6	47	529	antiferromagnetic
7	33	632	antiferromagnetic

magnetic property of the specimen

Ishikawa's sample compositions were determined by XRD. X-Ray diffraction method is one of the most commonly used techniques of physically characterizing a material, typically a crystal. Therefore the XRD method is very common amongst mineralogists. The XRD can determine lattice parameters, Miller indices $[hkl]$, relative intensities and in the above case, mole ratio of ilmenite to hematite in the IH samples.

3.2 Ilmenite-Manganese

Extensive studies of Ilmenite-Hematite are available in literature. Since IH has promising application possibilities, impurities other than hematite also yield promising results. Doping Ilmenite with manganese alters the electrical and magnetic properties of the material. Previous studies have been completed on the Manganese doped Ilmenite series at the University of Alabama. These studies can be found in reference [21]. These previous studies include physical, electrical and magnetic characterization and are fabricated from the same targets used in this thesis. Previous EDAX analysis in table 3.4

below shows the atomic percentages of FeTiO_3 and Mn_2O_3 for each ceramic sample according to Kale.

Table 3 4 Nominal and Actual Compositions of Manganese

% Mn	Nominal Composition	Actual Composition
0	$\text{Fe}_1\text{Ti}_1\text{O}_3$	$\text{Fe}_{1.07}\text{Ti}_{1.05}\text{O}_{2.86}$
15	$\text{Fe}_1\text{Ti}_1\text{O}_3.\text{Mn}_{0.30}$	$\text{Fe}_{1.08}\text{Ti}_{1.09}\text{O}_{3.09}.\text{Mn}_{0.33}$
40	$\text{Fe}_1\text{Ti}_1\text{O}_3.\text{Mn}_{0.80}$	$\text{Fe}_{1.18}\text{Ti}_{1.09}\text{O}_{3.82}.\text{Mn}_{0.90}$

The SEM micrographs found by Kale show grain boundaries in the samples between 15-20 microns.

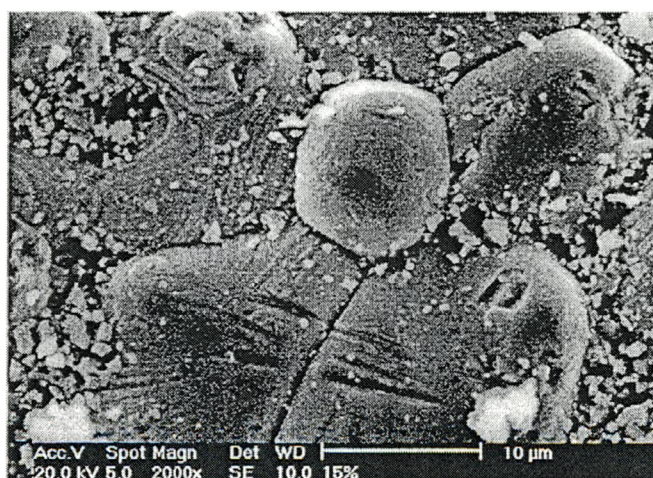


Figure 3 15 SEM Ilmenite-Mn(15%)²¹

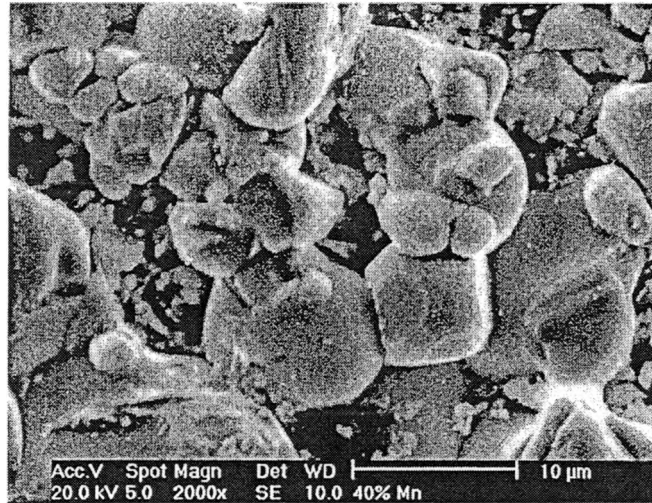


Figure 3.16 SEM Ilmenite-Mn(40%)²¹

Electrical characterization of the samples showed an anomaly at 15% Mn concentration where the resistivity behavior was dependant on the substitution mechanism of the Mn^{3+} ions in the Ilmenite lattice²¹. Table 3.5 below shows the resistivity at room temperature as a function of Mn concentration²¹.

Table 3.5 Resistivity versus Manganese Concentration

Mn %	Resitivity (Room Temperature)
0%	0.13 Ω -cm
15%	0.14418 Ω -cm
40%	4.05447 Ω -cm

Note that the resistivity of Ilmenite ceramic according to Kale is of orders of magnitude smaller than literature. Previous studies of Ilmenite ceramic have shown resistivity

measurements between 100 and 500 $\Omega\text{-cm}$ which is reasonable since Ilmenite is an insulator. Zhou published a resistivity of Ilmenite ceramic of 331.4 $\Omega\text{-cm}$ ²². Kale stated that this significant difference could be a consequence of the differences in processing techniques. Zhou prepared the ilmenite ceramic in vacuum while Kale prepared the ilmenite samples in Argon. Kale showed that the Ilmenite-Mn samples show semiconductor behavior by plotting the resistivity as a function of inverse temperature as shown below.

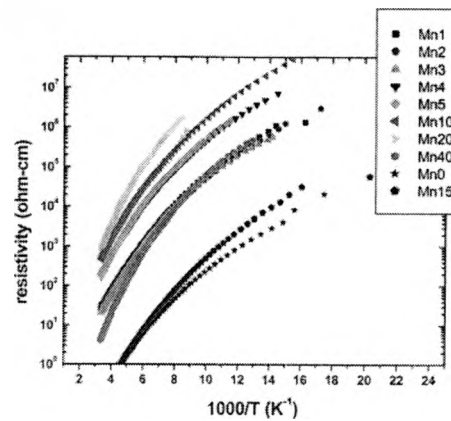


Figure 3 17 Resistivity vs Temperature for Ilmenite-Manganese Series²¹

Manganese doped Ilmenite is still semiconducting by nature. However these samples are extrinsic semiconductors therefore the material is doped by the presence of defects. The doping-nature is a consequence of the large quantity of defects. In this case the activation energy is of interest. The activation energy can give us quantitative results on the donor or acceptor levels and the ionization energy level. The activation energy, E_{ac} , can be found in the slope of the Wilson's formula. Pandey and Zhou referred to this as "hopping" where charged ions (positive or negative) hop from one lattice site to another, which completely depends on vacancies, under the influence of an electric field³.

The resistivity as a function of inverse temperature follows the Wilson's formula. Kale used the moderate temperature region (250K – 300K) to extract the activation energies as a function Manganese concentration. Table 3.6 below shows the results.

Table 3 6 Activation Energy versus Manganese Concentration

Mn mole %	Activation energy (eV)
0%	0.1206
15%	0.0896
40%	0.0792

Once again this only contains results that pertain to the samples in this thesis. Other results are available in reference [21]. Previous Seebeck effect measurements concluded that, similar to the Ilmenite-Hematite series, the Ilmenite-Mn series shows p-type for Mn concentration below 20% and n-type for Mn concentrations above 20%. Figures 3.18 and 3.19 below show the Seebeck coefficients as a function of dopant concentrations.

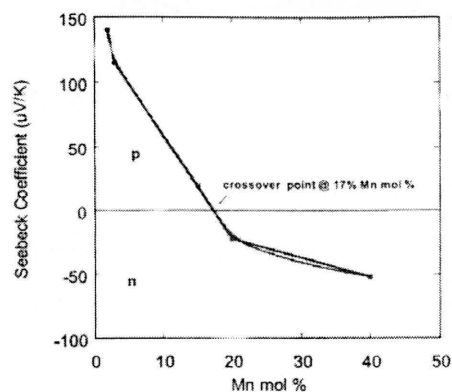


Figure 3 18 Transition from p- to n-type in I-Mn²¹

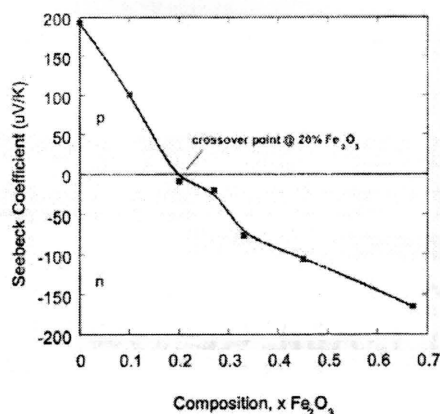


Figure 3.19 Transition from p- to n-type in IH^{21}

3.3 Pseudobrookite-Manganese

Although PsB is the lesser-known species of the iron-titanates, it is also a potential candidate for spintronics, magneto-electronics and radiation hard electronics²⁴. Since pure PsB is non-magnetic at room temperature doping with Mn^{3+} ions dissociated from Mn_2O_3 makes the material ferromagnetic. The single crystal and thin film for the PsB-Mn(40%) were fabricated from the PsB-Mn(40%) ceramic samples. Previous work focused on the crystals (both pure PsB and PsB-Mn(40%)) and film samples. For the manganese doped or substituted PsB, the resistivity measured was 0.294 kΩ.cm and the resistivity for the pure PsB crystal was found to be 2.197 kΩ.cm; both were found to be n-type semiconductor²⁴. Pandey *et al* found the activation energy (assumed to be determined from the Wilson's formula) to be 0.50eV for the pure PsB crystal and temperature dependent in other literature with results of 0.19 for $T < 500$ K and 0.46 for $T > 500$ K and in reference [24] an activation energy of 0.17 for the PsB-Mn(40%). The

PsB thin film fabricated by PLD at 450°C on MgO substrate from the ceramic targets was studied by Pandey *et al* and found be semiconductor in behavior and at room temperature to have a resistivity of 0.3 Ω .cm and an activation energy of 12meV. The graph below (figure 3.20) shows the resistivity as a function of inverse temperature.

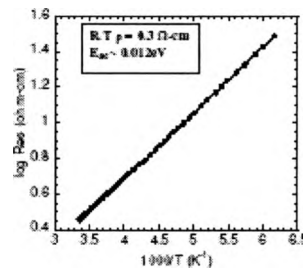


Figure 3.20 Resistivity versus Temperature for PsB-Mn(40%) Film²⁴

Literature discusses the possibility of the conduction of this material to be polaron mediated—strong coupling between the electron and the lattice, similar to phonon interaction. Pandey *et al* argued that the conductivity of this material is due to a small polaron conduction band therefore the small activation energy level is not due to intrinsic conduction but rather pointed to possible defects or interstitials in the material²⁴. Four point probe measurements in the PsB-Mn(40%) film showed strong linearity, however by subtracting the linear component Pandey *et al* were able to exploit a possible non-linear and field dependent resistivity in the sample at temperatures of 300K and 441K.

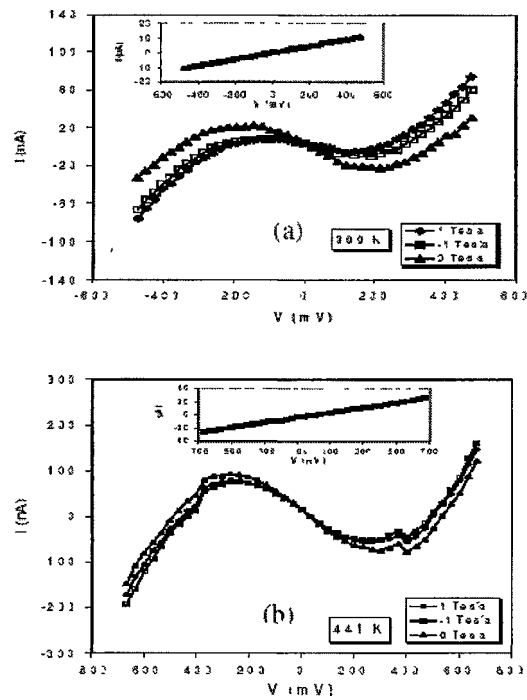


Figure 3.21 4pp I-V Non-Linear with Field Effects for PsB-Mn(40%) Thin Film at 300K and 441K²⁴

Note that the inserts in the graphs (figure 3.21) are the original 4pp results including both the non-linear components and the linear counterparts. Also note that the field shows an increase in current over a constant voltage thus showing a decrease in resistance. This result is polarity independent such that a plot of resistance versus applied magnetic field symmetric around zero H will produce an even function.

CHAPTER 4

MEASUREMENT TECHNIQUES

4.1 Electrical Characterization

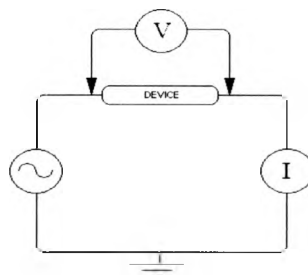
4.1.1 Two-Point Probe Method

In electrical characterization, the two-point method or direct method yields an I-V characteristic of a material, typically a conducting material. However as materials evolved through technology the demand for accurate measurements increased with it. With the discovery that resistance and conductance were not the fundamental parameters in materials, other measurement techniques became standard in industry.

Using Ohm's Law

$$V = IR \quad (4-1)$$

one can determine the voltage drop along a conductor with a uniform cross section of a current carrier.



Typical setup for I-V measurements for Ohmic devices

Figure 4 1 2pp I-V Set up

By letting

$$R = \frac{\rho L}{A} \quad (4-2)$$

one can determine the resistivity of the sample. This works well for a conductive sample, however metal to semiconductor contact creates a Schottky contact and not an Ohmic contact. Therefore a majority of the voltage drop is across the contacts and not the sample, this type of resistance is commonly called contact resistance. A typical solution to overcome contact resistant problems for certain semiconductors is to sweep the voltage. At high voltages, the total resistance ($R_{\text{contact}} + R_{\text{sample}}$) becomes constant. It is in this region where the resistivity can be measured. However, using this approach, the minority carriers may be injected from the contact and flooded into the semiconductor and lower the measured resistivity value ⁵.

4.1.2 Four-Point Probe Method

Another approach to avoid or minimize contact resistance is to employ a four-point probe measurement. Several strategies are employed to do four point probe measurements. The first to be discussed is sketched in Figure 4.2. This four-point probe contains two probes of a defined spacing that are free to move in unison along the surface of the sample and two fixed contacts.

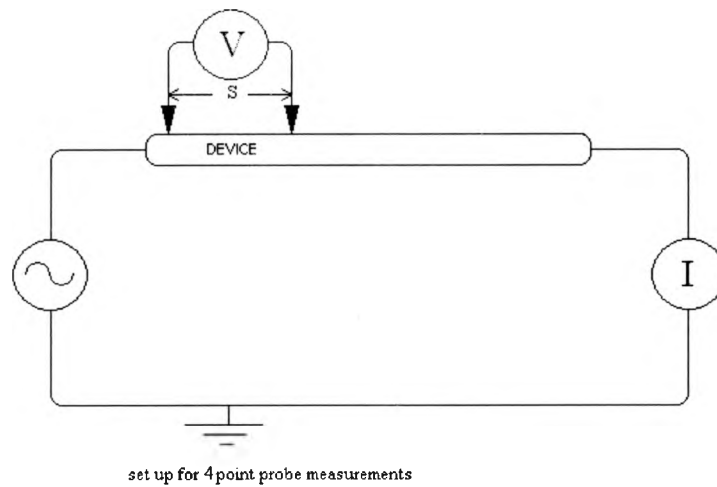


Figure 4 2 4pp Set up

This four-point probe set up measures an average resistivity of the sample. Although for these measurements a constant current is required, yet this set up still has contact issues and spreading resistance. A slightly different approach is where one of the two voltage electrodes is kept at a fixed position. This variation is sometimes referred to as the one-point probe. Instead of both probes scanning the sample in unison, one probe remains stationary while the other probe scans the sample in a lateral motion. In this situation one would measure voltage as a function of distance x along the sample.

Therefore resistivity can be calculated from

$$\rho = \frac{dV}{dx} \frac{A}{I} \quad (4-3)$$

where once again a constant current I is required.

As apposed to the two-point analysis, the four-point probe analysis (4pp) alleviates the metal-semiconductor contacts of current carrying wires and replaces them with electrodes or point probes. Although the four point probe technique, invented in

1916, was originally used to determine the Earth's resistivity. The four-point probe technique was coined the Wenner method—named after its inventor. In 1954 the Wenner method was adopted for semiconductors. In the semiconductor industry, the 4pp method is the most common technique for determining resistivity of a sample.

Figure 4.3 below shows the typical arrangement for the in-line 4pp

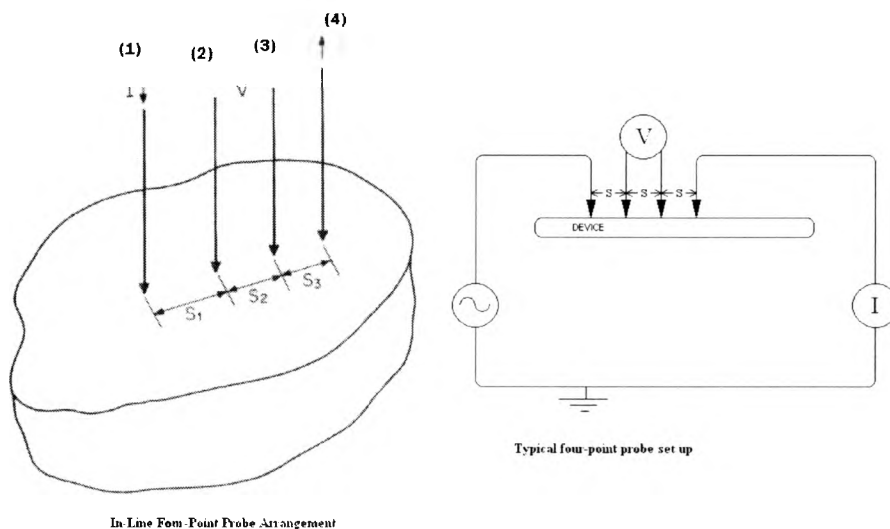


Figure4 3 4pp Arrangement and Set up

The four-point probe is preferable over a two-point probe because the contact resistance and spreading resistances typically associated with the two-point probe and direct measurement can be eliminated. Therefore the true sheet or bulk resistance can be accurately measured. The arrangement for the in-line or linear four-point probe consists of two current carrying probes (1 and 4), and two voltage measuring probes (2 and 3) as shown in figure 4.3 and S_1 , S_2 and S_3 defining the spacing between probes 1, 2, 3 and 4. Since very little contact and spreading resistance is associated with the voltage probes (2 and 3), one can obtain a reasonably accurate calculation of the sheet

resistance and in turn calculate the resistivity. Since the 4pp method is common in the semiconductor industry, the typical sample is a wafer. As long as the diameter of the wafer is considerably larger than the spacing distance between the probes, then the wafer can be considered to of semi-infinite size. The equation for the resistivity of a semi-infinite wafer measured with the linear four-point probe method is given by

$$\rho = 2\pi \frac{V}{I} \left[\frac{1}{S_1} - \frac{1}{(S_1 + S_2)} + \frac{1}{(S_2 + S_3)} \right]^{-1} \quad (4-4)$$

Where ρ is the resistivity, V is the measured electric potential, I is the measured current, and S_1 , S_2 , and S_3 are the inter-electrode distances. When the probes are of equal spacing the equation collapses to

$$\rho = 2\pi S \frac{V}{I} \quad (4-5)$$

The derivation for the resistivity equation starts with Laplace's equation—

$$\frac{\nabla E}{\rho} = \frac{\nabla^2 \varphi}{\rho} = 0 \quad (4-6)$$

Where E is the electric field and φ is the electric potential. One can solve for the potential in proximity to the electrodes under the following conditions: the equation of continuity ($I_{in} = I_{out}$), Ohm's Law and the relation between the electric field, E , and the electric potential, φ where E is the normal derivative of φ such that

$$E = \frac{-\partial \varphi}{\partial n} \quad (4-7)^8.$$

Assuming that the charges are injected into the material from a point probe in a semi-spherical manner, then

$$E = k \frac{Q}{r^2} \quad (4-8)$$

can be expressed as

$$E = \frac{I\rho}{2\pi r^2} \quad (4-9)$$

or in terms of potential

$$\phi = V = \frac{I\rho}{2\pi r} \quad (4-10)$$

When the distances between the four probes are equal, the potential difference measured between the two inner probes is equal to

$$\frac{I\rho}{2\pi s} \quad (4-11).$$

This is true for wafers of infinite length. However wafers are not infinite in length so correction factors are employed. For samples that are not large wafers, geometrical correction factors are used. In addition to the linear arrangement, there are several non-collinear four-point probe arrangements. Along with these variations of arrangements come variations of equations and correction factors. The square and rectangular array benefit the measurement because the arrangement may fit into a smaller area. As long as the probes have equal spacing between them (square array), the resistivity can be calculated as:

$$\frac{2\pi s}{2 - \sqrt{2}} \frac{V}{I} \quad (4-12).$$

Yet for the rectangular array

$$\rho = \frac{2\pi s}{2 - \left(\frac{2}{\sqrt{1+n^2}} \right)} \frac{V}{I} \quad (4-13)$$

where n is the ratio of the probe spacings.

In an attempt to develop a method of resistivity measurements for thin epitaxial layers—thin separate single crystalline layers—the delta arrangement made it possible to have only two probes of close spacing. However for the delta method, calculating the resistivity is a complex function of sample layer thickness, substrate thickness, probe spacing and correction factors⁵. Although the probe points used in the 4pp method are very small relative to the probe spacings and sample size, the points can be considered hemispheric or circular and not true points. Along with the points having a surface area, the points also have spreading resistance. The spreading resistance for a single, flat circular point of radius a can be determined by

$$R_{sp} = \frac{\rho}{4a} \quad (4-14)$$

and for a hemispheric point pressed into the surface of the sample

$$R_{sp} = \frac{\rho}{2\pi a} \quad (4-15).$$

Depending on the material of the points and the sample being measured, there may also be contact resistance in series with the spreading resistance. To eliminate spreading resistance non-contact methods can be employed. Especially in samples with shallow junction depths where surface scarring caused by probe measurements can severely damage the sample, the non-contact method becomes vital. There have been several methods used for non-contact measurements including the mercury drop method, the capacitance-couple method and the microwave measurement method.

As discussed previously, to determine the specific resistivity of a material using the linear or non-collinear methods of four-point probe techniques it requires a series of

correction factors and known geometries. A typical geometry employed was commonly known as the bridge-sample,

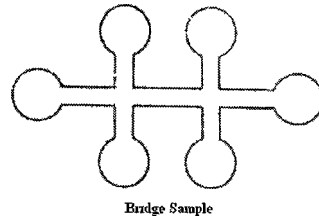


Figure 4.4 Bridge Sample⁹

Where the large areas at the ends served as low-Ohmic contacts. This particular geometry was designed to ensure that lines of current flow are sufficiently parallel.

4.1.3 van der Pauw Method

The van der Pauw technique allows the use of an arbitrary shape under specific conditions ⁹:

1. The contacts are at the circumference of the sample
2. The contacts are sufficiently small
3. The sample is homogeneous in thickness
4. The surface of the sample is singly connected

The van der Pauw method is useful for Hall measurements. The basic physical principle describing the Hall effect is the Lorentz force. When an electron moves through a sample perpendicular to an applied magnetic field, it experiences a force perpendicular to both the magnetic field and the internal electric field. For an n -type,

bar-shaped semiconductor sample as shown in figure 4.5 below, the majority carriers are electrons with a bulk density n .

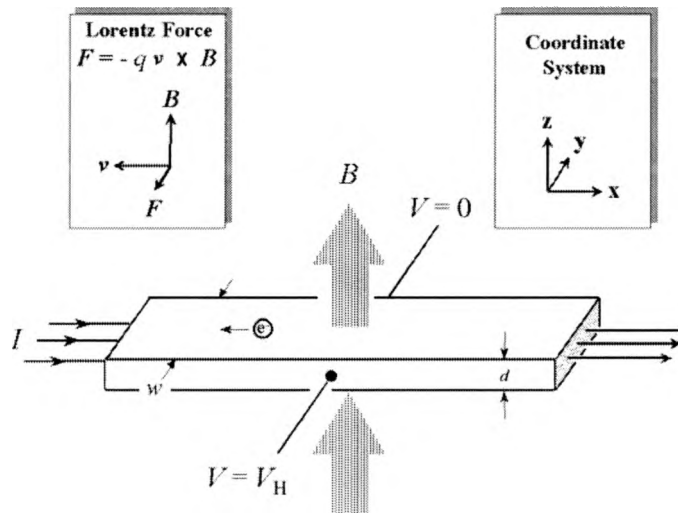


Figure 4.5 Lorentz Force¹⁰

By applying a constant current, I , in x -direction and a magnetic field, B , in positive z -direction, then the electrons will feel the Lorentz force and will build up on the negative y -direction resulting in an excess surface charge. The Hall voltage, V_H , is the potential drop across two sides of the sample which is also a consequence of the build up of negative charges. It is important to note that for holes, the same phenomenon occurs yet the build up has a positive potential. This transverse potential has unique components.

The V_H is equal to

$$\frac{IB}{qnd} \quad (4-16)$$

where q is the fundamental charge and d is the thickness of the sample. This can also be expressed as

$$n = \frac{IB}{qdV_H} \quad (4-17)$$

where the sign of the Hall voltage depicts the type of majority carriers.

Since $\sigma = ne\mu = \frac{1}{\rho}$ the mobility, μ , can be written as:

$$\mu = \frac{1}{ne\rho} \quad (4-18).$$

With a few substitutions one can determine the Hall mobility such that

$$\mu = \frac{1}{qn_s R_s} = \frac{V_H}{R_s IB} \quad (4-19)$$

where n_s is the sheet concentration ($n=n_s d$) and R_s is the sheet resistance. If the thickness of the sample is known then the concentration and resistivity can be determined.

However to determine the mobility, there are two measurements needed; the Hall voltage and the sheet resistance. To measure both parameters, it is convenient to employ the van der Pauw technique. As discussed earlier this technique is conditional. Figure 4.6 below shows the recommended sample configuration for this technique.

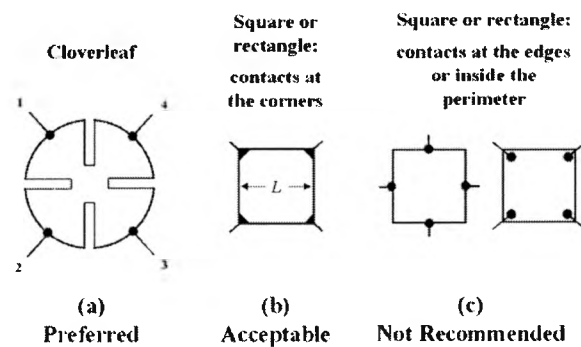


Figure 4.6 Contact Configurations for van der Pauw Technique⁹

For the sheet resistance, R_s , van der Pauw states that there are actually two parameters R_A and R_B that are needed to determine the sheet resistance. Figure 4.7 below shows how R_A , R_B , and V_H are measured.

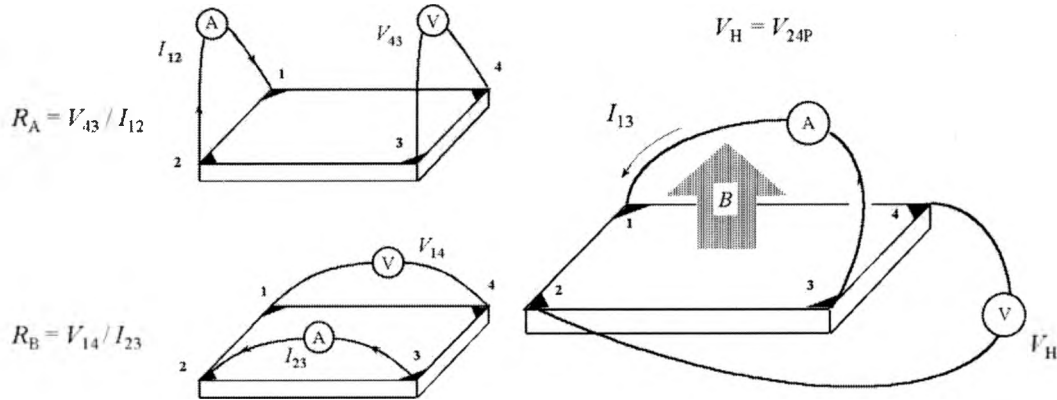


Figure 4.7 I-V Configurations for van der Pauw Technique¹⁰

Where 1, 2, 3 and 4 relate to the contact points and A and V are the ammeter and voltmeter. In addition, the van der Pauw equation (VDP) is needed to calculate R_s .

The VDP equation is as follows:

$$\exp\left(\frac{-\pi R_A}{R_s}\right) + \exp\left(\frac{-\pi R_B}{R_s}\right) = 1 \quad (4-20)^9.$$

Since the VDP equation is transcendental van der Pauw employed a correction factor that is related to the ratio of the R_A and R_B measurements to solve for R_s .

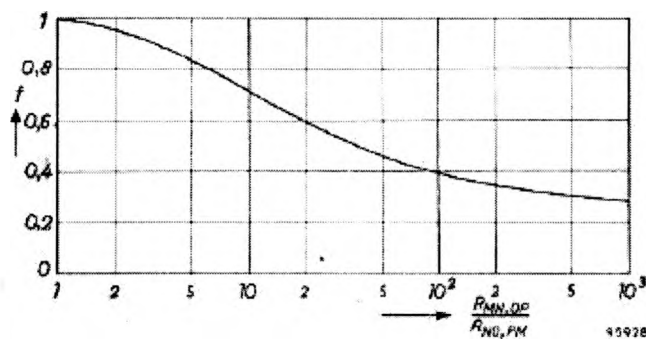


Figure 4.8 VDP Ratio Correction Factor⁹

If the sample is symmetric then the correction factor $f(R_A, R_B) = \text{unity}$. Otherwise R_s is simply

$$R_s = \frac{\pi}{\ln(2)} \frac{R_A + R_B}{2} f(R_A, R_B) \quad (4-21)^9.$$

The overall objective of the Hall measurement in the van der Pauw technique is to determine the sheet carrier density by measuring the Hall voltage. There are certain parameters that must be met when carrying out Hall and resistivity measurements. First the contacts need to be as Ohmic as possible. As noted earlier, metal to semiconductor contacts can create Schottky contacts. Methods of annealing assist in generating Ohmic contacts. It is also important that the contacts as small relative to the sample size. Second, the sample must be uniform in thickness. Finally, it is imperative to measure the sample in the absence of light due to possible photovoltaic effects and temperature gradients.

CHAPTER 5

SET UPS AND EQUIPMENT

For this thesis work several new setup were put together. After preliminary measurements using the four-point probe setup built by Chris Brown, we concluded that some of the electronics was not suitable to measure such high resistive samples. New electronic equipment was purchased including a switching unit, a current source that would enable us to source currents as low as a few femto amperes, and a nanovoltmeter. Also when we moved to the new building the power supply of the magnet failed. We found a replacement in two power supplies that were donated by Motorola. New software was written to control the new instruments and to enable 2pp and 4pp measurements as a function of the temperature and the magnetic field. The mechanics of the setup was also modified. We designed a hinge-based system that enables us to place the cryostat between the pole pieces of the magnet.

In this chapter the instrument specifics relevant for the conducted experimental setups are described. These set ups are dichotomized into Electrical Set ups and Optical Set ups. The purpose of the Optical Set up is to monitor any possible photovoltaic or photoconduction on the sample of interest as a consequence of incident light. The Electrical Set ups are for I-V measurements. The Electrical Set ups are further

dichotomized into 1) Low Level/Low Temperature electrical characteristics coupled with magnetic field effects and 2) High Temperature electrical characteristics.

5.1 Electrical Characterization Set ups and Equipment

Equipment used for low-level I-V, Temperature dependent I-V and Field effect I-V measurements included:

- 1 Keithley Model 2182A Nanovoltmeter and Model 6221 AC and DC Current Source
- 2 HP7001 Switch System
- 3 Model 22 CTI Cryogenics Cryostat and Model 8200 CTI Cryogenics Helium Compressor (Closed Cycle System designed by Janis Inc.)
- 4 Roughing Pump (Closed Vacuum System)
- 5 Lakeshore 331 Temperature Controller
- 6 Varian Electromagnet (1.1 Tesla)
- 7 Electromagnet Polarity Switch Unit and HP3488A Switch Unit
- 8 (2) HP6681A DC Power Supply for Electromagnet

For the Low Level/Low Temperature electrical characterization we employed the Keithley Model 2182A Nanovoltmeter and Model 6221 AC and DC Current Source. The two-channel 2182A Nanovoltmeter was chosen due its low noise voltage measurements at higher speeds over alternative low voltage measurement solutions (i.e. Lock-in Amplifier). The 2182A coupled with the 6221 Current proved advantageous with its GPIB interface and coupled triggering method. Guarded triax cables were also employed

to minimize leakage current for low-level signals. The Keithley system has a pulse and delta pulse feature that has advantages over other methods of low-level techniques.

5.1.1 Pulse mode versus Lock-in Amplifier

Due to the onset of nanotechnology, the devices under test (DUT) are becoming smaller and smaller such that their temperature can be raised significantly with very small amounts of applied power yielding inaccurate results. Consequently, for I-V measurements, measuring with DC signals would yield undesirable results. Even if the applied power is not the issue, devices or materials with extremely high or low resistance can have very low measurable currents or voltages. With low measurables one has to account for noise or errors. The objective to accurate low power measurements is to minimize the noise²⁸. A common technique for measuring low signals is by use of a lock-in amplifier. However it is still necessary to minimize the noise signal. In particular Johnson noise, which places a fundamental limit on resistance measurements²⁸. Johnson noise is a consequence of Brownian motion or the thermal motion of charged particles and has a white noise spectrum that is dependent on bandwidth frequency, resistance and temperature which can be expressed as

$$V_{rms} = \sqrt{4RkT\Delta f} \quad (5.1)$$

where V_{rms} is the root mean square voltage or $V_{rms} = \frac{V_f}{\sqrt{2}}$, R is the resistance, k is the Boltzmann constant, T is the absolute temperature and Δf is the bandwidth. Typical results from a 400 $k\Omega$ resistor at room temperature with a bandwidth from 100 to 17,000 cps is approximately 10 microvolts with a corresponding current of 25×10^{-6} microamps

which is significant for a high-gain amplifier with a $400\text{ k}\Omega$ resistor in the circuit²⁹.

Reducing the bandwidth (filtering) or reducing the temperature of the device can minimize the noise signal.

Other possible noise factors and errors include external noise sources, thermoelectric voltages, test lead resistance and the $1/f$ noise. Thermoelectric voltages can be attributed to temperature variations on non-uniform materials or at contacts. The $1/f$ noise is a term used to describe a noise signal that has an increase in magnitude with a decrease in frequencies²⁸. This is often a consequence of “drift”. The $1/f$ noise or Johnson noise does not have to originate from the device under the test. It can also originate from the measurement equipment. Most opamps and measurement amplifiers have a $1/f$ noise component which means that it is not possible to reduce the noise by endless averaging sessions. It is this $1/f$ noise which limits the measurement accuracy of the system.

In order to avoid the $1/f$ noise, often AC measurement techniques are employed. An example of an AC measurement technique is a lock-in amplifier which is capable of measuring small AC signals. This is unique since a lock-in can measure signals that are smaller than their noise signals. However this is not completely without limitations. As good AC current sources are not readily available one often uses an AC voltage source and includes a series resistance, R_{ref} , in the circuit. R_{ref} is chosen considerably larger than the DUT, thus creating an approximate current source of the form $A \sin(2\pi f_0 t)$. The voltage drop across the DUT is measured by a lock-in amplifier by multiplying the signal times a sine (real part of the AC voltage) and cosine wave (imaginary part of the AC voltage) of the same frequency and phase of the driven voltage source (read current

source). If the DUT is a clean resistor without capacitance and/or induction, the output of the upper channel in figure 5.1 will have a non-zero average output voltage while the lower channel will have a zero average output voltage. If one chooses for the time constant of the low pass filters a value much larger than the period of the voltage source, these output voltage will be constant. The upper output (labeled with real) will be proportional to the V_{rms} value of the AC-voltage that is in phase with the voltage source while the lower output (labeled with imaginary) will be proportional to the V_{rms} value of the AC-voltage that is 90 degrees out of phase with the voltage source. If one assumes that the impedance of the DUT is real, the lower channel will of course have a zero output. A lock-in amplifier can be considered to be an amplifier with a very narrow bandwidth. The bandwidth depends on the low pass filter after the multipliers. The larger their time constant the more narrow the bandwidth, and thus the lower the noise that is measured. Applying a lock-in technique often increases the signal noise ratio of the setup. In particularly for experimental setups that have a significant $1/f$ noise. Traditional averaging will not improve the signal to noise ratio of those setups, since averaging would mean looking at lower frequencies, and at lower frequencies there will be more noise.

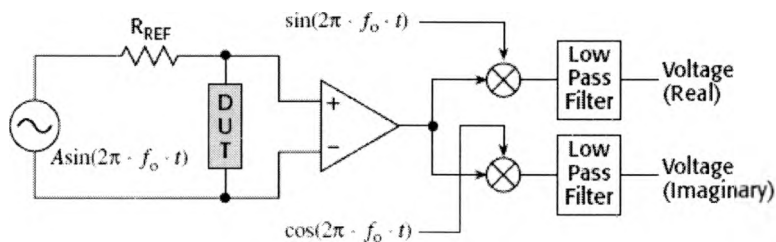


Figure 5.1 Schematic for a Lock-in Amplifier²⁸

An alternative to the lock-in is the DC reversal measurement method. This method is very similar yet this method employs an alternating DC signal of specified time intervals corresponding to a frequency. This method, often referred to as the “delta” method, applies a current to the device, takes a voltage measurement, then reverses the current and takes a voltage measurement. The difference between these two measurements divided by two is the voltage response of the device²⁹. The noise bandwidth is reduced by repeating the process and averaging the measurements. However this method is not without shortcomings. Thermoelectric voltages can still exist yielding a linearly changing difference. This method and the lock-in method only work for symmetric devices or devices whose I-V characteristics are symmetric. Mathematically the delta mode technique is similar to the lock-in technique. The voltmeter working in delta mode can be considered to be an AC voltmeter with a very narrow bandwidth filter. The width of the bandfilter depends on the number of delta-measurements that are averaged. So measurements are taken at a frequency above the onset of the $1/f$ noise of the device and the equipment. The noise is limited by limiting the bandwidth of the instrument by averaging over multiple delta-measurements.

A third method for low-level electrical characterization is the Pulse method. The pulse method is simply a heavy-side step function defined by a pulse width, which pulses a current for a defined time interval and then takes a short voltage measurement at a defined time in the interval, usually at the end of the pulse. The purpose of the low-level pulse method versus a DC method is to reduce thermal effects since a constant power source could heat or damage the DUT and yield undesirable results.

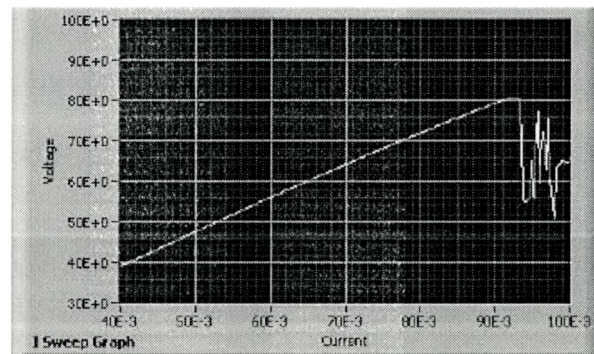


Figure 5a: DC I-V curve from 40mA to 100mA. Testing destroys the DUT.

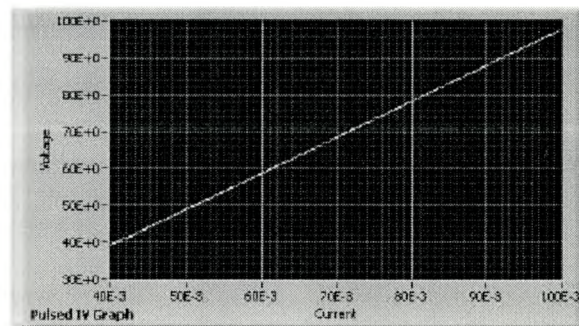


Figure 5b: Pulsed I-V curve over the same range.

Figure 5 2 Pulsed I-V Curve vs DC Curve²⁸

Previously the pulse method was executed manually at most one cycle per second. Current technology allows a computer to accurately control pulse intervals and widths at much higher frequencies and much shorter pulse widths. This method also has noise issues. Yet synchronizing the time intervals with the power line cycle reduces some signal noise. Also the method of repeating measurements and averaging reduces noise. However with microsecond pulse widths the pulse method introduces a new level of limitations.

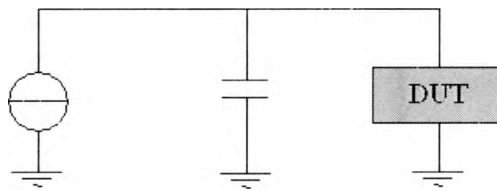


Figure 5.3 Schematic of DUT with parallel capacitor

Figure 5.3 shows a simple diagram of the current source shows the internal capacitance and the DUT symbolized as a load resistor. A Kirchoff current loop yields a differential equation whose solution is of the form:

$$V = Ae^{\alpha t} \quad (5-2)$$

The unique solution for the output voltage is:

$$V_{out} = IR(1 - e^{-t/RC}) \quad (5-3)$$

which is logical in the upper limit as t approaches infinity the solution collapses to Ohm's Law— $V=IR$. However for short defined pulse intervals there are several critical parameters: the resistance of the DUT and the time the output signal is evaluated at. For metals this is not much of an issue due to their low resistance and picosecond relaxation times, but for semiconductors and high resistant devices their carrier dynamics set limits to the pulse intervals. Roughly speaking the minimum pulse width has to be about 5 times the time constant. In particularly for high resistance devices, the pulse width becomes large and the measurement frequency will reduce to the part of the spectrum where the $1/f$ noise will be significant. It should be mentioned here that these charging effects will

also limit the applicability of the delta-mode technique in a similar matter to resistance values below 100 Mohm.

Through the evolution of new materials and devices follows the advancement in technology. The objective is smaller and faster and consequently the properties of the materials gives rise to limits on the characterizing of the devices.

5.1.2 Keithley 7001 Switch System

The Keithley switching unit allows us to change two-point and four-point probe configurations without changing cables or moving the sample. This is advantageous since many measurements are taken at specific temperatures or in the presence of an applied magnetic field. A LabView VI (see Appendix C), was prepared to interface with the switching unit to control the configurations. Each configuration was labeled with an alpha-numeric code that corresponds to a specific Current-Voltage electrode configuration. The following chart shows all configurations and their corresponding code and contact position on the sample. A systematic method was employed to insure consistency by numbering the contacts for every sample for this thesis in the following manner:

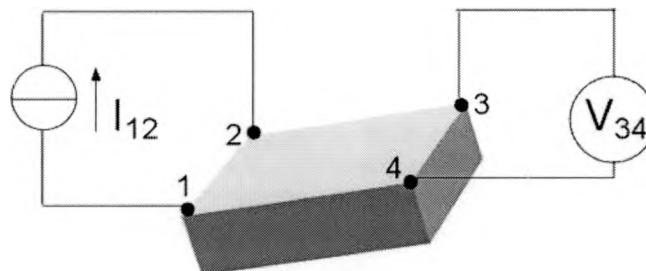


Figure 5.4 Sample Contact Numbers

The following chart (Table 5.1) shows all configurations used for the switching unit and for this thesis.

Table 5 5 Alpha-Numeric Contact Codes

Alpha-numeric Code	Current	Voltage
R1	21	34
R2	12	34
R3	32	41
R4	23	41
R5	43	12
R6	34	12
R7	14	23
R8	41	23
VH1	31	42
VH2	13	42
VH3	42	13
VH4	24	13
RR1	21	21
RR2	12	21
RR3	32	23
RR4	23	32
RR5	43	34
RR6	34	43
RR7	14	41
RR8	41	14
VVH1	31	13
VVH2	13	31
VVH3	42	24
VVH4	24	42

5.1.3 Model 22 CTI Cryogenics Cryostat and Model 8200 CTI Cryogenics Helium

Compressor

The Model 22 CTI Cryogenics Cryostat comes equipped with 6 triax connections.

A four-prong modified adapter at the top of the cryostat to connect samples to the cryostat and second stage thermocouple. The modified adapter has four connections that correspond to 4 of the 6 triax connection that connect directly to the Keithley 7001

Switch System. The Switch unit then connects directly to the Keithley Nanovoltmeter/Current Source. The cryostat base is mounted to a fixed hinge attached to an aluminum ground plate. This allows the cryostat to rotate between the pole pieces of an electromagnet.

The Model 8200 CTI Cryogenics Helium Compressor is a closed cycle refrigeration system attached to the cryostat. This (under vacuum, mTorr) will allow us to cool the sample to ~8 Kelvin. A series of valves between the cryostat and a roughing pump allows us to change samples without completely venting the system. This is advantageous when time is critical. It also enables us to vent the system with nitrogen instead of air which will drastically decrease the following pump down time since out-gassing will be considerably reduced.

5.1.4 Lakeshore 331 Temperature Controller

The Lakeshore 331 Temperature Controller is connected directly to the cryostat and has two temperature sensors; a thermocouple and a GaAs temperature sensor. The latter is more accurate but cannot be used for temperatures above 200 Celsius. The GaAs diode measures the temperature at the base of the cryostat generated by the helium compressor. The thermocouple is mounted between the base and the four-prong adapter at the top of the cryostat which measures the temperature of the sample holder. An internal heater controlled by the Lakeshore 331 allows us to vary the temperature of the sample while the helium compressor is running.

5.1.5 Electromagnet, Power Supply and Switch Unit

The cryostat has capability to rotate into a large Varian Electromagnet. The electromagnet is powered by two HP6681A DC Power supplies with GPIB interface. The power supplies have a maximum voltage output of 8 volt. In order to increase the maximum field we used two of the same power supplies in series, and we furthermore wired the two coils of the magnet in parallel. The two power supplies can provide a maximum of 120 Amperes at 16 volts which generate 1.1 Tesla from the electromagnet. A switching unit containing two high current relays controlled by a low signal relay was built to switch the polarity of the electromagnet. Since the magnet draws such high current, safety measures were employed to insure that zero current was drawn when the polarity was switched. In order to engage the large relays, one must enable the low signal relay. This was controlled by an HP3488A Switch Unit with GPIB interface. This combination of switching units allows us to control not only the magnitude of the electromagnet by computer but also the direction of the field. This is advantageous for MR measurement and Field effect I-V measurements.

For high temperature measurements the following equipment was used:

- 1 HP 4145B Semiconductor Parameter Analyzer
- 2 HP 16058A Test Fixture
- 3 Delta Model 6400 Temperature Chamber with modified circuit board to co-axial adapter

The HP 4145B semiconductor parameter analyzer (SCPA) comes equipped with voltage sources, current sources, voltage monitors, and current monitors. GPIB interface allows

control with Metric Software. This allows us to take two-point probe and four-point probe I-V measurements. The HP4145B comes with a shielded 16058A Test Fixture. The HP4145B contains four SMU# (Source Monitor Units). Each of these can be programmed to be a voltage source, a current source, or a ground as shown below in figure 5.5 by specifying the source mode field (V, I, COM)³⁰. SMU1, SMU2, SMU3, SMU4, Vs1, Vs2, Vm1, and Vm2 are available on the Test Fixture. We used SMUs

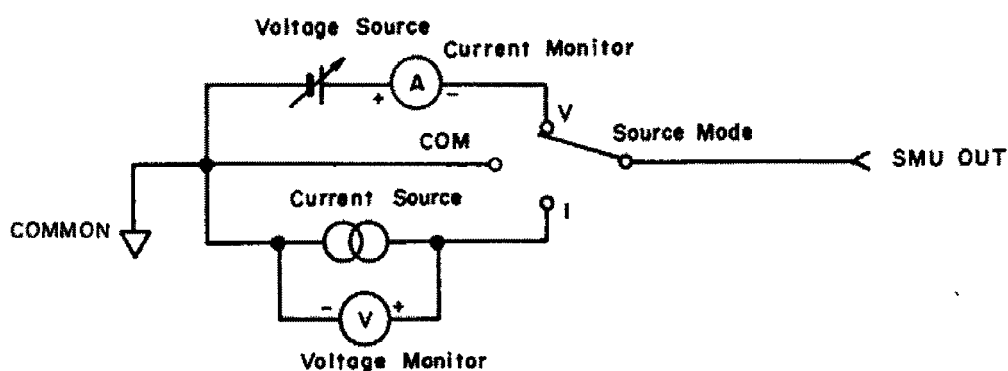


Figure 5.5 SMU Schematic³⁰

configured as zero ampere current sources to measure voltages because they have a much larger input impedance than the voltage monitors Vm1 and Vm2.

5.1.6 Delta Model 6400 Temperature Chamber

The Delta Model 6400 Temperature Chamber with modified circuit board to coaxial adapter attached to the HP 4145B in lieu of the test fixture. This allowed us to take I-V measurements at various high temperatures. The Delta 6400 heated by convection and when coupled with the cooling system has a range of -184°C to 315°C .

5.2 Optical Characterization Set ups and Equipment

The equipment used in this experiment to illuminate the sample consisted of a Xenon 6251 lamp as a light source, a light filterwheel containing six filters, an Oriel digital light intensity controller 68950, the ARC SpectraPro 300i Monochromator, a focusing lens, and an aluminum box that would shield the sample from stray-light, EM noise, and direct exposure of the sample to the airflow caused by the air conditioning. The electric measuring equipment for this experiment contained an HP4140A PicoAmmeter, a Kiethley 2182A Nanovoltmeter, a Keithley 6221 current source, and a Keithley 6514 electrometer (Keithley Nanovoltmeter and Current Source are described in section 5.1).

The ARC 300i SpectraPro monochromator contains two 1200 g/mm gratings numbered 1 and 2 with parameters 300nm blaze and 750nm blaze respectively. The gratings are mounted on a turret which is controlled by a PC running LabView software. Figure 5.6 shows the efficiency versus wavelength graph of several gratings from Richardson Grating Laboratory.

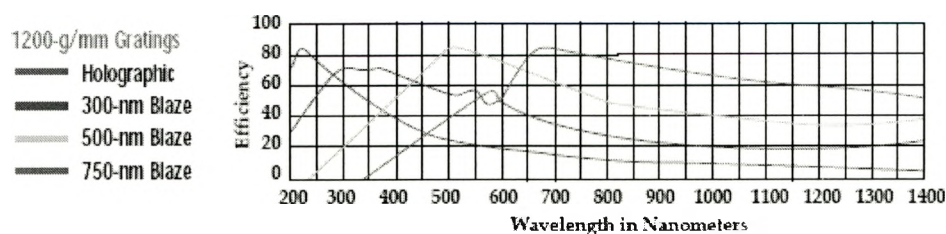


Figure 5.6 Efficiency vs Wavelength³³

The gratings are not flat but have a triangular shaped line pattern and are called blaze-gratings (see also Figure 5.7). This particular profile will result in a larger portion of the incident light being diffracted in the first-order diffracted beam. Grating 1 (300 nm blaze) was used below 560 nm and grating 2 (750 nm blaze) was used above 560 nm. The filter wheel is used to remove the light from 2nd and higher order diffraction beams. Figure 5.7 below shows how more than one wavelength can occupy the same. The use of a pass filter can remove the higher order diffracted beams and therefore only a specific wavelength will be selected. The six filters used, numbered 1 through 6 (see table 5.2), are high pass filters, allowing only the wavelength above a certain cutoff value to pass.

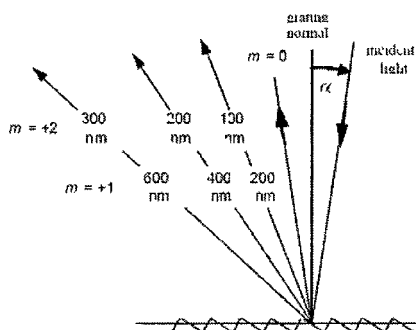


Figure 5.7 Higher Order Diffraction Beams³³

Table 5.2 Wavelength Cut offs

Filter position	Minimum Transmitted λ [nm]	Wavelength range [nm]
1	no filter	All wavelengths according to lamp
2	320	320-469
3	470	470-589
4	590	590-664
5	665	665-714
6	715	715-1430

The Xenon 6251 75 Watt bulb and the Oriel digital light intensity controller allowed a stable light source for the experiments. The Xenon 6251 was chosen for its UV output. Normally an ozone-free bulb is used in this setup, but as we expect the effect to be stronger in the UV, a bulb that emits light up to 200-250 nm was purchased.

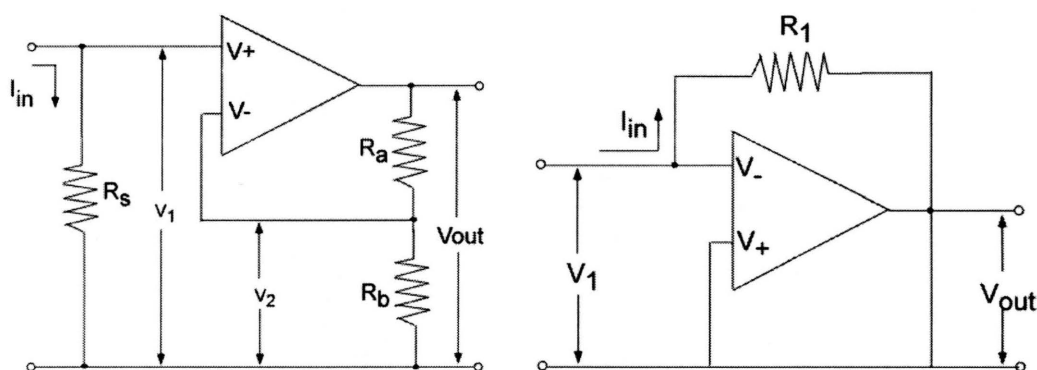


Figure 5 8 Shunt ammeter (left) and feedback ammeter (right)

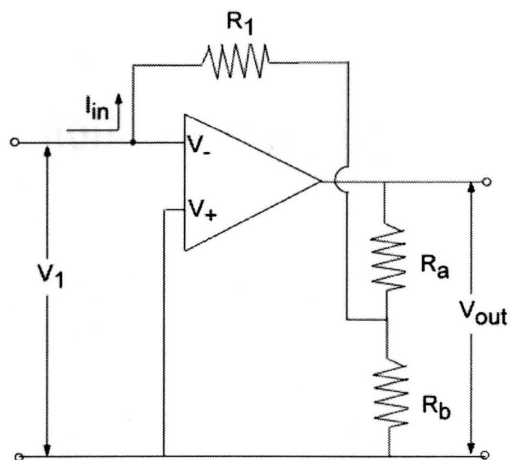


Figure 5 9 Picoammeter

The choice of the picoammeter allows for low signal measurements. The traditional ammeter uses a shunt resistor as shown in figure 5.8 on the left. The current is determined by measuring the voltage over a resistor, typically 1-100 Ohm. This will result in a rather large voltage drop over the ammeter. The feedback ammeter (See figure 5.8-right) allows for more accurate measurement since the voltage drop over the meter is very low (of the order of 10 μ V). The low voltage burden of the feedback ammeter can be understood from figure 5.8-right. Since the Opamp has negative feedback, the two input leads of the input are virtually at the same electric potential. A real picoammeter has an internal voltage divider to control the amplification of the op amp and ultimately to increase the sensitivity to the femto-range depending on the current to be measured (see figure 5.6). Below are the output voltage equations from the Keithley Low-Level Measurements Handbook that are associated with the above ammeter schematics.

$$\text{Shunt ammeter:} \quad V_{\text{out}} = I_{\text{in}} R_{\text{shunt}} (1 + R_a/R_b) \quad (5-3)$$

$$\text{Feedback ammeter:} \quad V_{\text{out}} = -I_{\text{in}} R_1 \quad (5-4)$$

$$\text{Picoammeter:} \quad V_{\text{out}} = -I_{\text{in}} R_1 (1 + R_a/R_b) \quad (5-5)$$

Note that for the feedback ammeter and the picoammeter, the V_{out} equations initially had a V_{in} component. However since V_{in} is equal to the voltage difference of the op amp, V_{in} is virtually zero leaving only $-I_{\text{in}} R_1$. Also note that the picoammeter is similar to the feedback ammeter yet has a voltage divider to control the sensitivity.

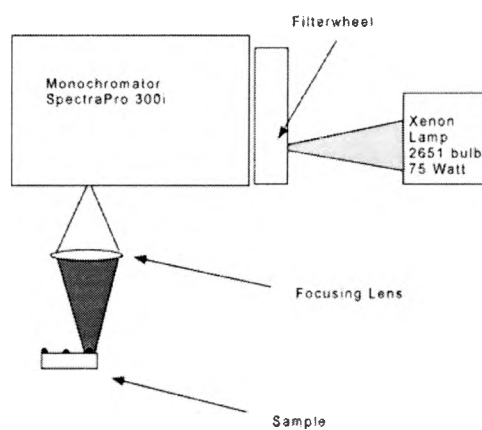


Figure 5.10 Light over right Contact

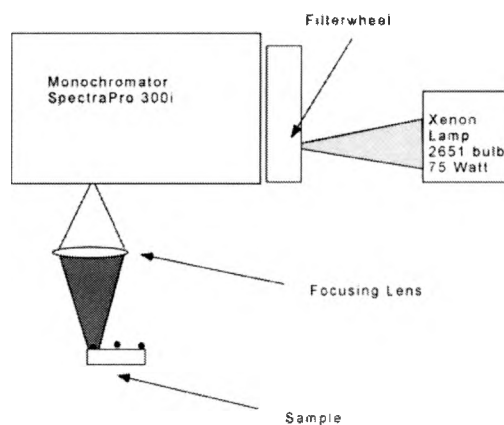


Figure 5.11 Light over left Contact

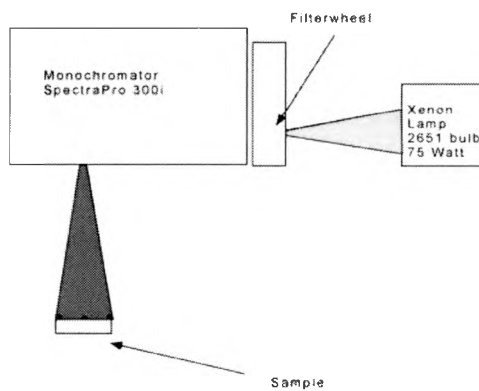


Figure 5.12 Flooded Sample

Figures 5.10, 5.11 and 5.12 show the set up for the optical characterization experiments. Figure 5.10 shows light focused on a single contact and figure 5.11 shows how light is focused on the other contact to measure possible photoeffects at the metal to semiconductor contact. Figure 5.12 is where the sample is flooded to measure possible photoconduction.

CHAPTER 6

MEASUREMENT RESULTS

6.1 Electrical Characterization

6.1.1 Ilmenite Ceramic Sample

The I-V relation for ceramic Ilmenite has been investigated and available in literature. In this experiment we evaluated the two-point probe measurements and the four-point probe measurements. We can assume that the voltage measurements from the two-point measurement can be expressed as the sum of the voltage drops over the contacts and the voltage drop over the sample (see picture below).

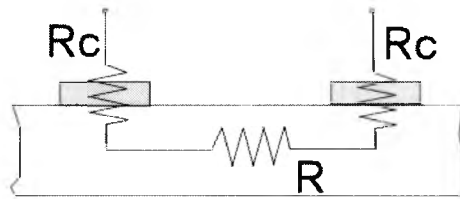


Figure 6.1 Series Resistance

Or in other words:

$$V_{2pp} = 2 * V_{contact} + V_{sample} = 2 * V_{contact} + I * R = 2 * V_{contact} + \frac{\rho}{RCF_{2pp}} I \quad (6-1)$$

Where ρ is the resistivity of the material, RCF_{2pp} is the 2pp-correction factor for the sample geometry (which will be defined below), I is the current, and V_{contact} is the voltage drop over the contacts. Strictly speaking the V_{contact} term contains and the voltage drop over the semiconductor-metal contact and a term originating from the spreading resistance under the contacts. Since the contacts are rather larger we ignore the latter term. From two-point probe measurement we can see a large non-linearity consistent with literature. However the resistivity measurements from the four-point probe configurations are almost completely linear. The non-linearity is smaller than 1%. This small linearity can be due by Ohmic heating effects in the sample or by a voltage dependent resistivity. The latter can be intrinsic or extrinsic due to the p-n-p properties of grain boundaries¹¹.

6.1.1.1 Determination of I-V Relation of Contacts

The I-V characteristics of the contacts can be derived from the 2pp and 4pp probe measurements, by calculating the voltage drop over the Ilmenite thin film from the 4pp measurement results and subtracting this from the 2pp measurement results using above given equation. The remaining I-V relation is characteristic for the contacts. The resistivity was determined from the 4pp data using two different methods: (1) by using the van der Pauw equation as described in section 4.1.2 (2) by calculating the 4pp-correction factors using the theory of images as described in appendix A. The former technique assumes a 2-dimensional current distribution in the sample while the latter technique assumes a 2-dimensional current distribution or a 3-dimensional current

distribution in the sample depending on the sample thickness. The figures below show the assumed current distribution for the 2-dimensional and the 3-dimensional samples.

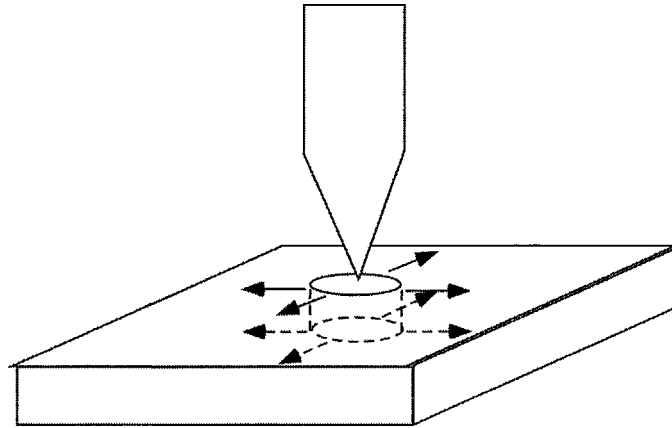


Figure 6 2 2-Dimensional Current Distribution

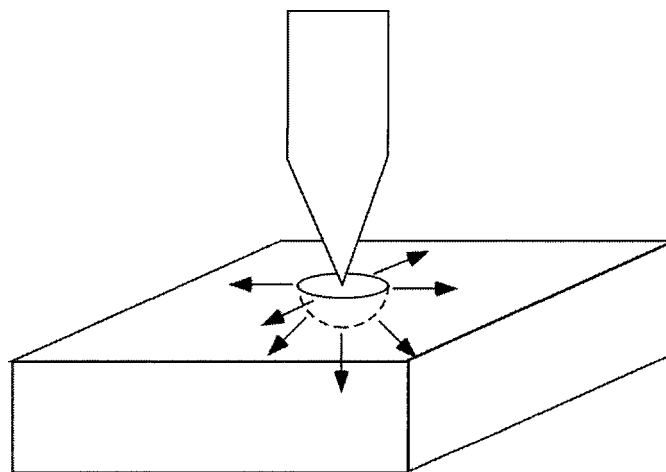


Figure 6 3 3-Dimensional Current Distribution

Since the 2pp measurements yield strong non-linearity and the 4pp measurements are mostly linear and contacts are metal-semiconductor, it is possible that the non-linearity is a consequence of Schottky barriers. This result shows strong non-linear behavior in both forward and reverse bias. We characterized the I-V relation of each contact and determined the work function of the Ilmenite sample and barrier heights of

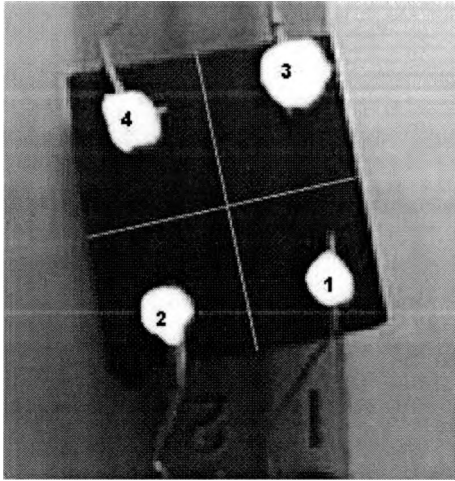
the metal-semiconductor contacts. The first reasonable approximation for the work function of Ilmenite ceramic is $4.81\text{eV}\pm 0.02$.

The sample of interest for this experiment is labeled as a FeTiO_3 ceramic sample and was fabricated at the University of Alabama. The sample is mounted on a circuit board and has four small silver contacts at the corners. The HP 4145B Semiconductor Parameter Analyzer, the HP 16058A Test Fixture, and the Metrics software were used to conduct 2pp and 4pp experiments and collect the data onto a spreadsheet. We used the source monitoring units on all four contacts labeled SMU#1 through SMU#4 due to the high input impedance (10^{12} Ohm) in lieu of the voltage monitors. Measurements were taken at room temperature ~ 300 K and also the measurements were taken in the dark to eliminate any possible photovoltaic effects. For the 2pp measurements only two SMUs were used at a time. One SMU contained the current sweep and monitored both the current and voltage while the other SMU was held at zero potential. For the 4pp measurements one SMU was held at zero potential while the other three SMUs were programmed to be current sources. Of the three remaining SMUs one was used for a current sweep and monitored the current while the other two had zero current and monitored the potential with respect to the zero potential (i.e. these two SMUs acted as voltage monitors)

The Ilmenite ceramic sample has dimensions of $5.7 \times 6.1 \times 2.2 \text{ mm}^3$. Using Canvas 8.0.3 software we imported a digital photo of the Ilmenite sample and determined the dimensions of the sample and the contacts, and the exact position of the contact. To do so we set the ruler units in the Canvas software to reflect the exact dimensions of the sample in mm and drew polygons around each contact. The Canvas software was used to

tell us the exact surface area and perimeter length of each polygon. The position of each contact was determined by approximating the polygon by a circle and determining the position of the circle's center.

Area4 = 1.034 sq mm Area3 = 1.459 sq mm



Area2 = 0.861 sq mm Area1 = 0.731 sq mm

Ilmenite Ceramic	Contact 1	Contact 2	Contact 3	Contact 4
Position (x mm)	4.794	1.359	4.611	1.150
Position (y mm)	1.161	1.183	5.649	5.359
Contact Area (mm ²)	0.731	0.861	1.459	1.034

Figure 6.4 Photo of Ilmenite Sample with Contact Areas and Positions

The two-point probe measurements for all configurations showed non-linear behaviors. The results are summarized in the graph below. Not all curves are the same, which is logical since all contacts have different surface areas, and also the distance between each two contacts varies slightly.

I-V for 2pp Configurations Ilmenite Ceramic

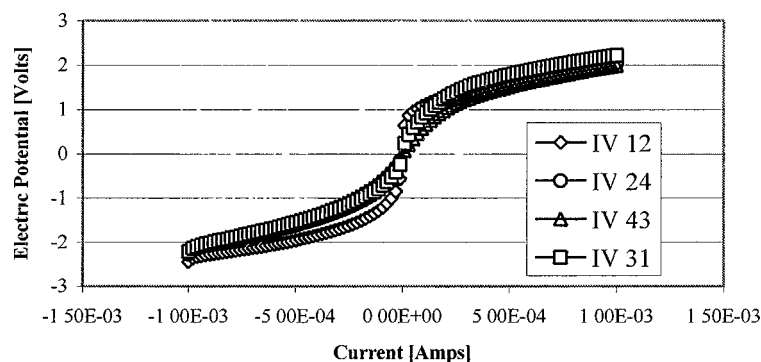


Figure 6 5 I-V for 2pp Configurations Ilmenite Ceramic

The raw measurement data for the four-point probe measurements also yielded non-linear behavior and is shown in the figure below. If we plot the electric potential difference between the two voltage contacts as a function of the current a linear behavior is observed. Although the graph is noisy one can still determine a linear fit to the graph where the slope of the graph corresponds to the non-corrected sheet resistance.

I-V for Independent Probes

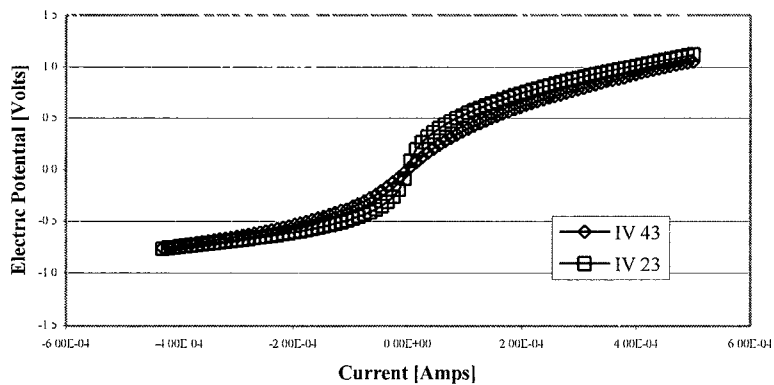


Figure 6 6 I-V for Independent Probes

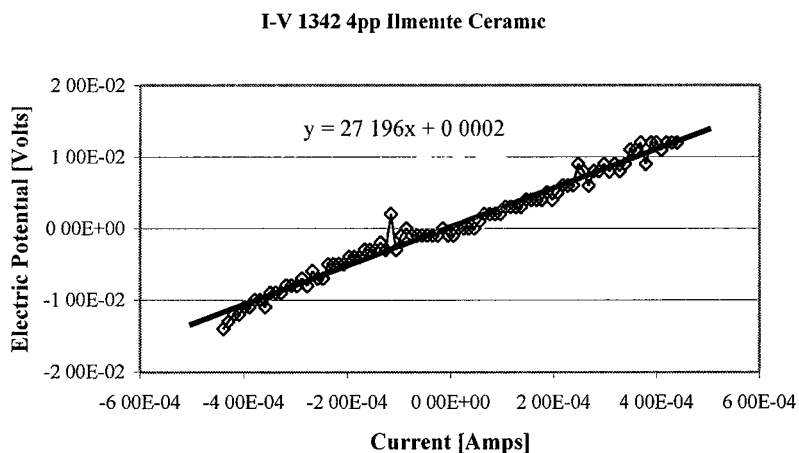


Figure 6 7 I-V 1342 4pp Ilmenite Ceramic

Four configurations were evaluated using this method. Using the van der Pauw technique and solving the van der Pauw equation (Appendix B) we determined the resistivity of this sample to be $21.7 \, \Omega \cdot \text{cm}$. Since strictly speaking the VDP equation is only true for very thin samples there is possible error in the resistivity calculation since the Ilmenite sample is bulk ceramic. A derived four-point probe correction factor based on the geometry of the sample and the positions of the contacts was employed to calculate the resistivity (Appendix A). The derived correction factor yielded consistent results with van der Pauw— $22.3 \, \Omega \cdot \text{cm}$. This is possible since the distances between the contacts are larger than the thickness of the sample. However these results were inconsistent with literature which showed a resistivity between $100\text{--}500 \, \Omega \cdot \text{cm}$. Since pure Ilmenite ceramic is difficult to produce, there is a possibility of a contaminated sample. These results were also inconsistent with previous results of the sample. The labeled resistivity calculated at the University of Alabama stated $0.13 \, \Omega \cdot \text{cm}$ which is also inconsistent with literature. Future test can conclude the sample's composition. The table below shows the calculated

correction factors (CRF) and slopes that correspond to the four 4pp configurations and calculated sheet resistance and resistivity.

Table 6 1 Ilmenite Ceramic Data

4pp Configurations (I,V)	Correction Factors	Slope of Graph	Sheet Resistance $R_s (\Omega/\square)$	Sample Thickness (mm)	Resistivity ($\Omega.cm$)
13,42	3.723	27.272	101.53	2.2	22.34
12,43	5.829	17.139	99.90	2.2	21.98
42,13	3.732	26.991	100.73	2.2	22.16
43,12	5.829	17.811	103.82	2.2	22.84
Average			101.50		22.33

The voltage measurements from the two-point probe technique can be expressed as the sum of the voltage drops across the two contacts and voltage drop across the sample as follows: $V_{2pp} = V_{c1} + V_{c2} + V_{sample}$. Since the voltage drop across each contact is the area of interest we can subtract the voltage drop across the sample from the 2pp measurements and exploit the I-V behavior of the contacts. The results from the 4pp measurements show us the sheet resistance of the sample without the contact resistance thus eliminating the voltage drop across the contacts. However we cannot simple subtract the 4pp data from the 2pp data since the voltage is measured at other locations in the sample. For the 2pp technique current is injected at the same location as the potential is monitored. For the 4pp technique the voltage is measured at a different locations then the current is injected. Yet if we assume that for the 2pp technique the current is injected at the center of the contacts and the voltage is monitored at the periphery we can generate a correction

factor for this geometry and use the calculated resistivity to approximate a set of voltage data that corresponds to the 2pp current distribution as follows:

$$V_{2pp} = V_{c1} + V_{c2} + \frac{\rho_s}{CRF_{2pp}} I_{measured} \quad (6-2)$$

where $\frac{\rho_s}{CRF_{2pp}}$ is the ratio of the sheet resistance and 2pp correction factor yielding a resistance value of the sample only. We first evaluated the I-V relation over contacts 1 and 2 on the Ilmenite ceramic and calculated $\frac{\rho_s}{CRF_{2pp}}$ from the sheet resistance average and the following geometry of contacts 1 and 2:

Table 6 2 Contact 1 and 2 Data

	Center Contact 1	Center Contact 2	Periphery Contact 1	Periphery Contact 1
Position (x mm)	4 794	1 359	4 249	1 858
Position (y mm)	1 161	1 183	1 187	1 211

Based on the contact positions the CRF for the 2pp resistance was 0.696. In the figure below the I-V characteristics of the contacts (dotted line) and the I-V characteristics of the Ilmenite ceramic (solid line) are plotted.

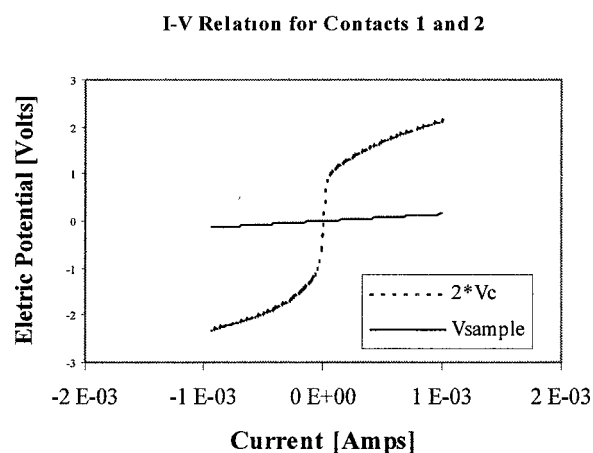


Figure 6 8 I-V Relation for Contacts 1 and 2

In the following graph the I-V characteristic of both contacts is shown again with the two axes switched. This clearly shows the non-linear behavior of the contacts. The I-V characteristics of the contacts are clearly non-linear and suggest that the metal-semiconductor contacts have Schottky barriers. Note that the I-V curve of the figure below is the I-V characteristic of two metal semiconductor contacts in series. So if the contacts are Schottky diodes, the diodes are biased oppositely.

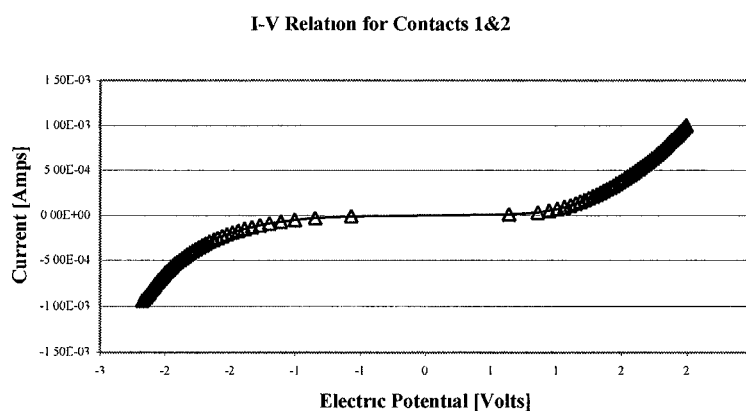


Figure 6 9 I-V Relation for Contacts 1 and 2 Corrected

In order to check if the observed I-V relation could be caused by two opposite biased Schottky diodes we did a PSpice simulation. Since the contacts have Schottky barriers they behave as diodes and the I-V relation can be modeled as two diodes with parallel resistors (modeling leaky Schottky contacts) in series with a resistor (modeling the Ilmenite) according to the following model.

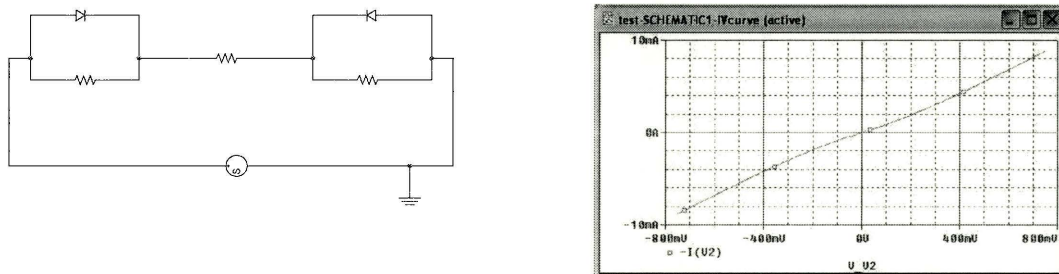


Figure 6 10 PSpice Schematic and Simulation

The above figure shows a P-Spice simulation of the previous schematic which clearly shows the non-linear behavior. No attempt was made to maximize the non-linearity of the simulated results by adapting the model parameters. Although the P-Spice simulation does not match the I-V relation of the Ilmenite ceramic contacts, this does show that each contact could be modeled as a diode with a parallel resistor. Now that the contacts have been modeled we can characterize each contact. This is not straight forward as each I-V curve represents a forward biased and reverse biased diode. Some of the corrected 2pp I-V curves are clearly non-symmetrical around zero and thus show rectifying properties. We believe that this is due to the different size of the contacts. The graph below shows the asymmetry of the forward and reverse bias between contact 1 and 2.

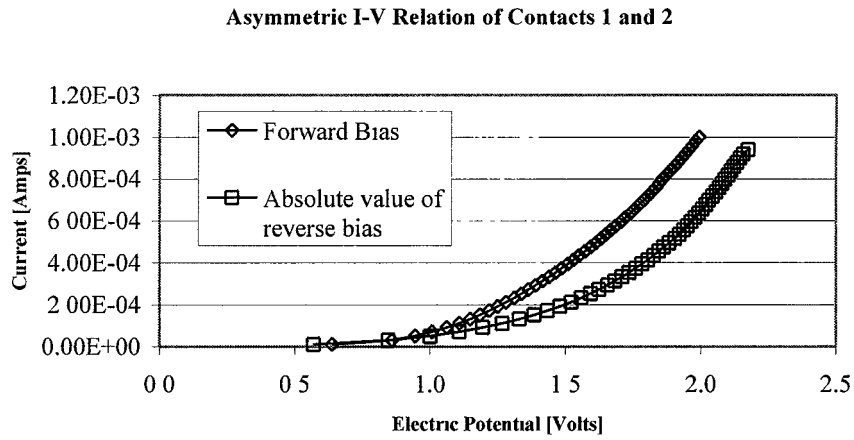


Figure 6.11 Asymmetric I-V Relation of Contacts 1 and 2

Since we measured six I-V characteristics, i.e. I-V₁₂, I-V₂₄, I-V₄₃, I-V₃₁, I-V₁₄, I-V₂₃, it should be possible to calculate the individual contact voltages from the measurement results, If we assume that the contact voltage over each contact is independent of the position of the other current electrode we can state the following:

$$\begin{aligned}
 V_{12} &= V_{c1} + V_{c2} \\
 V_{24} &= V_{c2} + V_{c4} \\
 V_{43} &= V_{c4} + V_{c3} \\
 V_{31} &= V_{c3} + V_{c1} \\
 V_{14} &= V_{c1} + V_{c4} \\
 V_{23} &= V_{c2} + V_{c3}
 \end{aligned}
 \tag{6-3}$$

Where V₁₂, etc are the 2pp voltages corrected for the voltage drop over the sample.

Inverting those equations by plug and play gives:

$$\begin{aligned}
V_{c1} &= \frac{1}{2} [V_{31} + V_{12} - V_{32}] \\
V_{c2} &= \frac{1}{2} [V_{12} + V_{24} - V_{14}] \\
V_{c4} &= \frac{1}{2} [V_{24} + V_{43} - V_{23}] \\
V_{c3} &= \frac{1}{2} [V_{43} + V_{31} - V_{41}]
\end{aligned} \tag{6-4}$$

Since we have 6 measured voltage values for each current, the contact voltages can be calculated also via the equations listed below:

$$\begin{aligned}
V_{c1} &= \frac{1}{2} [V_{31} + V_{14} - V_{34}] & V_{c1} &= \frac{1}{2} [V_{41} + V_{12} - V_{42}] \\
V_{c2} &= \frac{1}{2} [V_{12} + V_{23} - V_{13}] & V_{c2} &= \frac{1}{2} [V_{32} + V_{24} - V_{34}] \\
V_{c4} &= \frac{1}{2} [V_{24} + V_{41} - V_{21}] & V_{c4} &= \frac{1}{2} [V_{14} + V_{43} - V_{13}] \\
V_{c3} &= \frac{1}{2} [V_{43} + V_{32} - V_{42}] & V_{c3} &= \frac{1}{2} [V_{23} + V_{31} - V_{21}]
\end{aligned} \tag{6-5, 6}$$

Those equations are only valid if we assume that the potential difference across the contacts is independent of the position of the 2nd current electrode, i.e. V_{ca} ($a=1,2,3,4$) is independent of the measurement configuration.

6.1.1.2 Model Contacts

If the I-V plot of two contacts is the superposition of two bias dependant rectifiers with parallel resistors then theoretically solving for the individual contacts from the derived equation above (i.e. $V_{c1}, \dots, V_{c4}$) should yield rectifying behavior similar to the P-Spice simulation. The P-Spice simulation figure below shows the I-V behavior of the independent contacts and the superposition of the two contacts identified by the markers.

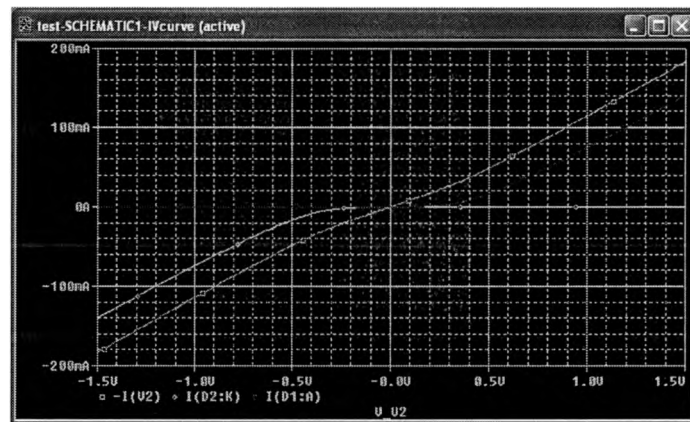


Figure 6.12 PSpice Simulation of Rectifying Behavior

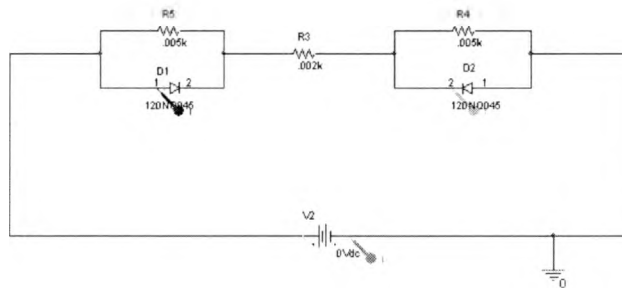


Figure 6.13 PSpice Schematic

The figure below shows the results of this analysis for one set of equations (6-5):

$$V_{c1} = \frac{1}{2}[V_{31} + V_{12} - V_{32}], V_{c2} = \frac{1}{2}[V_{12} + V_{24} - V_{14}], V_{c4} = \frac{1}{2}[V_{24} + V_{43} - V_{23}], V_{c3} = \frac{1}{2}[V_{43} + V_{31} - V_{41}]$$

Although we clearly see a non-linear behavior, the plots do not show the expected I-V characteristic of a Schottky diode. Some rectifying effect is observed though. Since the curves are asymmetric, it could mean that breakdown does occur.

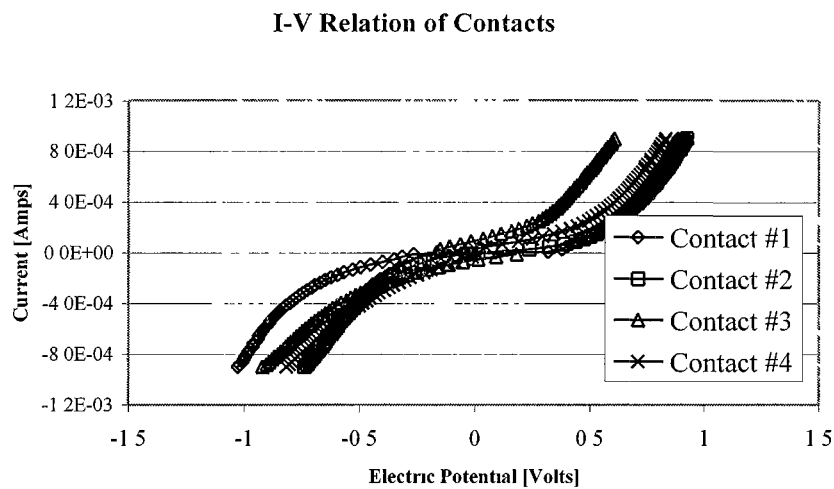


Figure 6 14 I-V Relation of Contacts from Eq (6-5)

The derived equations for determining independent contact I-V relations yielded three equations per contact. Ideally each would generate the exact same solution. Although close, each resulted in different values. Therefore an average of the results will be used to characterize each contact. The graph below shows the averaging results.

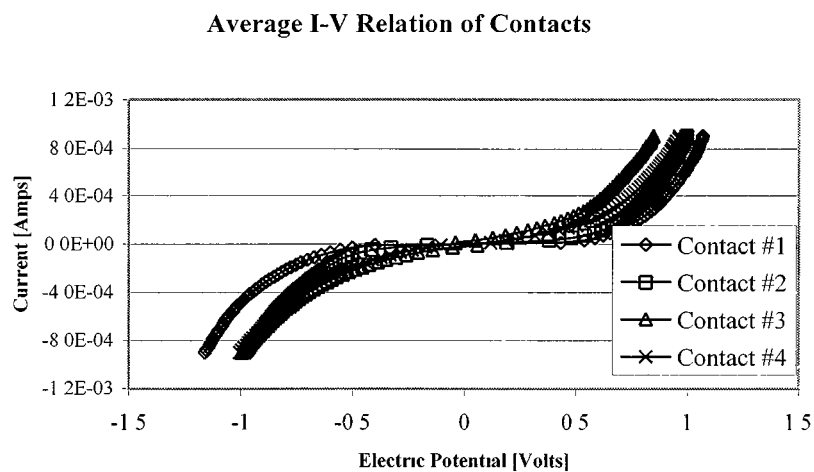


Figure 6 15 Average I-V Relation of Contacts

Ilmenite ceramic according to literature is p-type therefore the Schottky barrier energy band diagram can be represented as:

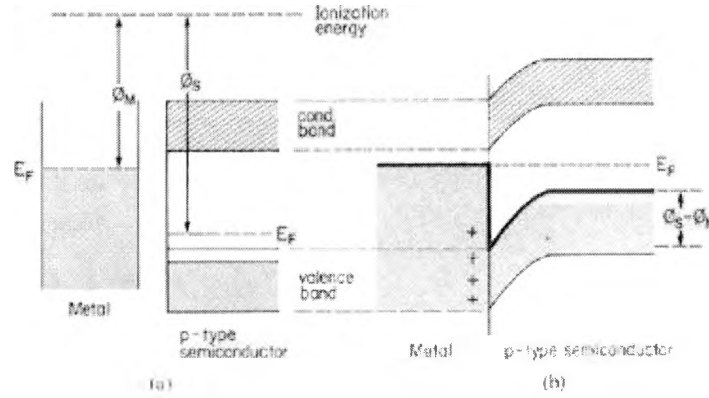


Figure 6.16 Metal to p-type Band Diagrams and Contact³

where $q\phi_B$ is the barrier height which is the difference between the work function of the semiconductor and the work function of the metal. The barrier height is reached when forward biased. As expressed earlier the simple I-V equation for the Schottky barrier diode can be expressed as

$$I = I_s \left(\exp\left(\frac{qV}{nkT}\right) + 1 \right) \quad (6-7)$$

where I_s is the saturation or leakage current and can be expressed as

$$I_s = AA^* T^2 \exp\left(\frac{-q\phi_B}{kT}\right) \quad (6-8)$$

and n is the ideality factor which can be determined by

$$\frac{1}{n} = 1 - \frac{\partial \phi_B}{\partial V} \quad (6-9)$$

or by evaluating the slope of the semi-logarithmic graph. A refers to the contact area and A^* (Richardson's constant) can be expressed as

$$A^* = 120 \left(\frac{m^*}{m} \right) \frac{\text{Amps}}{\text{cm}^2 \text{K}^2} \quad (6-10)$$

The I-V equation for a Schottky barrier diode can be expressed as

$$I = I_s \exp \left(\frac{qV}{nkT} \right) \left(1 - \exp \left(\frac{-qV}{kT} \right) \right) \quad (6-11)$$

By examining the $\ln(I)$ as a function of V for the contact I-V graphs we can determine I_s at the y-intercept. However in figure 21 this is evident that there exists more than one y-intercept. An ideal diode will yield a linear profile on a semi-logarithmic ($\ln[y]$ -axis, current) scale such that the y-intercept yields a value for the leakage current. In our case it is evidently clear that the Schottky diode has two modes; one at low bias and one at high bias. Since at low bias voltage the influence of the parallel resistors will be large, we used in our analysis the high bias voltage data. By extrapolating a line consistent with the high bias mode we can determine I_s and its components. To find the slopes of the two bias modes we can set the graph to linear axes and plot $\ln(I)$ versus potential and find equations to fit both modes.

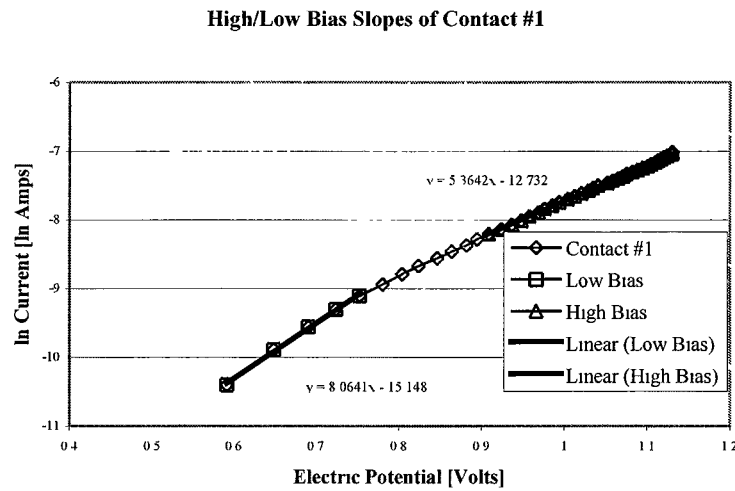


Figure 6.17 High/Low Bias Slopes of Contact #1

We used the high bias slope to determine the ideality constant— n . By evaluating at high bias we can assume that $I(V) \gg I_s$ such that

$$\frac{I(V)}{I_s} - 1 = \frac{I(V) - I_s}{I_s} \approx \frac{I(V)}{I_s} \quad (6-12)$$

which can approximate

$$y = \ln \left[\frac{I(V)}{I_s} \right] = \text{slope} * (V) \quad (6-13)$$

where the slope is equal to $\frac{q}{nk_bT}$. The ideality constant can be solved for algebraically.

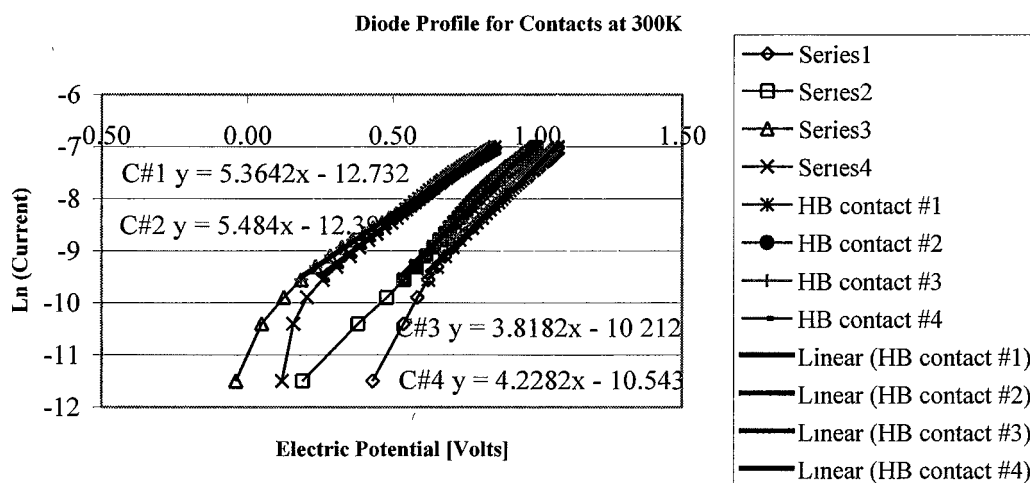


Figure 6 18 Diode Profile for Contacts at 300K

The above graph shows the high bias equations for all four contacts on the Ilmenite ceramic sample at room temperature and the high bias linear trend. The n-values calculated from the slopes and the I_s values are summarized in tables 6.3 and 6.4.

The next step is to show that each contact consists of a parallel resistor and a diode. Using MathCad we can simulate the I-V behavior of a diode and then compare to the simulation of a diode parallel to a resistor as shown in the figure below using parameters determined in the previous graph figure 6.18.

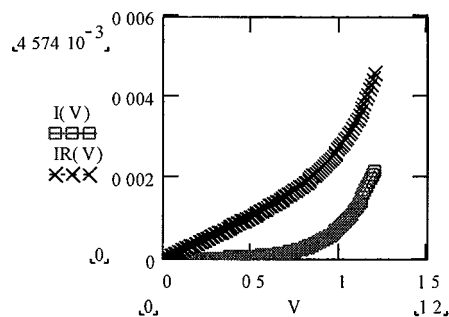


Figure 6 19 MathCad Simulation

The equations plotted in the MathCad simulation (appendix A), where the x-axis is Volts and the y-axis is Current as a function of Volts, are as follows:

$$I(V) = I_s \left(\exp \frac{qV}{nkT} - 1 \right) \quad (6-14)$$

and

$$IR(V) = I_s \left(\exp \frac{qV}{nkT} - 1 \right) + \frac{V}{R} \quad (6-15)$$

where equation (6.5) contains a parallel resistor. The two equations (6-14) and (6-15) have similar characteristics however when the derivatives, or slope, are evaluated at $V=0$ we can see the two differences. The slope of the I-V curve at zero voltage for a single Schottky contact is given by:

$$\left. \frac{\partial I}{\partial V} \right|_{V=0} = \frac{q}{nkT} \quad (6-16)$$

The slope of the I-V curve at zero voltage for a leaky Schottky contact is however:

$$\left. \frac{\partial I}{\partial V} \right|_{V=0} = \frac{q}{nkT} + \frac{1}{R} \quad (6-17)$$

So the parallel resistor has a clear effect on the slope at zero voltage as also indicated in the figure above. The values used for the simulation are available in appendix A. The value for the parallel resistor was arbitrary yet believed within the range of the actual value and clearly shows the bias dependence. The ideality constant, n , although excessively high was generated from the diode evaluation in figure 21. The larger the resistor value, the smaller the slope at $V=0$. Note that the profiles of $I(V)$ and $IR(V)$ at high bias are very similar and the profiles at low bias are quite different. The profile for $IR(V)$ can be explained as having two modes; one for low bias where the parallel resistor

is influential and one for high bias where the current is primarily through the diode. This two-mode profile is consistent with our data. This was convincing evidence to use the high bias profile when determining the ideality constant. The low bias profile should reveal information about the parallel resistor. As discussed earlier, evaluating at zero bias and determining the slope we can find an approximation for the parallel resistor.

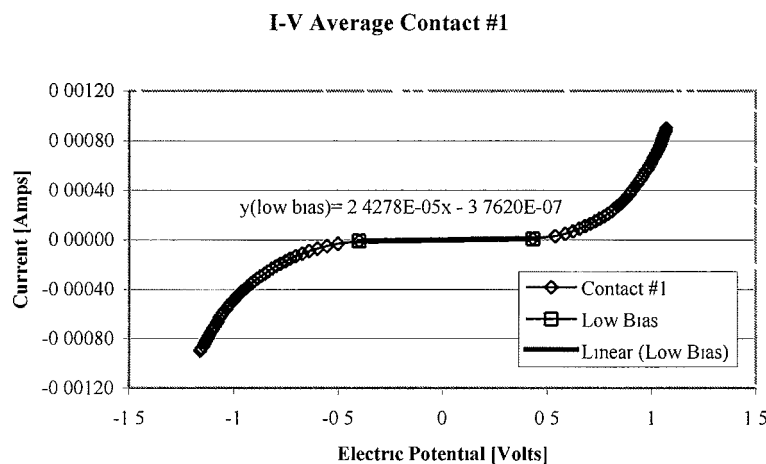


Figure 6 20 I-V Average Contact #1

The evaluation of the low bias data on contact #1 yielded a parallel resistance value $41.2 \text{ k}\Omega$ which was considerably larger than the predicted value. However this value is still conceivable since there is a large voltage drop over the contacts. Next we can plot a theoretical I-V relation using the generated equation for a Schottky diode with a parallel resistor:

$$I(V) = I_s \left(\exp \frac{qV}{nkT} - 1 \right) + \frac{V}{R} \quad (6-18)$$

and compare this to the experimental data. The graph below shows the forward bias, both high and low, comparison between the two.

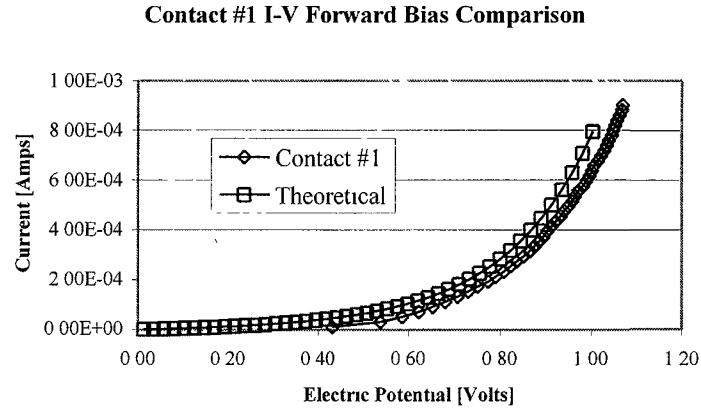


Figure 6.21 Contact #1 I-V Forward Bias Comparison

Convincingly the experimental data in forward bias closely fit the theoretical data. This is evidence that there is a depletion contact between the metal contacts and the semiconductor.

6.1.1.3 Resistivity Measurements

For the Ilmenite ceramic sample I-V measurements were taken at 8, 20, 40, 80, 160, 300, 323, 348 and 373 Kelvin. For the measurements from 8 to 160 Kelvin the Cryostat setup was employed and for the I-V measurements from 300 to 373 Kelvin the furnace and SCPA were employed, details can be found in Chapter 5.1. First a plot resistivity, ρ , vs $1000/T$ was produced. This plot was fairly consistent with literature and corresponded to the Wilson's formula

$$\rho = \rho_0 \exp\left(\frac{E_{ac}}{2kT}\right) \quad (3-1)$$

such that the activation energy level can be determined from the slope of the graph below. We found for $E_{ac} = 73 \text{ meV}$ (80-373 °C) for all data point shown in figure 6.12

and 153 meV for the three highest temperatures, i.e. 323-373 °C which is comparable to that found by Kale (Section 3.1.3).

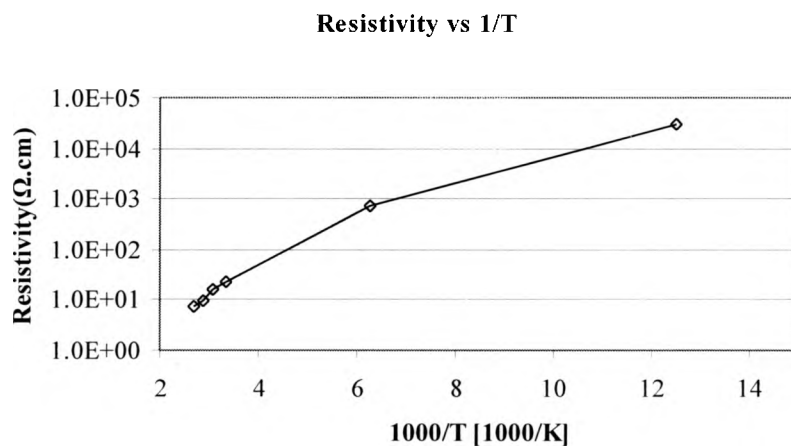


Figure 6 22 Resistivity vs 1/T

The above chart shows the resistivity versus 1000/T within a range from 80 to 373 Kelvin. The next chart shows the resistivity versus 1000/T over a range of temperatures from 8 to 450 Kelvin.

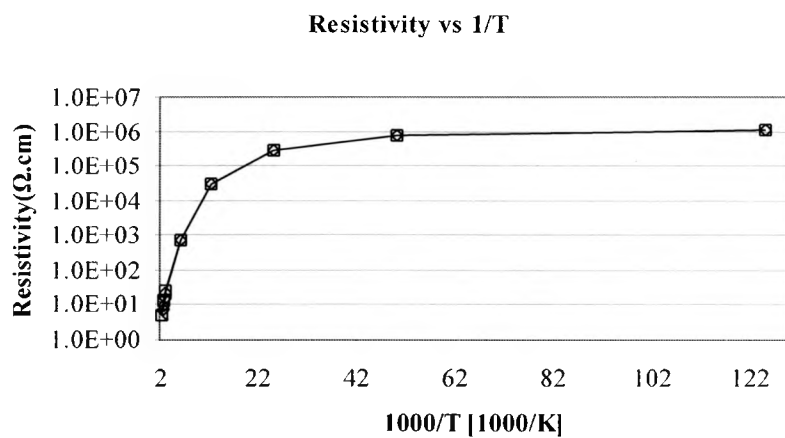


Figure 6 23 Resistivity vs 1/T

6.1.1.4 Estimation of the Barrier Height and Workfunction

The next process is to determine the first approximation of the work function of the Ilmenite ceramic sample. Now that we have a working model that is consistent with experimental data we can make the first estimation to find the barrier heights and the effective electron mass.

According to Schottky theory, the saturation or leakage current can be represented as

$$I_s = AA^*T^2 \exp\left(\frac{-q\phi_B}{kT}\right) \quad (6-8)$$

whose components were described earlier⁴. Since this is a first attempt to determine the work function of Ilmenite ceramic, the Richardson's constant for Ilmenite is not published. We can make one assumption that the A^* is dependent on the material so that A^* is constant for all four contacts. Therefore we can derive this equation to find the difference between two contact barrier heights:

$$\frac{k_B T}{q} \ln \left[\frac{I_{s1} A_2}{I_{s2} A_1} \right] = \phi_{B1} - \phi_{B2} = \Delta \phi_B \quad (6-19)$$

which we will assume to be small since the barrier heights should be very close in value. Since any combination of $\Delta \phi$ is linearly dependent of another a matrix representation of a set of equations has no inverse and consequently no solutions for the unknown variables (i.e. ϕ_{B1} , ϕ_{B2} , ϕ_{B3} , ϕ_{B4}).

A second approach is to employ the modified Norde plot. A Norde plot defines a function H such that

$$H = V - \frac{nkT}{q} \ln \left(\frac{I}{I_s} \right) = Ir_s + n\phi_B \quad (6-20)$$

where r_s is a series resistance (which we corrected for) and where the H-intercept of H versus I is equal to $n\phi_B$. However knowledge of A^* is necessary for this operation. Yet from a modified Norde plot one can extract both $n\phi_B$ and A^* ⁴. By allowing

$$F1 = \frac{V}{2kT/q} - \ln\left(\frac{I}{T^2}\right) \quad (6-21)$$

we can plot F1 as a function of V for each contact at varying temperatures. Since these plots are non-linear there exists a minimum for each temperature plot. From this minimum we can find $F1_{\min}$, $V_{\min}$ and $I_{\min}$ at different temperatures. From the following equation

$$2F1_{\min} + (2-n) \ln\left(\frac{I_{\min}}{T^2}\right) = 2 - n[\ln(AA^*) + 1] + \frac{n\phi_B}{kT/q} \quad (6-22)$$

we can make a linear plot of $2F1_{\min} + (2-n) \ln\left(\frac{I_{\min}}{T^2}\right)$ as a function of q/kT where the

slope will yield $n\phi_B$ and the y-intercept will yield $2 - n[\ln(AA^*) + 1]$. As discussed

earlier the ideality constant, n, can be solved for by evaluating the corrected I-V data at

high bias and assuming that $I(V) \gg I_s$ such that (6-12) $\frac{I(V)}{I_s} - 1 = \frac{I(V) - I_s}{I_s} \approx \frac{I(V)}{I_s}$ which

can approximate (6-13) $y = \ln\left[\frac{I(V)}{I_s}\right] = \text{slope} * (V)$ where the slope is equal to $\frac{q}{nk_bT}$.

The ideality constant can be solved for algebraically. It is noted in literature that values for n, which are typically between 1 and 2 can change for different temperatures.

For the modified Norde plot method we first determined values for the ideality constant for each contact at varying temperatures extracted from the high bias voltage linear equation from each diode profile. Figures 6.24 and 6.25 show the I-V behavior of

the contacts as determined by the method laid out in section 6.1.1.1 for $T=40$ Kelvin and $T=373$ Kelvin.

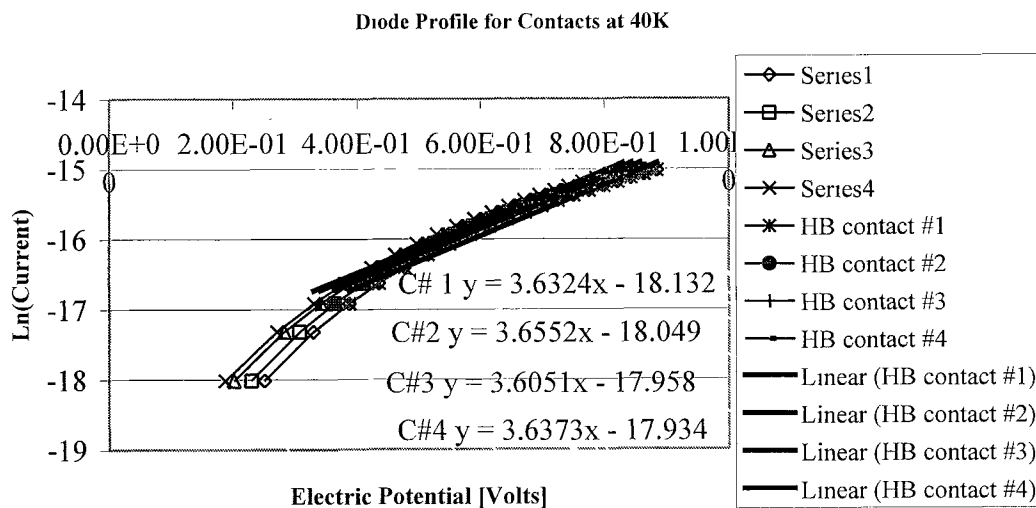


Figure 6 24 Diode Profile for Contacts at 40K

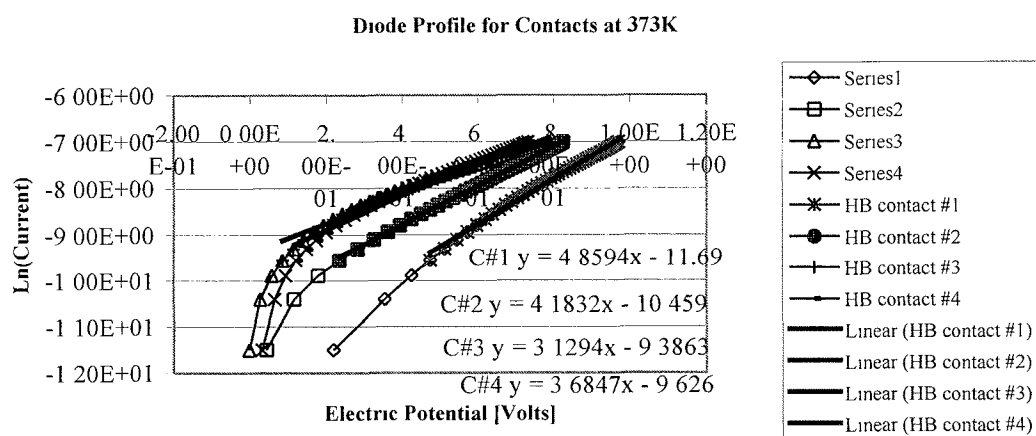


Figure 6 25 Diode Profile for Contacts at 373K

Note that at low temperature, the diode profiles conform while at higher temperatures there is larger spread. At this moment it is not clear what causes this effect. Also note

that the I_s increases as a function of temperature as expected from theory. The electric potential monitored in the 40K graph is one order of magnitude smaller than the electric potential monitored in the 373K graph. The followings chart shows the values for the ideality constants and the I_s for varying temperatures as extracted from the graphs above.

Table 6 3 Ideality Constants at Varying Temperatures

Temperature Kelvin	Ideality Constant for Contact #1	Ideality Constant for Contact #2	Ideality Constant for Contact #3	Ideality Constant for Contact #4
8	602.509	638.757	649.958	687.806
20	391.749	87.420	578.380	411.375
40	79.797	79.299	80.401	79.690
80	18.335	17.908	18.466	19.110
160	4.321	3.069	1.660	0.570
300	7.205	7.047	10.122	9.140
323	5.775	6.427	9.210	7.450
348	6.659	6.747	10.506	9.149
373	6.397	7.431	9.933	8.436

Table 6 4 Leakage Currents at Varying Temperatures

Temperature Kelvin	I_s Contact #1	I_s Contact #2	I_s Contact #3	I_s Contact #4
8	1.26E-08	1.47E-08	1.51E-08	1.58E-08
20	1.88E-08	6.27E-09	2.17E-08	2.00E-08
40	1.33E-08	1.45E-08	1.59E-08	1.63E-08
80	8.84E-09	1.14E-08	1.78E-08	3.93E-08
160	1.27E-08	1.86E-08	2.02E-08	4.45E-09
300	2.96E-06	4.16E-06	3.67E-05	2.64E-05
323	3.60E-06	1.14E-05	5.08E-05	3.49E-05
348	7.50E-06	1.37E-05	7.26E-05	4.83E-05
373	8.38E-06	2.87E-05	8.39E-05	6.60E-05

An anomaly occurred at 160 Kelvin such that the corrected I-V data no longer followed diode behavior. This could be because this temperature is close to T_N for this sample. In

literature for Ilmenite ceramic the $T_N \sim 60 \text{ K}$ ¹². Note that as expected the ideality constants were not so constant and are inversely related to the temperature. These excessively large values of n cause difficulties in employing the modified Norde plot. Since only a few variations in temperature are required for this method we used the high temperature measurements (i.e. 300 to 373 Kelvin). The plot below shows $F1$ as a function of V for contact #4 at 300, 323, 348 and 373 Kelvin where equation (6-21)

$$F1 = \frac{V}{2kT/q} - \ln\left(\frac{I}{T^2}\right) \text{ and } V \text{ is the forward bias voltages.}$$

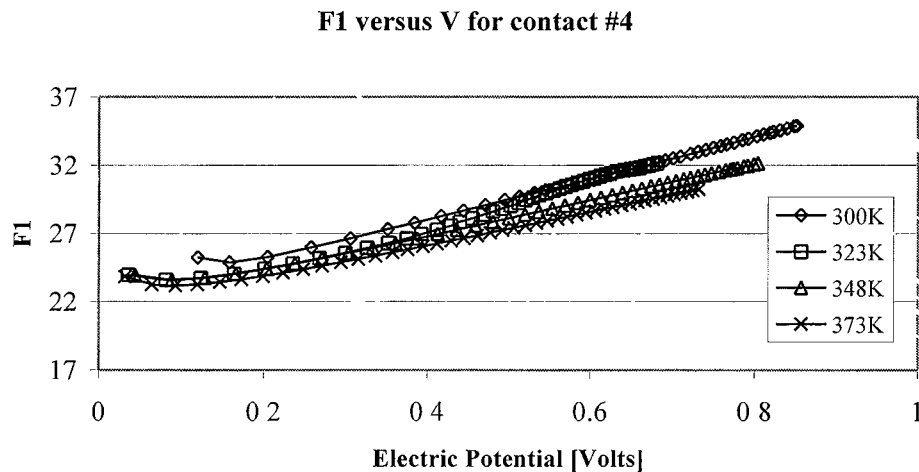


Figure 6 26 F1 versus V for contact #4

Since these plots are non-linear there exists a minimum for each temperature plot. From this minimum we can find $F1_{\min}$, $V_{\min}$ and $I_{\min}$ at different temperatures and plot equation

$$(6-22) F2 = 2F1_{\min} + (2-n) \ln\left(\frac{I_{\min}}{T^2}\right) \text{ as a function of } q/kT \text{ for } T=300, 323, 348 \text{ and}$$

373K where the slope will yield $n\phi_B$ and the F2-intercept will yield $2 - n[\ln(AA^*) + 1]$.

The following chart shows the modified Norde plot for contact #3 and #4.

Modified Norde Plot for Contacts #3 and #4

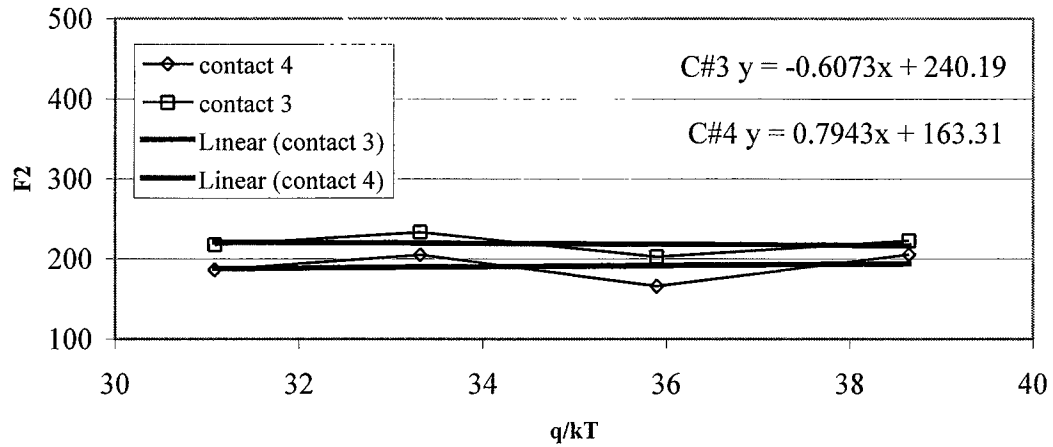


Figure 6 27 Modified Norde Plot for Contacts #3 and #4

Using average n values for each contact we determined two barrier heights: 1) 0.061eV for contact #3 and 0.093eV for contact #4. This is a first approximation. We expected the results to be very similar. The average of the two $\pm$ the relative difference give us a reasonable value for the barrier height: 0.077eV $\pm$ 0.02. Several assumptions were made on the way to generate these values.

For A^* where (6-10) $A^* = 120 \left(\frac{m^*}{m} \right) \frac{\text{Amps}}{\text{cm}^2 \text{K}^2}$ and $2 - n[\ln(AA^*) + 1]$ equals the F2-

intercept we can determine a first approximation for A^* and subsequently the effective mass of an electron. The F2 intercepts from the modified Norde plot above yielded two

values for A^* : $0.998 \frac{\text{Amps}}{\text{cm}^2 \text{K}^2}$ for contact #3 and $0.997 \frac{\text{Amps}}{\text{cm}^2 \text{K}^2}$ for contact #4. Although

these values are very small and give rise to a small value for m^*/m (~ 0.01), published

values for A^* for various semiconductors range from $0.41(\pm 0.15)$ for n-GaAs to $112(\pm 6)$ for n-Si⁴.

For p-type semiconductors we can say that the work function of the semiconductor is greater than the work function of the metal or $\phi_s > \phi_m$. To determine the work function of the semiconductor we can say that the barrier height plus the work function of the metal equals the work function of the semiconductor such that $\phi_s = \phi_m + \phi_B$. From literature, the accepted work function value for silver is 4.73eV ³⁰. However tabulated values for silver can range between 3.0 to 4.75eV depending on the material preparation and the Miller indices. Bulk crystal for silver from literature has varied between 4.64eV to 4.52eV ²⁰. Assuming the work function of silver to be 4.73 eV , the first reasonable approximation for the work function of Ilmenite ceramic is $4.81\text{eV} \pm 0.02$.

This experiment and analysis was a first approximation for determining the work function of Ilmenite ceramic bulk based on both 2pp and 4pp I-V measurements. There were several assumptions in the determination of these values. First we assumed that for 2pp correction factors the current was injected at the center of the contacts and the voltage was monitored at the periphery, second that the potential difference across the contacts is independent of the position of the 2nd current electrode, i.e. V_{ca} ($a=1,2,3,4$) is independent of the measurement configuration and thirdly that we can characterize the forward bias I-V of each contact as a Schottky diode.

6.1.2 Ilmenite-Manganese(15%) Ceramic Sample

As mentioned earlier, Ilmenite is a natural semiconductor. By convention semiconductors can be doped with impurities to add energy levels and alter the material's electrical properties, amongst other properties. The next material of interest is Ilmenite-Manganese(15%) (atomic percentage). We employed the same method of characterizing as performed on the Ilmenite ceramic sample in section 6.1. As in the Ilmenite sample, the doped Ilmenite also has non-linear two-point probe I-V characteristics and predominately linear four-point probe I-V characteristics with a non-linearity of less than 3%. Once again we believe that the large non-linearity is a consequence of a metal-semiconductor contact on the surface or moreover a Schottky barrier. The calculated resistivity of 15% manganese doped Ilmenite ceramic at room temperature was $14.84 \Omega \cdot cm$. By making several reasonable assumptions we determined the contact barrier heights and the work function of the 15% manganese doped Ilmenite. The calculated value for the work function was $5.25 eV \pm 0.02$.

Once again the sample was fabricated by the conventional method of ceramics and mounted on a Lakeshore printed circuit board at the University of Alabama. The sample has dimensions of $6.0 \times 5.9 \times 1.75 \text{ mm}^3$ and has silver contacts. The HP 4145B Semiconductor Parameter Analyzer, the HP 16058A Test Fixture, the Delta Temperature chamber, and the Metrics software were used to generate 2pp and 4pp measurements at room temperature and high temperature and collect the data onto a spreadsheet. As in the experiment in section 6.1 we used the source monitoring units on all four contacts labeled SMU#1 through SMU#4 due to the high input impedance in lieu of the voltage monitors. Measurements taken at room temperature were taken in the dark to eliminate any possible

photovoltaic effects in the HP 16058A Test Fixture and for high temperatures (323 – 373 Kelvin) we employed the Delta Temperature Chamber. For the 2pp measurements only two SMUs were used at a time. One SMU contained the current sweep and monitored both the current and voltage while the other SMU was held at zero potential. For the 4pp measurements one SMU was held at zero potential while the other three SMUs were programmed to be current sources. Of the three remaining SMUs one was used for a current sweep and monitored the current while the other two had zero current and monitored the potential with respect to the zero potential (i.e. these two SMUs acted as voltage monitors). We swept the current between -1.000mA to 1.000mA and monitored the voltage in the manor mentioned above.

The 2pp measurements for all configurations showed strong non-linear I-V relations as shown in the graph below.

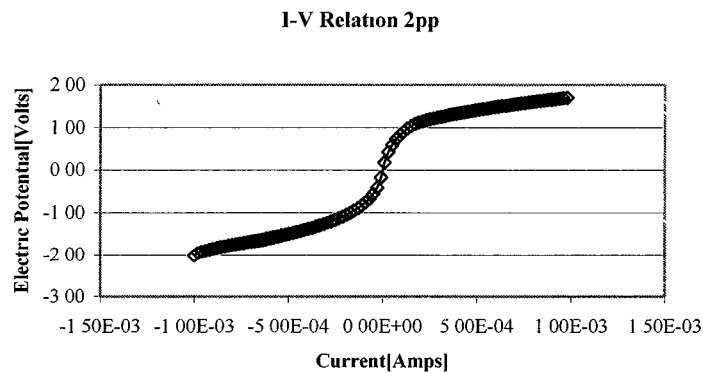


Figure 6.28 I-V Relation 2pp

The 4pp probe measurement shows the uncorrected resistivity of the sample which clearly shows a strong linearity as shown in the graph below.

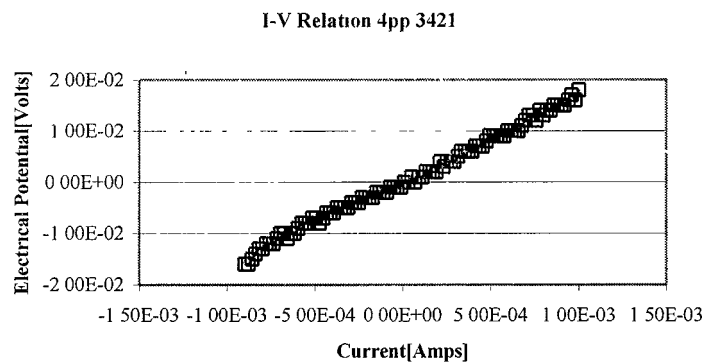


Figure 6 29 I-V Relation 4pp 3421

Using the geometric correction factors determined by the sample dimensions and contact positions we were able to determine the resistivity of the sample. The method of determining CRF—calculated correction factor—can be found in Appendix A. The contact positions in Cartesian coordinates and sample sizes were determined by importing a digital photo of the sample into Canvas 8.0.3. With these correction factors we were able to determine the resistivity of the Ilmenite-Mn(15%) ceramic sample as $\sim 14.84 \Omega \text{ cm}$. The chart (table 6.5) below shows the collected and calculated data.

Table 6 5 Ilmenite-Mn(15%) Data

4pp Configurations (I,V)	Correction Factors	Slope of Graph	Sheet Resistance $R_s (\Omega/\square)$	Sample Thickness (mm)	Resistivity ($\Omega \cdot \text{cm}$)
13,42	4.173	19.973	83.35	1.75	14.59
12,43	5.165	17.749	91.67	1.75	16.04
42,13	4.173	19.073	79.59	1.75	13.93
43,12	5.165	16.36	84.50	1.75	14.79
Average			84.78		14.84

6.1.2.1 Determination of I-V Relation of Contacts

To determine the I-V characteristic of each contact independently we employed the same method as in section 6.1.1.1. First we determined a 2pp correction factor by making two assumptions: (1) the current is injected at the center of the contacts and (2) that the potential is measured from the periphery of the contacts. Next we determined an I-V profile of the material only scaled with the current sweep of the 2pp measurements—in this case at $\pm 1.000\text{mAmps}$. Using the equations (6-2), (6-4, 5, and 6) we were able to correct for the sample resistance also referred to as the series resistance and solve for each contact I-V characteristic. Figure 6.30 shows the results for these calculations.

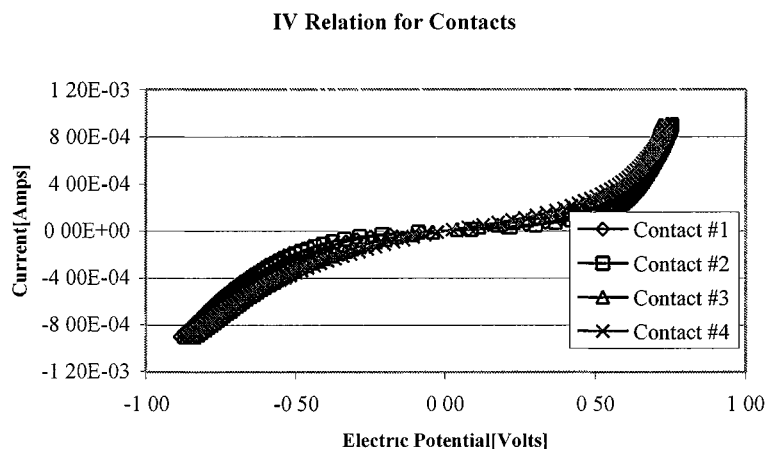


Figure 6.30 IV Relation for Contacts

6.1.2.2 Model Contacts

We can define the contacts in the same manner as in section 6.1.1.2 as a diode with a parallel resistor. The next step is to evaluate the forward bias on a semi-log scale and determine the diode properties.

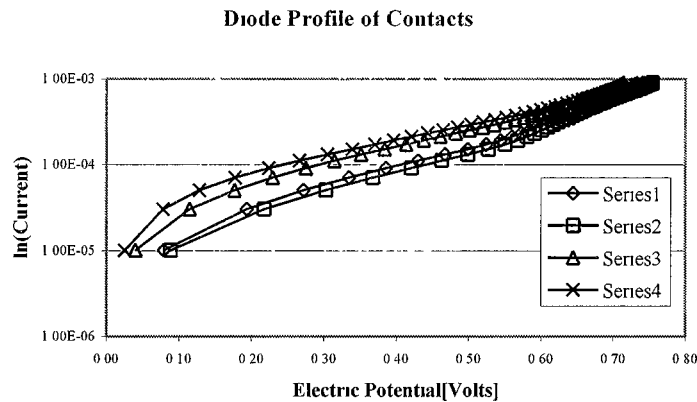


Figure 6.31 Diode Profile of Contacts

The profile of the contacts by observation has two modes, a high bias mode and a low bias mode which can be determined by their slopes. The high bias mode is consistent with a Schottkey diode and the low bias slope can imply current through the resistor. By observing the slope at high bias and the y-intercept we can determine the leakage current of the diode where I_s is the leakage current. The ideality constant in the following

equation (6-7) $I = I_s \left(\exp\left(\frac{qV}{nkT}\right) + 1 \right)$ can be solved for in the following manner. By

evaluating at high bias we can assume that $I(V) \gg I_s$ such that (6-12)

$$\frac{I(V)}{I_s} - 1 = \frac{I(V) - I_s}{I_s} \approx \frac{I(V)}{I_s} \text{ which can approximate (6-13) } y = \ln \left[\frac{I(V)}{I_s} \right] = \text{slope} * (V)$$

where the slope is equal to $\frac{q}{nk_b T}$. The ideality constant can be solved for algebraically.

The chart below shows the diode profile for all four contacts at room temperature.

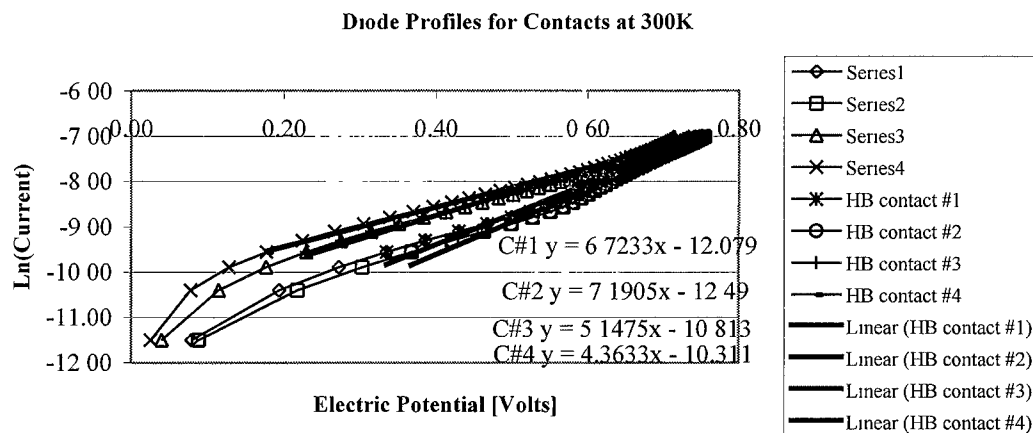


Figure 6.32 Diode Profiles for Contacts at 300K

By evaluating contact #4 at high bias we see the equation $y = 4.3633x - 10.311$ where y is $\ln(\text{current})$ and x is the electrical potential. The y -intercept is -10.311 and the exponent(y -intercept) is 3.3×10^{-5} and is the value for the leakage current. The slope is inversely proportional to the ideality constant and can be defined as $\text{slope} = \frac{q}{nk_bT}$ where q , k and T are known values. The parallel resistor can be determined by evaluating the I-V relation at (6-17) $\left. \frac{\partial I}{\partial V} \right|_{V=0} = \frac{q}{nkT} + \frac{1}{R}$. This is possible since the diode is by convention highly resistive at low bias so the current is predominately through the resistor. A value of $24.0 \text{ k}\Omega$ was found for the parallel resistor and a value of 8.858 was found for the ideality factor.

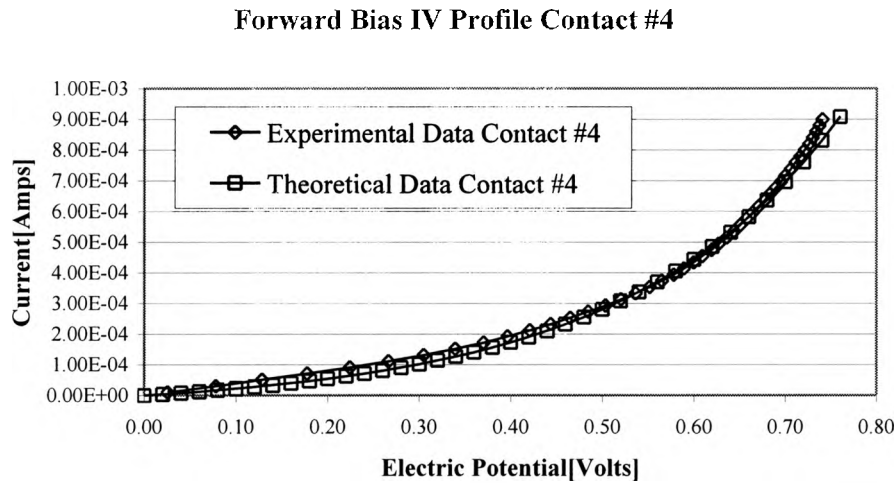


Figure 6 33 Forward Bias IV Profile Contact #4

The above graph in figure 6.33 shows how closely the theoretical model compares to the experimental data. This experimental set is from contact #4 where the theoretical data is from equation (6-18) where values for n , R and I_s were determined earlier.

6.1.2.3 Resistivity Measurements

For the Ilmenite-Manganese(15%) ceramic sample high temperature I-V measurements were taken at 323, 348 and 373 Kelvin using the Delta furnace and the SCPA, equipment details can be found in Chapter 5. A plot of resistivity, ρ , vs $1000/T$ was produced which corresponds to the Wilson's formula, (3-1) $\rho = \rho_0 \exp\left(\frac{E_{ac}}{2kT}\right)$, such that the activation energy level can be determined from the slope of the graph below. We found for $E_{ac}=99.5$ meV (300-373°C).

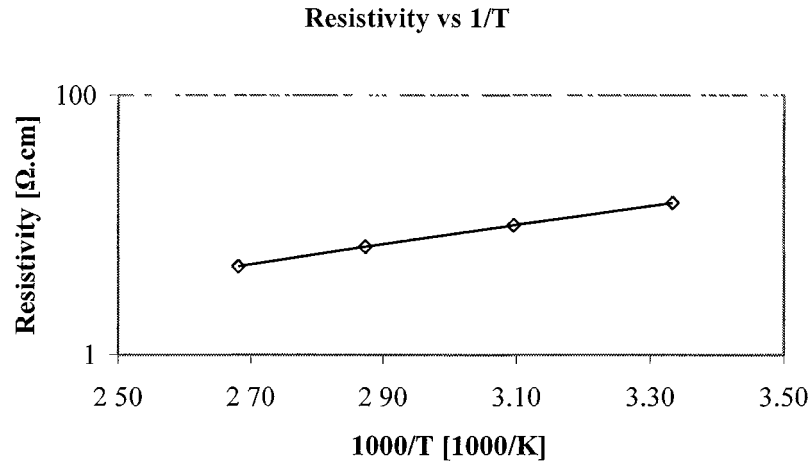


Figure 6.34 Resistivity vs 1/T

6.1.2.4 Estimation of the Barrier Height and Workfunction

The next process is to determine the first approximation of the work function of the Ilmenite-15% Manganese ceramic sample in the same manner as the Ilmenite ceramic sample in section 6.1.1.4.

Using the modified Norde plot we can again extract both $n\phi_B$ and A^* ⁴. By

allowing (6-21) $F1 = \frac{V}{2kT/q} - \ln\left(\frac{I}{T^2}\right)$ we can plot F1 as a function of V for each contact

at varying temperatures. Finding $F1_{\min}$, $V_{\min}$ and $I_{\min}$ at different temperatures we can employ the following equation (6-22)

$$2F1_{\min} + (2-n) \ln\left(\frac{I_{\min}}{T^2}\right) = 2 - n[\ln(AA^*) + 1] + \frac{n\phi_B}{kT/q} \text{ and from a linear plot of (6-22) as a}$$

function of q/kT we can extract a value for $n\phi_B$ and A^* from $2 - n[\ln(AA^*) + 1]$.

As discussed earlier the ideality constant, n, can be solved for by evaluating the corrected I-V data at high bias and assuming that $I(V) \gg I_s$ such that (6-12)

$$\frac{I(V)}{I_s} - 1 = \frac{I(V) - I_s}{I_s} \approx \frac{I(V)}{I_s} \text{ which can approximate (6-13) } y = \ln \left[\frac{I(V)}{I_s} \right] = \text{slope} * (V)$$

where the slope is equal to $\frac{q}{nk_b T}$.

For the modified Norde plot method we first determined values for the ideality constant for each contact at varying temperatures extracted from the high bias voltage linear equation from each diode profile. The followings charts show the values for the ideality constants and the I_s for varying temperatures.

Table 6 6 Ideality Constants at Varying Temperatures

Temperature Kelvin	Ideality Constant for Contact #1	Ideality Constant for Contact #2	Ideality Constant for Contact #3	Ideality Constant for Contact #4
300	5.748	5.375	7.508	8.857
323	7.943	8.027	8.116	11.287
348	7.595	7.614	7.090	8.909
373	7.427	7.564	6.841	6.288

Table 6 7 Leakage Currents at Varying Temperatures

Temperature Kelvin	Is Contact #1	Is Contact #2	Is Contact #3	Is Contact #4
300	5.68E-06	3.76E-06	2.01E-05	3.33E-05
323	2.38E-05	2.50E-05	3.94E-05	7.30E-05
348	3.38E-05	3.75E-05	5.00E-05	9.06E-05
373	5.84E-05	5.69E-05	6.87E-05	9.99E-05

The plot below shows $F1$ as a function of V for contact #4 at 300, 323, 348 and 373 Kelvin where $F1$ and V is the forward bias voltages.

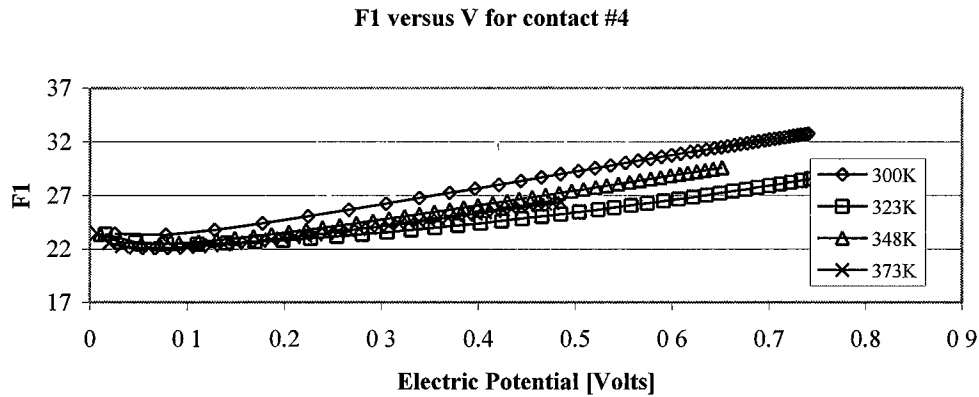


Figure 6.35 F1 versus V for contact #4

Since these plots are non-linear there exists a minimum for each temperature plot. From this minimum we can find $F1_{\min}$, $V_{\min}$ and $I_{\min}$ at different temperatures and plot (6-22)

$$F2 = 2F1_{\min} + (2-n) \ln \left(\frac{I_{\min}}{T^2} \right) \text{ as a function of } q/kT \text{ for } T=323, 348 \text{ and } 373\text{K where}$$

the slope will yield $n\phi_b$ and the F2-intercept will yield $2 - n[\ln(AA^*) + 1]$. The following chart shows the modified Norde plot for contact #1 and #2. Note that the room temperature measurement was omitted from the data set. Only three values are needed to employ the Modified Norde plot method and the room temperature measurements were taken with the sample in the HP16058A Test Fixture instead of the Delta Temperature chamber.

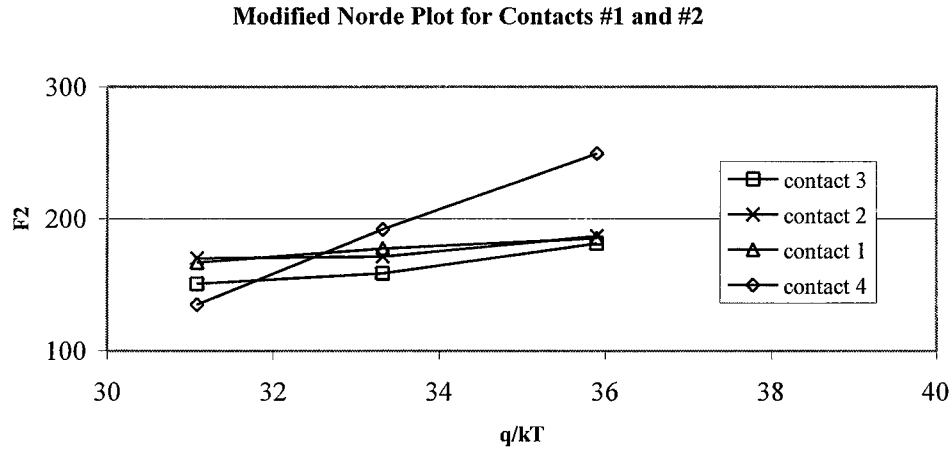


Figure 6.36 Modified Norde Plot for Contacts #1 and #2

Using average n values for contacts 1 and 2 we determined two barrier heights: 1) 0.532eV for contact #1 and 0.503eV for contact #2. This is a first approximation. The average of the two $\pm$ the relative difference give us a reasonable value for the barrier

height: $0.518\text{eV} \pm 0.02$. For A^* where (6-10) $A^* = 120 \left(\frac{m^*}{m} \right) \frac{\text{Amps}}{\text{cm}^2 \text{K}^2}$ and

$2 - n[\ln(AA^*) + 1]$ equals the F2-intercept we can determine a first approximation for A^* and subsequently the effective mass of an electron. The F2 intercepts from the modified

Norde plot above yielded two values for A^* : $5.62 \frac{\text{Amps}}{\text{cm}^2 \text{K}^2}$ for contact #1 and

$2.62 \frac{\text{Amps}}{\text{cm}^2 \text{K}^2}$ for contact #2 and gives rise to a small value for m^*/m (~ 0.03).

Since this is still a p-type semiconductor, we can say that the work function of the semiconductor is greater than the work function of the metal or $\phi_s > \phi_M$ such that

$\phi_s = \phi_M + \phi_B$. The accepted work function value for silver is 4.73eV therefore the first

reasonable approximation for the work function of Ilmenite-Manganese(15%) ceramic is $5.25\text{eV} \pm 0.02$.

Since this experiment and analysis employed the same protocol as the analysis in section 6.1 then the same assumptions for the determination of these values was also employed. First we assumed that for 2pp correction factors the current was injected at the center of the contacts and the voltage was monitored at the periphery, second that the potential difference across the contacts is independent of the position of the 2nd current electrode, i.e. V_{ca} ($a=1,2,3,4$) is independent of the measurement configuration and thirdly that we can characterize the forward bias I-V of each contact as a Shottky diode.

6.1.3 Ilmenite-Manganese(40%) Ceramic Sample

The final material of interest in the Ilmenite-Manganese ceramic series is the Ilmenite-40% Manganese. We employed the same method of characterizing as performed on the Ilmenite ceramic sample in section 6.1. As in the Ilmenite sample, the doped Ilmenite also has non-linear two-point probe I-V characteristics and predominately linear four-point probe I-V characteristics with a non-linearity of less than 3%. The calculated resistivity of Ilmenite-40% Manganese ceramic at room temperature was $445.37\Omega \cdot \text{cm}$. By making several reasonable assumptions we determined the contact barrier heights and the work function of the 40% manganese doped Ilmenite. The calculated value for the work function was $3.78\text{eV} \pm 0.15$.

The sample has dimensions of $6.9 \times 5.8 \times 2.0 \text{ mm}^3$ and has silver contacts. This sample however is n-type where as the previous samples of the Ilmenite ceramic series have been p-type. The HP 4145B Semiconductor Parameter Analyzer, the HP 16058A

Test Fixture, the Delta Temperature chamber, and the Metrics software were used to generate 2pp and 4pp measurements at room temperature and high temperature and collect the data onto a spreadsheet. As in the experiment in section 6.1 we used the source monitoring units on all four contacts labeled SMU#1 through SMU#4 and measurements taken at room temperature were taken in the dark to eliminate any possible photovoltaic effects in the HP 16058A Test Fixture.

The 2pp measurements for all configurations showed strong non-linear I-V relations where as the 4pp probe measurements show strong linearity as shown in the graph below (figure 6.37).

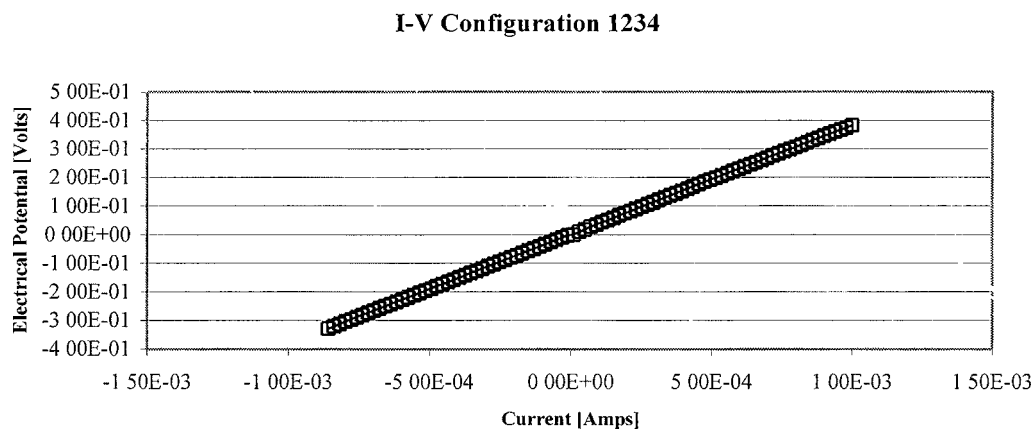


Figure 6.37 I-V Configuration 1234

Using the geometric correction factors determined by the sample dimensions and contact positions we were able to determine the resistivity of the sample. The method of determining CRF—calculated correction factor—can be found in Appendix A. The contact positions in Cartesian coordinates and sample sizes were determined by importing

a digital photo of the sample into Canvas 8.0.3. With these correction factors we were able to determine the resistivity of the Ilmenite-40% Mn ceramic sample as $\sim 445.37 \Omega \cdot \text{cm}$. The chart below shows the collected and calculated data for determining the resistivity at room temperature.

Table 6 8 Ilmenite-Mn(40%) Data

4pp Configurations (I,V)	Correction Factors	Slope of Graph	Sheet Resistance $R_s (\Omega/\square)$	Sample Thickness (mm)	Resistivity ($\Omega \cdot \text{cm}$)
13,42	5.197	496.910	2582.44	2	516.49
12,43	4.464	383.64	1712.57	2	342.51
42,13	5.197	508.88	2644.65	2	528.93
43,12	4.464	440.79	1967.69	2	393.54
Average			2226.84		445.37

6.1.3.1 Determination of I-V Relation of Contacts

To determine the I-V characteristic of each contact independently we employed the same method as in section 6.1.1.1. First we determined a 2pp correction factor by making two assumptions: (1) the current is injected at the center of the contacts and (2) that the potential is measured from the periphery of the contacts. Next we determined an I-V profile of the material only scaled with the current sweep ($\pm 1.000 \text{mAmps}$) of the 2pp measurements. Using the same protocol as in section 6.1.2.1 we were able to determine the corrected I-V characteristic for each contact on the Ilmenite-Mn(40%) ceramic sample.

6.1.3.2 Model Contacts

We can define the contacts in the same manner as in section 6.1.1.2 as a diode with a parallel resistor. The next step is to evaluate the forward bias on a semi-log scale and determine the diode properties.

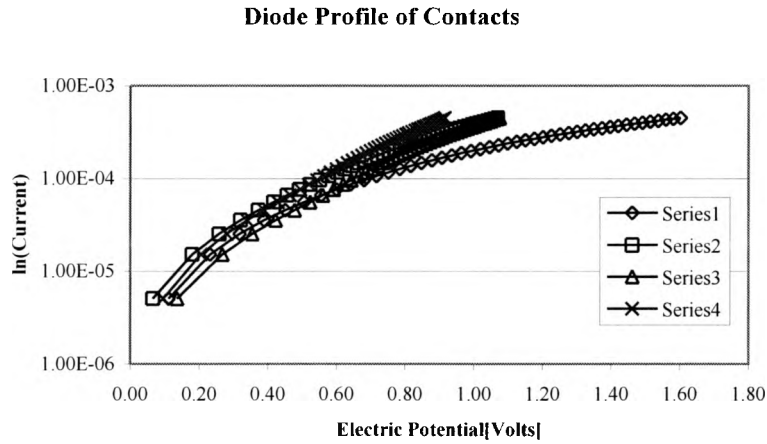


Figure 6 38 Diode Profile of Contacts

The profile of the contacts by observation has two modes, a high bias mode and a low bias mode which can be determined by their slopes. The high bias mode is consistent with a Schottky diode and the low bias slope can imply current through the resistor. By observing the slope at high bias and the y-intercept we can determine the leakage current of the diode where I_s is the leakage current. The ideality constant, n , and the leakage current in equation (6-7) can be solved for by evaluating the slope and the y-intercept

which can be approximated by (6-8) $y = \ln \left[\frac{I(V)}{I_s} \right] = \text{slope} * (V)$ where the slope is equal

to $\frac{q}{nk_b T}$ and the leakage current is equal to the y-intercept.

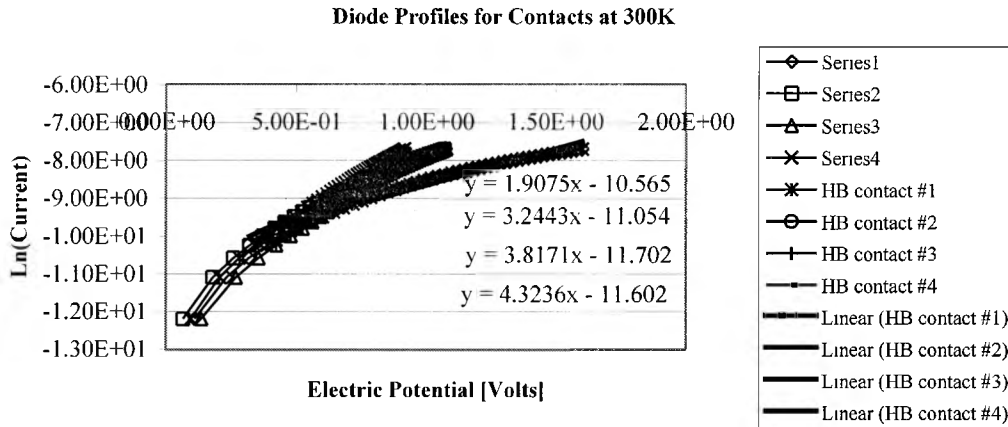


Figure 6 39 Diode Profiles for Contacts at 300K

By evaluating contact #4 at high bias we see the equation $y = 4.3236x - 11.602$ where y is $\ln(\text{current})$ and x is the electrical potential. The y -intercept is -11.602 and the exponent(y -intercept) is 9.5×10^{-6} and is the value for the leakage current. The slope is inversely proportional to the ideality constant and can be defined as $\text{slope} = \frac{q}{nk_bT}$ where q , k and T are known values and the ideality constant for contact #4 at room temperature is 8.939. The parallel resistor can be determined by evaluating the I-V relation at (6-17)

$$\left. \frac{\partial I}{\partial V} \right|_{V=0} = \frac{q}{nkT} + \frac{1}{R}. \text{ A value of } 401 \text{ k}\Omega \text{ was found for the parallel resistor. Note that the}$$

parallel resistor for this sample is an order larger than the other Ilmenite ceramic samples.

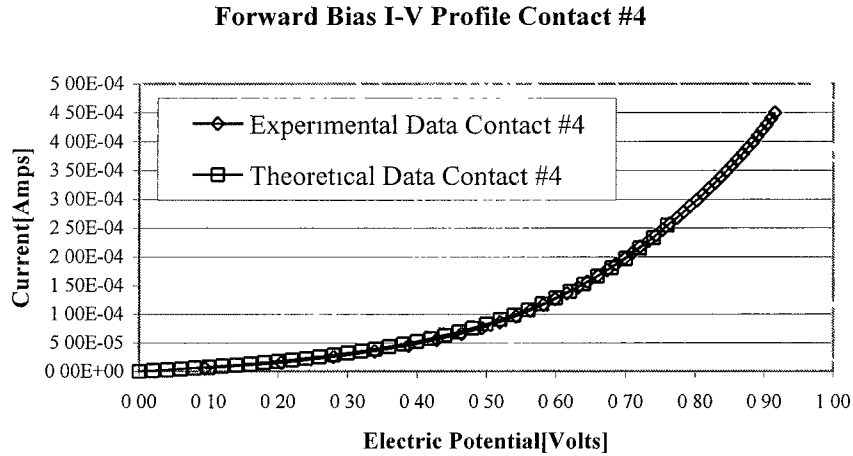


Figure 6 40 Forward Bias I-V Profile Contact #4

This experimental set is from contact #4 where the theoretical data is from equation (6-18) where values for n , R and I_s have been calculated.

6.1.3.3 Resistivity Measurements

For the Ilmenite-Manganese(40%) ceramic sample high temperature I-V measurements were taken at 323, 348 and 373 Kelvin using the Delta furnace and the SCPA and in the HP16058A Test Fixture for the 300 Kelvin measurement. A plot of resistivity, ρ , vs $1000/T$ was produced which even though has only four data points can still correspond to the Wilson's formula, (3-1) $\rho = \rho_0 \exp\left(\frac{E_{ac}}{2kT}\right)$, such that the activation energy level can be determined from the slope of the graph below. We found for $E_{ac}=65.7\text{meV}$ (300-373 °C).

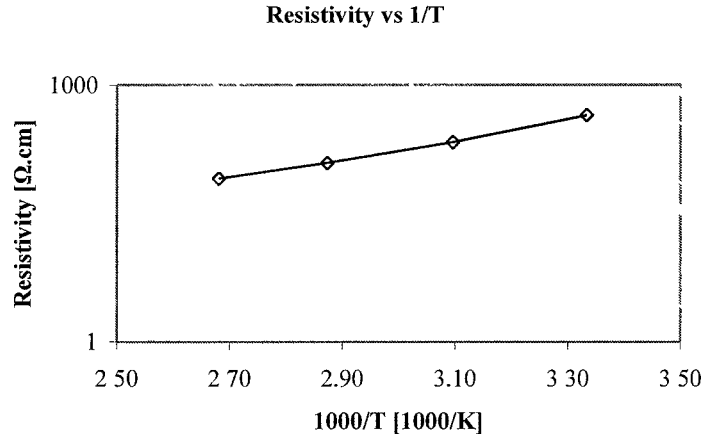


Figure 6.41 Resistivity vs 1/T

6.1.3.4 Estimation of Barrier Height and Workfunction

The next process is to determine the first approximation of the work function of the Ilmenite-Manganese(15%) ceramic sample in the same manner as the Ilmenite ceramic sample in section 6.1.1.4.

Using the modified Norde plot we can again extract both $n\phi_B$ and A^* .⁴ By

allowing $F1 = \frac{V}{2kT/q} - \ln\left(\frac{I}{T^2}\right)$ we can plot F1 as a function of V for each contact at

varying temperatures. Finding $F1_{min}$, V_{min} and I_{min} at different temperatures we can

employ equation (6-22) and from a linear plot of $2F1_{min} + (2-n)\ln\left(\frac{I_{min}}{T^2}\right)$ as a function

of q/kT we can extract a value for $n\phi_B$ and A^* from $2 - n[\ln(AA^*) + 1]$. As

discussed earlier the ideality constant, n, can be solved for by evaluating the corrected I-

V data at high bias and assuming that $I(V) \gg I_s$ such that (6-12)

$$\frac{I(V)}{I_s} - 1 = \frac{I(V) - I_s}{I_s} \approx \frac{I(V)}{I_s} \text{ which can approximate (6-13) } y = \ln \left[\frac{I(V)}{I_s} \right] = \text{slope} * (V)$$

where the slope is equal to $\frac{q}{nk_b T}$.

For the modified Norde plot method we first determined values for the ideality constant for each contact at varying temperatures extracted from the high bias voltage linear equation from each diode profile. The followings charts show the values for the ideality constants and the I_s for varying temperatures.

Table 6 9 Ideality Constants for Varying Temperatures

Temperature Kelvin	Ideality Constant for Contact #1	Ideality Constant for Contact #2	Ideality Constant for Contact #3	Ideality Constant for Contact #4
300	5.748	5.375	7.508	8.857
323	7.943	8.027	8.116	11.287
348	7.595	7.614	7.090	8.909
373	7.427	7.564	6.841	6.288

Table 6 10 Leakage Currents for Varying Temperatures

Temperature Kelvin	Is Contact #1	Is Contact #2	Is Contact #3	Is Contact #4
300	5.68E-06	3.76E-06	2.01E-05	3.33E-05
323	2.38E-05	2.50E-05	3.94E-05	7.30E-05
348	3.38E-05	3.75E-05	5.00E-05	9.06E-05
373	5.84E-05	5.69E-05	6.87E-05	9.99E-05

The plot below shows F1 as a function of V for contact #4 at 300, 323, 348 and 373

Kelvin where $F1 = \frac{V}{2kT/q} - \ln \left(\frac{I}{T^2} \right)$ and V is the forward bias voltages.

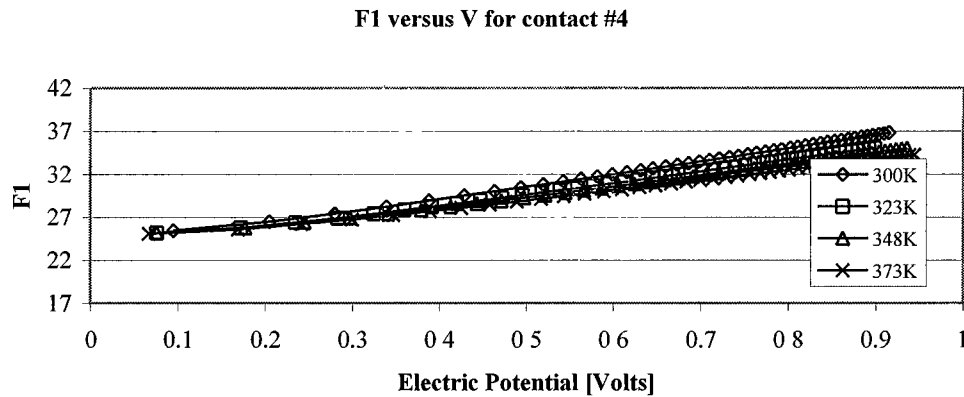


Figure 6.42 F1 versus V for contact #4

Since there is not a definitive minimum for each temperature plot, a close look at the data can determine a close approximation by extrapolating the data according to previous trends. Of course it is strongly recommendable that in the future these experiments are repeated and more data points are taken so extrapolation is not necessary. From this minimum we can plot equation (6-22) as a function of q/kT for $T=300, 323, 348$ and 373K where the slope will yield $n\phi_B$ and the F2-intercept will yield $2 - n[\ln(AA^*) + 1]$.

The following chart shows the modified Norde plot for contact #1, 2, 3 and 4.

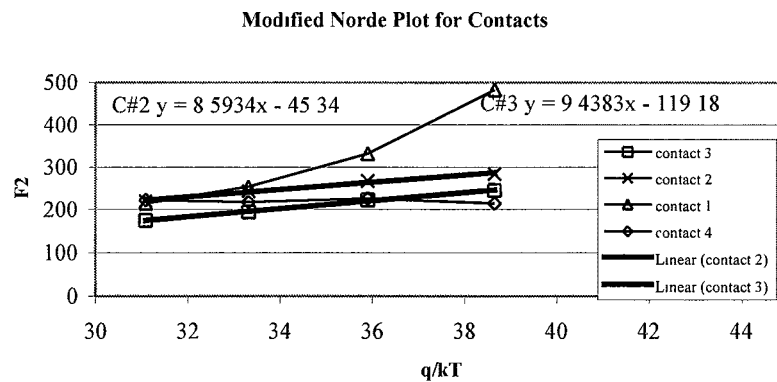


Figure 6.43 Modified Norde Plot for Contacts

For contacts #2 and #3 we determined two barrier heights: 1) 0.80eV for contact #2 and 1.09eV for contact #3. This is a first approximation. The average of the two $\pm$ the relative difference give us a reasonable value for the barrier height: $0.95\text{eV} \pm 0.15$. The F2 intercepts from the modified Norde plot above yielded two unrealistic values for A^* :

$4.12 \times 10^5 \frac{\text{Amps}}{\text{cm}^2 \text{K}^2}$ for contact #2 and $1.29 \times 10^{10} \frac{\text{Amps}}{\text{cm}^2 \text{K}^2}$ for contact #3. Since the upper

limit for a Richardson's constant is $120 \frac{\text{Amps}}{\text{cm}^2 \text{K}^2}$ this gives a value for m^*/m greater than

unity. By observation of the Modified Norde plot, contacts #2 and #3 had apparent minimums. The barrier heights and work functions were evaluated from these two contacts. The barrier heights were consistent yet the value for the Richardson's constant was orders of magnitude too large and consequently the effective mass to mass of an electron ratio exceeded unity. A modification of this Norde plot with known $R_{//}$ values could yield better results. It is also recommendable to repeat experiments and to gather data point at lower voltages so the minimum of the Nordon plots can be found without extrapolation.

Since this is an n-type semiconductor, we can say that the work function of the metal contact is grater than the work function of the semiconductor or $\phi_M > \phi_S$ such that $\phi_M = \phi_S + \phi_B$. Using the accepted work function value for silver—4.73eV—the first reasonable approximation for the work function of Ilmenite-Manganese(40%) ceramic is $3.78\text{eV} \pm 0.15$.

6.1.4 Ilmenite-Manganese Ceramic Series Summary

Physical and Electrical characteristics of the Ilmenite-Manganese samples have been studied previously in the thesis by Kale. In this thesis we re-examined these properties and expanded to find a first approximation for barrier heights and work functions of the samples.

SEM and EDAX concluded the existence of grain boundaries and determined the composition of the samples which is compared to Kale in the chart below.

Table 6 11 Composition of Manganese by EDAX

% Mn	Nominal Composition	Kale Composition	O'Brien Composition
0%	$\text{Fe}_1\text{Ti}_1\text{O}_3$	$\text{Fe}_{1.07}\text{Ti}_{1.05}\text{O}_{2.86}$	$\text{Fe}_{1.01}\text{Ti}_{1.01}\text{O}_{2.98}$
15%	$\text{Fe}_1\text{Ti}_1\text{O}_3.\text{Mn}_{0.30}$	$\text{Fe}_{1.08}\text{Ti}_{1.09}\text{O}_{3.09}.\text{Mn}_{0.33}$	Inconclusive
40%	$\text{Fe}_1\text{Ti}_1\text{O}_3.\text{Mn}_{0.80}$	$\text{Fe}_{1.18}\text{Ti}_{1.09}\text{O}_{3.82}.\text{Mn}_{0.90}$	$\text{Fe}_{1.00}\text{Ti}_{1.03}\text{O}_{3.14}.\text{Mn}_{0.70}$

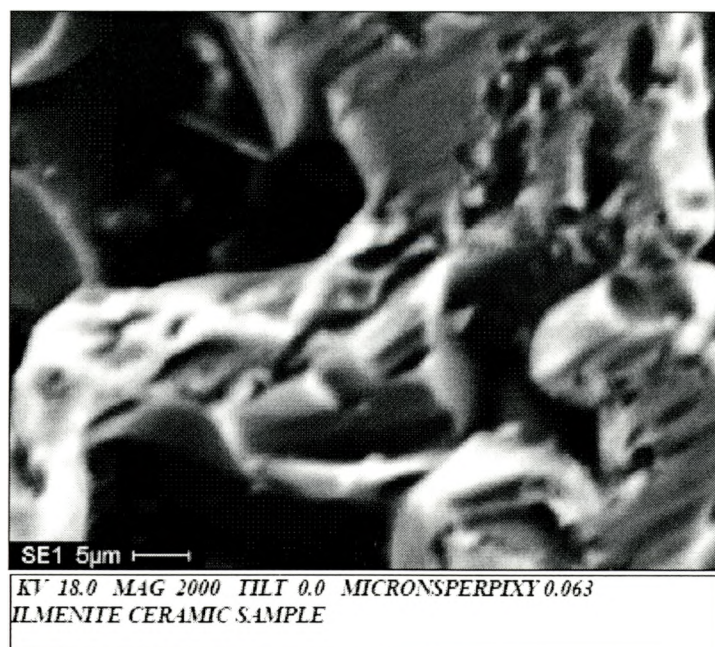


Figure 6 44 SEM mage of Ilmenite Ceramic

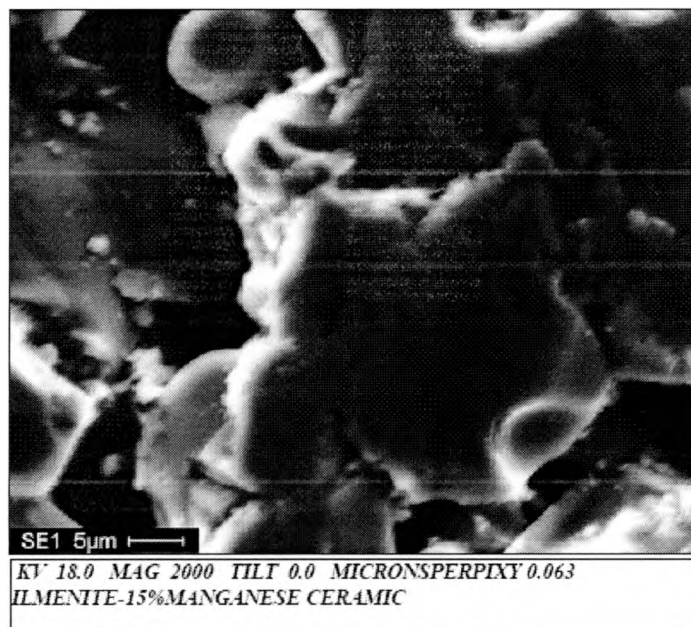


Figure 6.45 SEM Image of Ilmenite-Mn(15%)

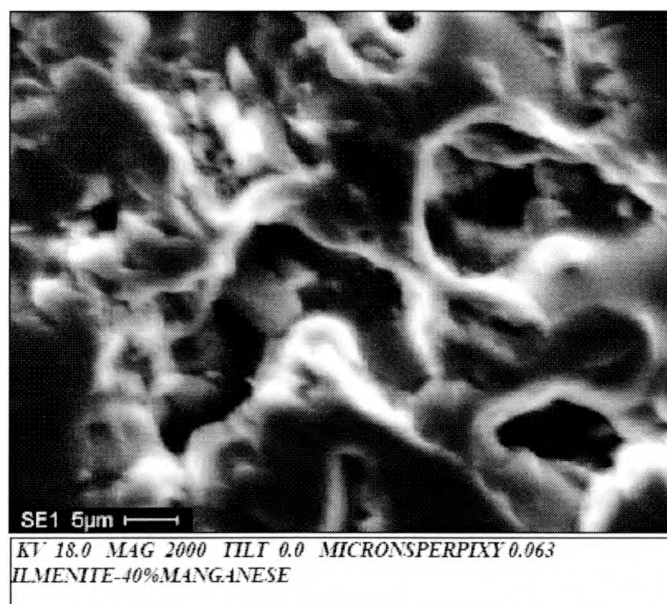


Figure 6.46 SEM Image of Ilmenite-Mn(40%)

Table 6 12 Resistivity of Ilmenite-Manganese Series

Mn %	Kale Resitivity (300K)	O'Brien Resitivity (300K)
0%	0.13 Ω -cm	22.3 Ω -cm
15%	0.14418 Ω -cm	14.84 Ω -cm
40%	4.05447 Ω -cm	445.37 Ω -cm

The resistivity measured in this thesis although two orders of magnitude higher than Kale's measured resistivity still follows the same trend and shows an anomaly at 15% manganese concentration.

The resistivity as a function of inverse temperature follows the Wilson's formula. By comparing to Kale, the activation energies at high temperatures from this thesis are consistent. Even though the resistivity results differ by orders, the activation energies are obtained from the slope of the resistivity versus $1/T$ which is consistent with Kale.

Table 6 13 Activation Energies of Ilmenite-Manganese Series

Mn mole %	Kale Activation energy (eV)	O'Brien Activation energy (eV) (High Temp~300-373K)
0%	0.1206	0.1530
15%	0.0896	0.0995
40%	0.0792	0.0657

Barrier heights, work functions, Richardson's constants and effective electron masses were determined for the Ilmenite-Manganese ceramic series. These values were first

approximations. There were several assumptions made (discussed in sections 6.1.1.1. and 6.1.1.4) before determining these values.

Table 6.14 Transport Properties of Ilmenite-Manganese Series

Mn %	Barrier Height (eV)	Work Function (eV)	Effective Electron mass(m^*/m)	Richardson's Constant Amps.cm ⁻¹ K ⁻¹
0%	0.077 ± 0.02	4.81 ± 0.02	(~0.01)	0.997 ± 0.001
15%	0.518 ± 0.02	5.25 ± 0.02	(~0.03)	4.12 ± 1.50
40%	0.95 ± 0.15	3.78 ± 0.15	Inconclusive	Inconclusive

6.1.5 PsB-Manganese(40%) Thin Film

Manganese doped Pseudobrookite is a new material and has little available literature. Pseudobrookite is considered the most stable of the iron titanates and is nonmagnetic in its single crystal state. However by adding manganese to the material changes its electrical and magnetic properties.

In this thesis we will examine electrical properties of two materials: 1) PsB-Mn(40%) thin film and 2) PsB-Mn(40%) single crystal. Section 2.3 contains a detailed description on the fabrication of these materials. We employed the Keithley set up for low level/low temperature testing described in section 5.1 for electrical characterization and possible magnetic field effects for the single crystal and thin film sample. The van der Pauw technique was used to determine the resistivity at varying temperatures for both samples.

6.1.5.1 Resistivity Measurements

Since the target for the PLD thin film was a PsB-Mn(40%) ceramic sample we first determined the resistivity at room temperature of the ceramic. The PsB-Mn(40%) ceramic had dimensions of 4.8mm x 5.0mm x 1.5mm with silver contacts. Since this was a bulk sample we determined the resistivity by employing a derived 3D four-point probe correction factor based on the sample dimensions and contact positions (see appendix A).

I-V Configuration 1234

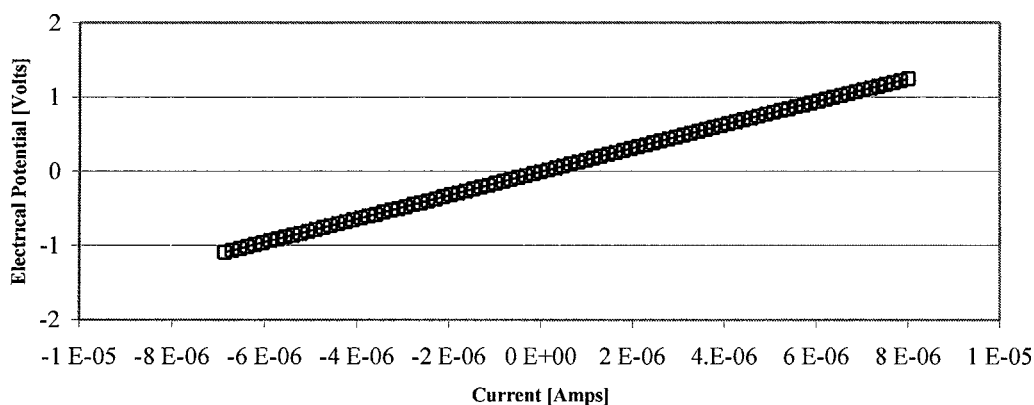


Figure 6 47 I-V Configuration 1234

A resistivity of 169.6 k Ω .cm was found for the ceramic sample.

The PsB-Mn(40%) thin film has a thickness of 500nm. For this sample we employed the Keithley set up for low level/low temperature measurements. This was necessary since the HP4145 SCPA has measurement limitations. The graph below shows a 4pp I-V measurement from the SCPA at room temperature.

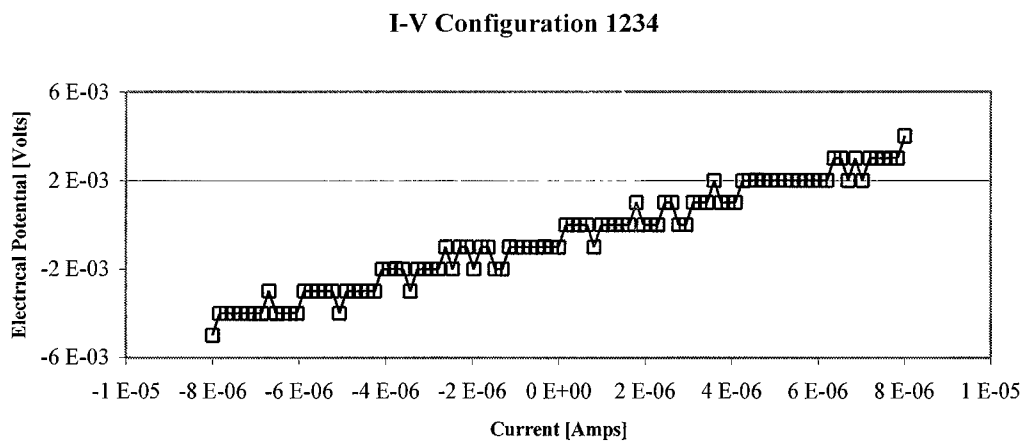


Figure 6 48 I-V Configuration 1234

The discrete data points show the limitation of the SCPA equipment. The I-V plot below shows the 4pp I-V measurement of the same configuration and range as the SCPA at room temperature using the Keithley set up.

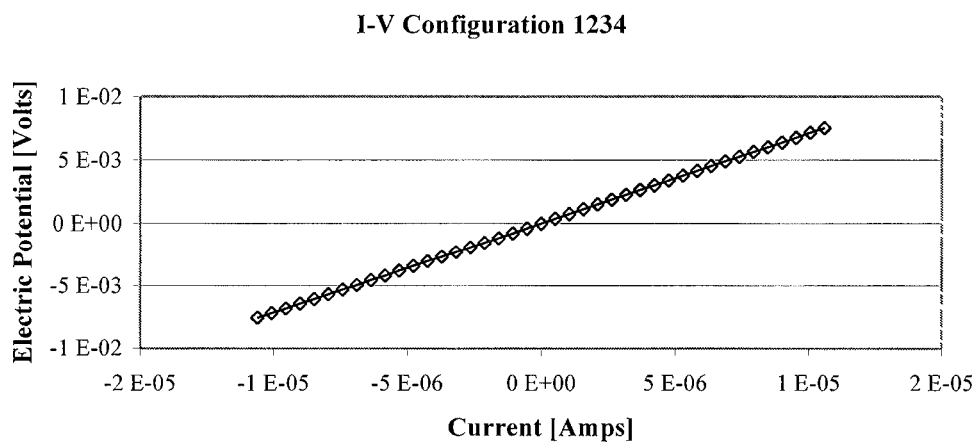


Figure 6 49 I-V Configuration 1234

Clearly the Keithley set up is advantageous for the thin film measurements. Four-point probe measurements were taken at temperatures of $T=100, 200, 300, 320, 380$ and 441K . the resistivity was determined by the van der Pauw technique. Previous studies show a resistivity at room temperature of $3\ \Omega\cdot\text{cm}$. The plot below shows the resistivity of the thin film as a function of inverse temperature and follows the Wilson's formula.

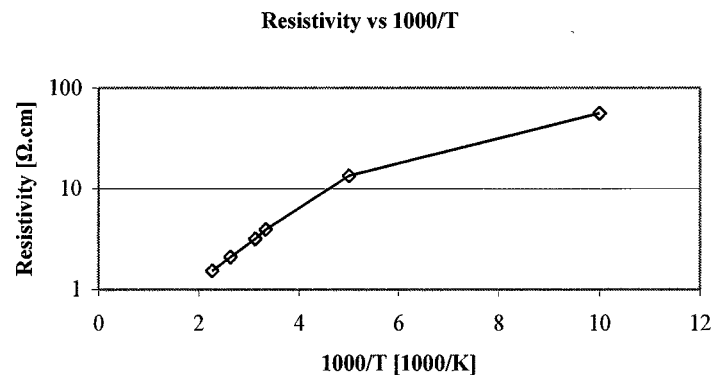


Figure 6.50 Resistivity vs $1000/T$

The room temperature resistivity was found to be $3.91\ \Omega\cdot\text{cm}$ which is consistent with previous study. From the $1/T$ plot we determined the activation energy to be 136meV .

6.1.5.2 Magnetic Field Effects

Another area of interest for the new materials is how the I-V characteristic behaves when exposed to a magnetic field. For this experiment we examined 4pp I-V measurements at 1, zero and -1 Tesla at varying temperatures. We chose 4pp measurements instead of 2pp measurements to eliminate possible contact influences.

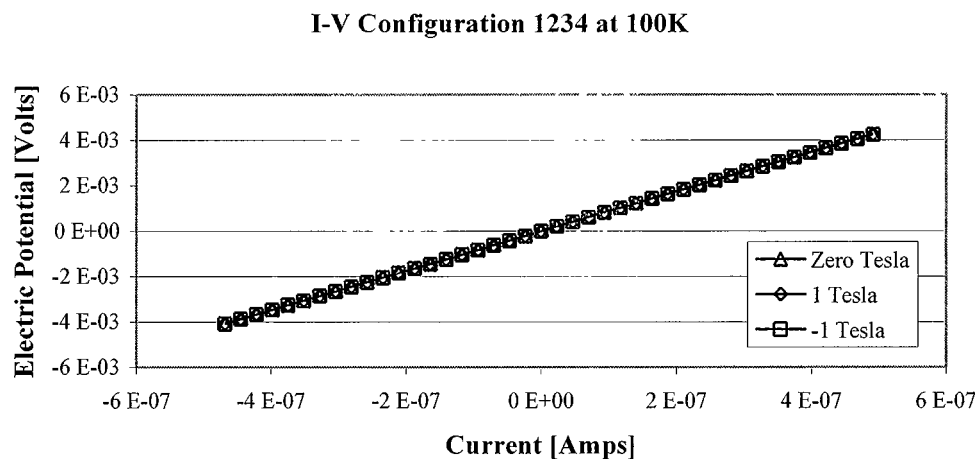


Figure 6 51 I-V Configuration 1234 at 100K

From the low temperature linear 4pp graph above (figure 6.51) there is no obvious field effect. By subtracting the linear component of the above graph we exploited the non-linear component and possible field effect.

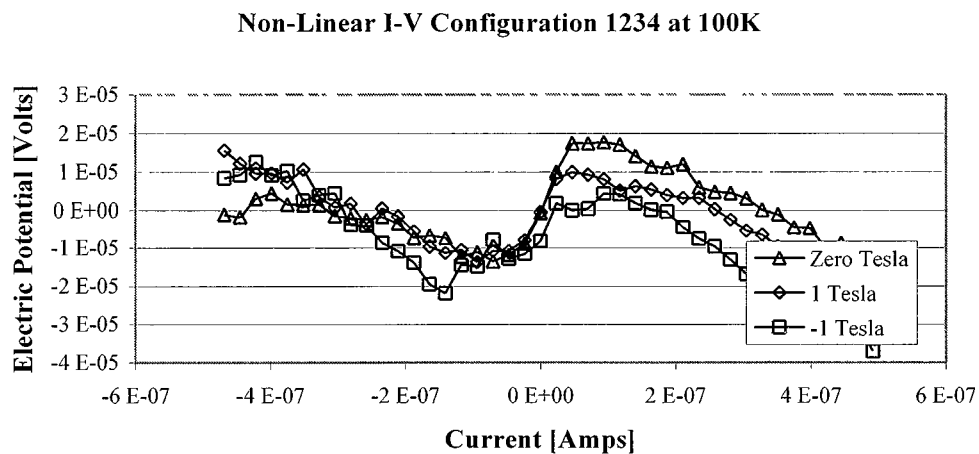


Figure 6 52 Non-Linear I-V Configuration 1234 at 100K

Although the field effect shown in the non-linear 4pp graph above (figure 6.52) is not convincing evidence that a field effect exists, the room temperature graph below (also the non-linear component from the same configuration) shows an obvious offset at 1 and -1 Tesla (figure 6.53). The behavior implies an even function such that the field effect is independent of the direction of the applied field. This effect is evident at the outer limits of the graph.

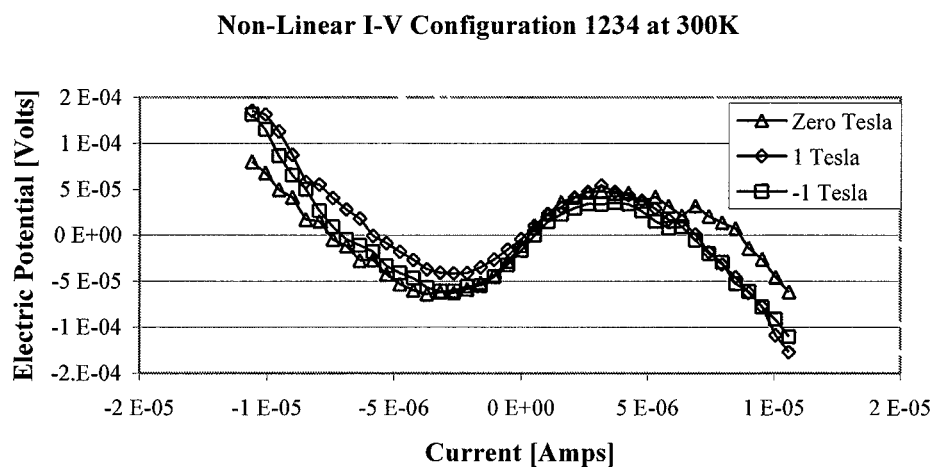


Figure 6 53 Non-Linear I-V Configuration 1234 at 300K

6.1.6 PsB-Manganese(40%) Single Crystal

The PsB-Mn single crystal has four silver contacts at the periphery and has a thickness of 2.1mm. Since the sample is of arbitrary shape we employed the van der Pauw technique to determine the resistivity at various temperatures.

6.1.6.1 Resistivity Measurements

Four-point probe measurements were taken at temperatures of $T=100, 200, 300, 310$ and 320 Kelvin. The plot of resistivity versus inverse temperature in the figure

below follows the Wilson's formula such that the activation energy of the PsB-Mn(40%) x'tal sample was found to be 326 meV. The room temperature resistivity was found to be 2355 $\Omega\cdot\text{cm}$

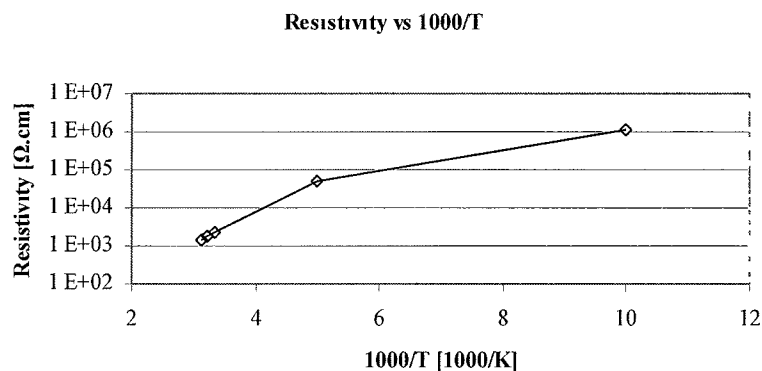


Figure 6 54 Resistivity vs 1000/T

6.1.6.2 Magnetic Field Effects

The 4pp I-V measurements show strong linearity and negligible field effect by observation in the room temperature plot below.

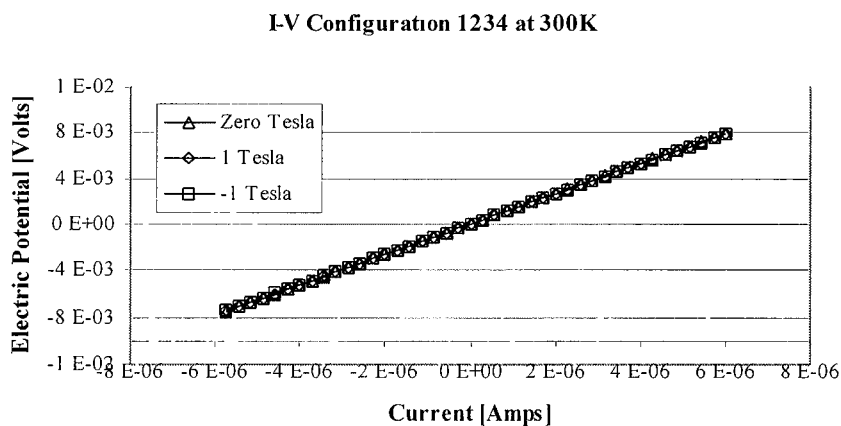


Figure 6 55 I-V Configuration 1234 at 300K

However by subtracting the linear component and exploiting the non-linear counterpart we can see a field effect in the I-V relation.

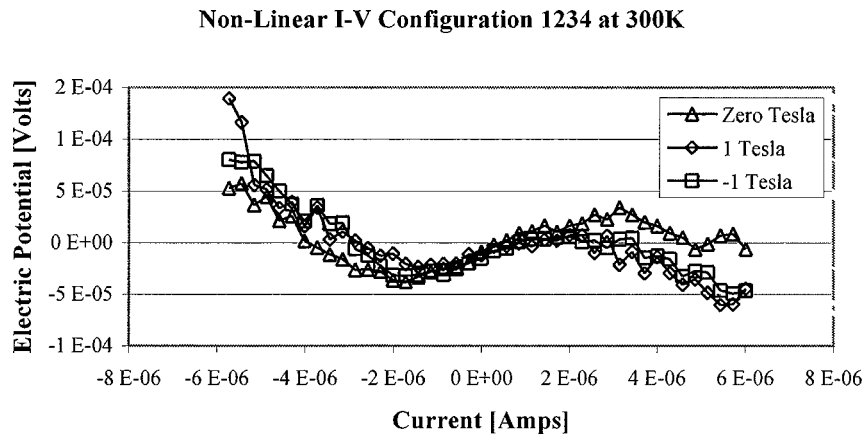


Figure 6 56 Non-Linear I-V Configuration 1234 at 300K

By employing the same technique of subtracting the linear component, we can also see a field effect at 100K that also implies a field effect independent of magnetic field direction.

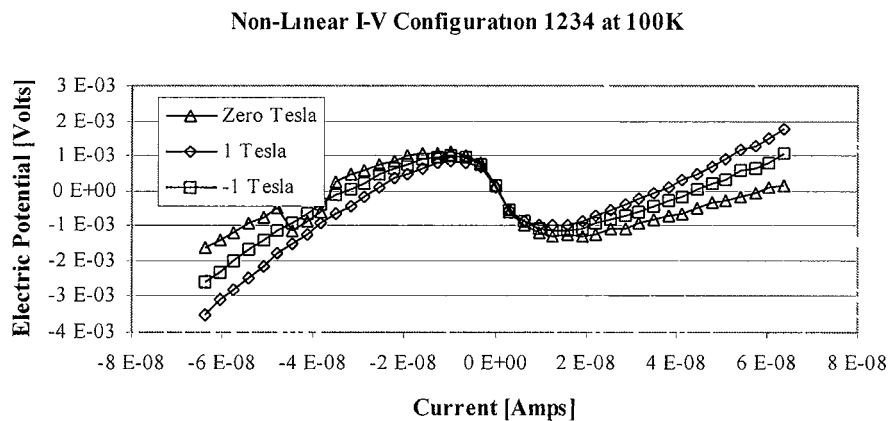


Figure 6 57 Non-Linear I-V Configuration 1234 at 100K

6.1.7 Pseudobrookite-Manganese Series Summary

In this thesis we determined the resistivity and the activation energies in the PsB-Mn samples as shown in the table below.

Table 6 15 Transport Properties of PsB-Mn(40%) Series

PsB-Mn(40%) (Type)	Resistivity (300K)	Activation Energy (meV)
Ceramic	169.6 k Ω .cm	Not Available
Thin Film	3.91 Ω .cm	136
Single Crystal	2355 Ω .cm	326

SEM and EDAX confirmed the type and composition of the three samples, PsB-Mn(40%) ceramic, thin film and single crystal. The table below shows the nominal and measured concentrations.

Table 6 16 Element Composition of PsB-Mn(40%) Series

Material Type	Nominal Composition	Actual Composition
Ceramic	Fe ₂ Ti ₁ O ₅ .Mn _{0.80}	Fe _{1.87} Ti _{1.57} O _{3.90} Mn _{0.81}
Thin Film	Fe ₂ Ti ₁ O ₅ .Mn _{0.80}	Fe _{0.67} Ti _{0.78} O _{5.16} .Mn _{0.25}
X'tal	Fe ₂ Ti ₁ O ₅ .Mn _{0.80}	Fe _{2.84} Ti _{3.03} O _{2.78} .Mn _{0.14}

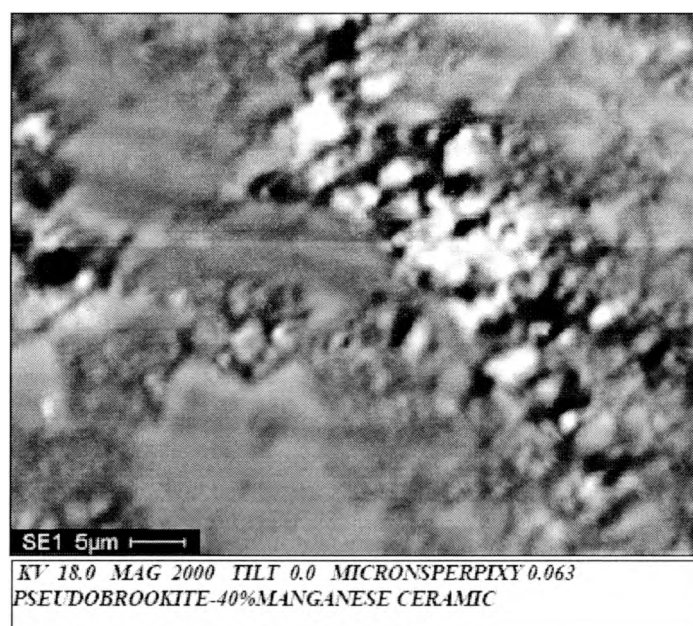


Figure 6.58 SEM Image of PsB-Mn(40%) Ceramic

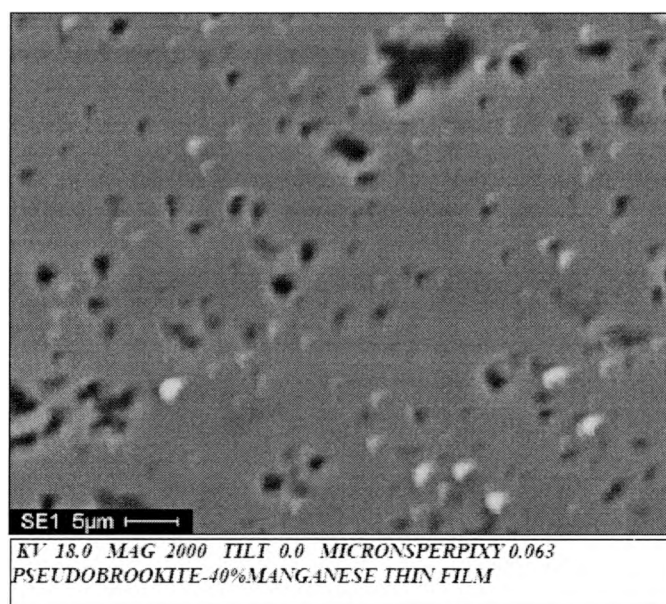


Figure 6.59 SEM Image of PsB-Mn(40%) Thin Film

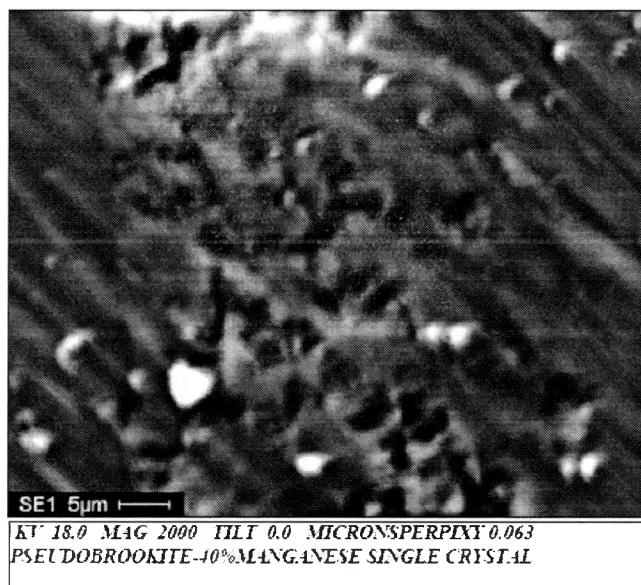


Figure 6.60 SEM Image of PsB-Mn(40%) x'tal

6.2 Optical Characterization

6.2.1 Ilmenite-Manganese Thin Film

For the manganese doped Ilmenite thin film we explored the possibility of a photovoltaic and photconductive effect in the thin film semiconductor sample. By illuminating the contacts with a small beam of light around one of the contacts we would expect the photovoltaic effect to result in an electric potential or current. Comparable to a solar cell, we expect that the absorbed photons will create electron-hole pairs which when created in the depletion area under the contacts will be separated by the internal electric field. We expect that a Schottky barrier exists under and around the metal contacts. Also, since the material is a semiconductor by nature we would expect that photons absorbed through the whole film will create additional charge carriers resulting in a decrease of the resistance. Three different experiments were performed. We measured the two-point

resistance with an electrometer and a current source. We measured the open terminal voltage with a nanovoltmeter. The final measurements were made with a picoammeter by measuring the short circuit current. For all experiments we exposed the whole sample or only the material around one of the contacts with monochromatic light (monochromator – Xenon lamp).

The Ilmenite-Manganese thin film has an assumed band gap of approximately 3.0eV therefore for a photo-effect we would need photons with enough energy to jump the band gap or moreover wavelengths in the UV range:

$$E=hc/\lambda=1239.8/3=413 \text{ nm}$$

This is at the edge of the visible light. Photoconductive and Photovoltaic effects might be larger at shorter wavelength since ilmenite is an indirect bandgap material.

We measured the intensity of the light exiting the monochromator with a calibrated Coherent SmartSensor detector from 405 –1065 nm. Both the entrance and exit slits of the monochromator were set at 2 mm corresponding to a bandwidth of 2 nm. The distance of the Xenon lamp to the monochromator entrance slit was 30 cm. The condenser lens on the Xenon lamp was used to focus the lamp on the entrance slit. Figure 5 shows the measured intensity of the Xenon 6251 lamp as a function of wavelength. Clearly the Xenon 6251 has significant output down to 405 nm as well as up and above 1000 nm. Clear peaks are present in the infrared. Figure 5 also shows the effects of an alteration in the grating setting at around 520nm to 600nm where grating 2 is selected versus grating 1.

As the detector could not be used to measure the intensity below 405 nm figure 6 shows the intensity versus wavelength graph as provided by the manufacturer. The

manufacturer's data shows not only a more detailed graph but also the y-axis is on a log scale to suppress the large peaks. Clearly the 6251 has significant output all the way down to 200-250 nm.

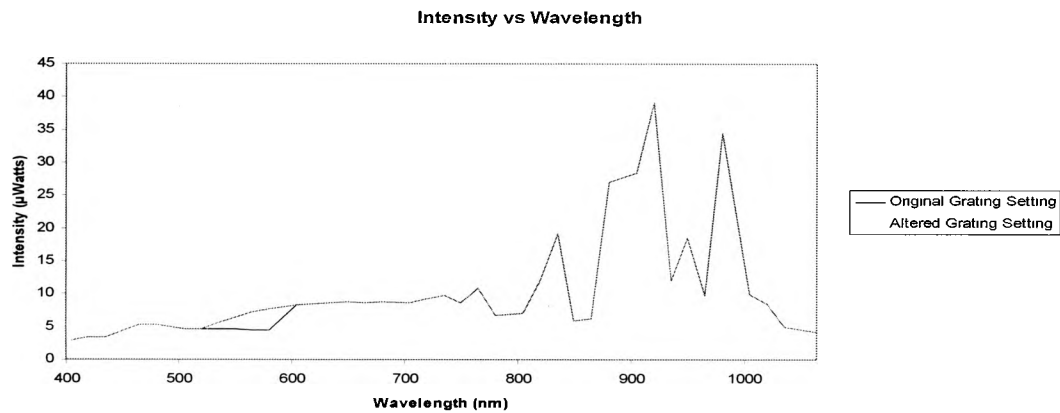


Figure 6 61 Intensity vs Wavelength

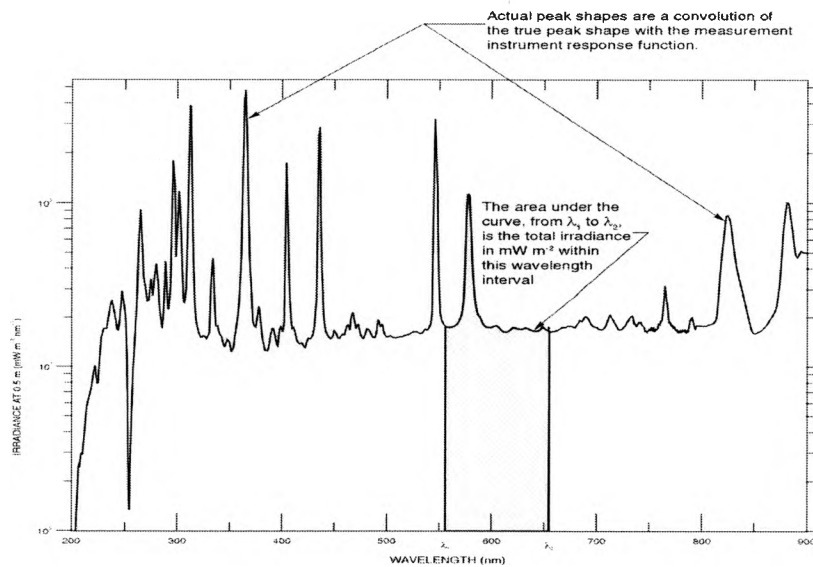


Figure 6 62 Intensity vs Wavelength from Factory³²

The Oriel digital light intensity controller 68950 allows a constant light output. Certain conditions can cause power variances over time. Figure 6.63 shows the relative intensity over a large time interval of the Xenon 6251 with and without the 68950 Controller as provided by the manufacturer.

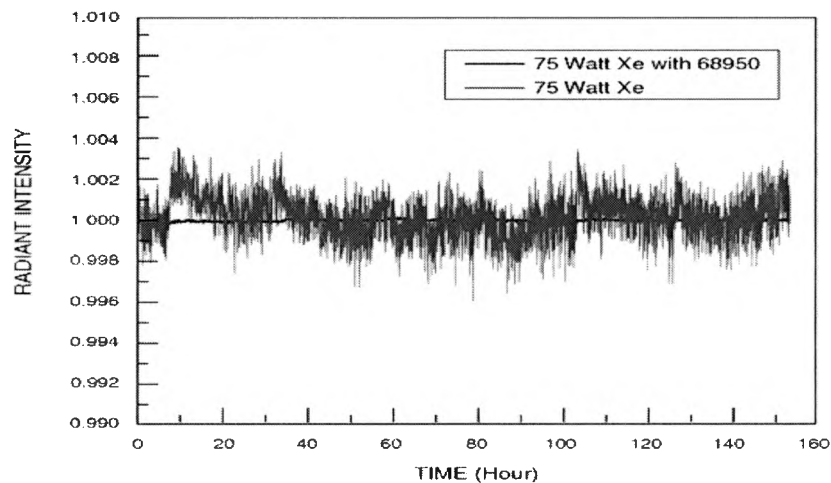


Figure 6.63 Radiant Intensity vs Time from Factory³²

Figure 6.64 shows experimentally the relative intensity as a function of time over a shorter interval of the Xenon 6251 with and without the flux controller. Unfortunately our experimental data was not as successful as the manufacturer's data. It looks like the controller is not working properly. Closer examination of the equipment showed an error in the setting thus causing the controller to not operate correctly.

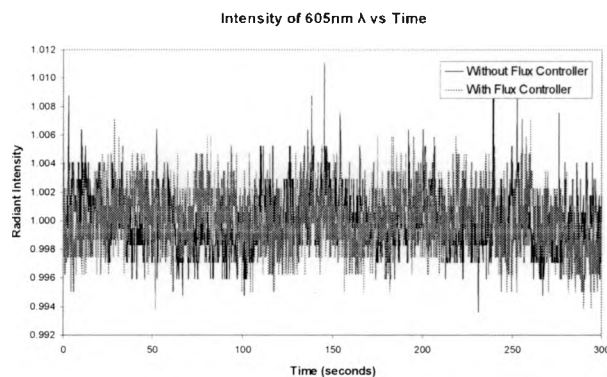


Figure 6.64 Radiant Intensity vs Time

The Keithley 2182a Nanovoltmeter was used to measure the open terminal voltage while the material around one of the contacts was exposed to light. The high input impedance of 10 Gohm was just sufficient to avoid loading of the circuit. An HP4140a picoammeter was selected in lieu of a shunt ammeter to measure the short circuit current while the material around one of the contacts was exposed to light.

Figures 5.10 and 5.11 show the set ups for measuring the photovoltaic properties of the Schottky contacts. The light source is focused first on and around the right contact, then on and around the left contact and finally the entire sample is flooded with light. For all these configurations the open terminal voltage and the short circuit current were measured. The open terminal voltage was measured across two contacts (One illuminated and the other not) using the Keithley 2182a nanovoltmeter. The short circuit current was measured using the HP 4140a picoammeter. Photoconductive measurements were only performed for the case where the sample was flooded with light. A Keithley 6221 current source and Keithley 6514 electrometer were used to determine the IV relation. It is important to note several controls in all the experiment.

1. The thin film was deposited on sapphire and thus more or less transparent in the visible range. A silicon wafer covered with aluminum was placed behind the sample. Aluminum has a high reflection coefficient (0.87 – 0.93) in the wavelength range we were working with. As the light would travel twice through the sample, thus increasing the photon absorption.
2. The sample was absent of stray light because of the aluminum box. The box also prevented influence of the airflow coming out of the air-conditioning vents, and provided some form of EM shielding.
3. A float table minimized vibrations.

The results for the voltage measurements showed no effect on the sample or the contacts. Illuminating each contact independently yielded no effect. We expected the measurement from one illuminated contact to have the opposite sign of the other contact. The voltage measurements maintained in the negative millivolt range and fluctuated ± 10 percent and showed no significant change in the three configurations. Also current measurement showed no noticeable effect.

6.2.2 Ilmenite-Hematite Thin Film

For the Ilmenite-Hematite thin film sample we further examined the possibility of a photoeffects by illuminating the sample with white light and varying the intensities at specific time intervals and taking IV measurements. We first took a measurement with no light and then illuminated the sample with a Quartz-Halogen Fiber-Lite source and then increased the intensity and measured followed by a final measurement with no light and looked for a hysteresis. The purpose of the hysteresis is to account for thermal

effects. Next we explored the possibility of a photoeffect on a Ilmenite-Hematite(33%) thin film sample by spanning a series of wavelengths with defined intensities using a Zenon lamp, a monochromator and a focusing lens and taking IV measurements. The results of the Ilmenite-Hematite film measurements showed some effects. The IV measurements for all four settings showed a decrease in resistance or an increase in conductivity proportional to the increase in intensity of the light. However the results showed a hysteresis therefore it is conclusive that the effect, or at least a large component of the effect is contributed to thermal effects or an increase in temperature causing a decrease in resistance characteristic to semiconductors. A similar approach to examine the photoeffect by extracting the resistance of the film from the IV characteristic as a function of wavelength instead of the open terminal voltage and short circuit current as a function of wavelength as employed on the Ilmenite-Mn film sample was used for the IH film sample. Unfortunately the measurements showed no noticeable change or photoeffect on the sample.

For the Ilmenite-Hematite(33%) film we illuminated the sample with a Fiber-Lite Model 190 Fiber Optic Illuminator. The sample was mounted and positioned on a float table and covered with a metal cage and black cloth to minimize stray radiation. The Fiber Optic Illuminator comes with four intensity settings and uses a 30-Watt quartz-halogen vibrationless source. The flexible fiber optic pipe allows for easy configuration and remains at ambient temperature for safe handling. First a series of three measurements were taken. An IV measurement using the Keithly 6228 Current Source and the 8218 Nanovoltmeter was taken with no light. The IV sweep took approximately 90 seconds followed by engaging the low level setting on the Fiber Optic Illuminator and

immediately the next IV measurements was taken followed by engaging the medium level setting and an immediate IV sweep followed by the high level setting IV sweep and then immediately a repeat measurement with no light. The purpose of the two “no light” measurements was to see if a hysteresis exists. This method was employed again yet with a two-minute delay between measurements which allowed any thermal effects to reach a steady state. This method was employed one more time with a five-minute delay to see if there were any noticeable differences between the two delay test.

The wavelength sweep on the IH film sample used the same set up as in section 6.2.1 with the Xenon lamp, monochromator and a series of pass filters for wavelength selections. In this experiment the light was focused to a spot size and centered between the two contacts. An IV sweep was made at a specific wavelength of incident light and the slope of the I-V relation determined the resistance. This technique was employed with wavelengths from 200nm to 1000nm paying close attention to wavelengths around the UV range since these wavelengths have corresponding energies at the band gap ~ 3.0 eV from literature. Energies from longer wavelengths can still contribute by exciting electrons from the donor level.

The nanovoltmeter measurements yielded no significant results. We focused the light source on each contact and measured the voltage across the two contacts as a function of wavelength between 250nm and 750nm. Since there is a depletion area under the contact we would expect to see a photovoltaic effect from photons being absorbed in the depletion area and causing an electron-hole pair. Figure 6.65 shows the voltage measurements for the left and right contact measurements. The error bars depict the upper and lower fluctuations in the voltage measurements. In essence the data points are

merely an average measurement. A measurement was also taken without a light source and yielded a measured voltage of $-2.52\text{mV} \pm 0.05$ which is similar to the illuminated measurements. Figure 6.65 also shows the results of flooding the sample with a near homogeneous light source and once again measuring the voltage over the two contacts. Although it appears that there is a significant difference in the flooded measurements versus the contact measurements, this could be contributed to thermo-electric effects in the connectors and or EM-effects originating from slightly moved cables. When blocking the light entering the monochromator the voltage stayed the same, i.e. $-2.17\text{mV} \pm 0.03$ which is similar to the results when the sample is exposed to light.

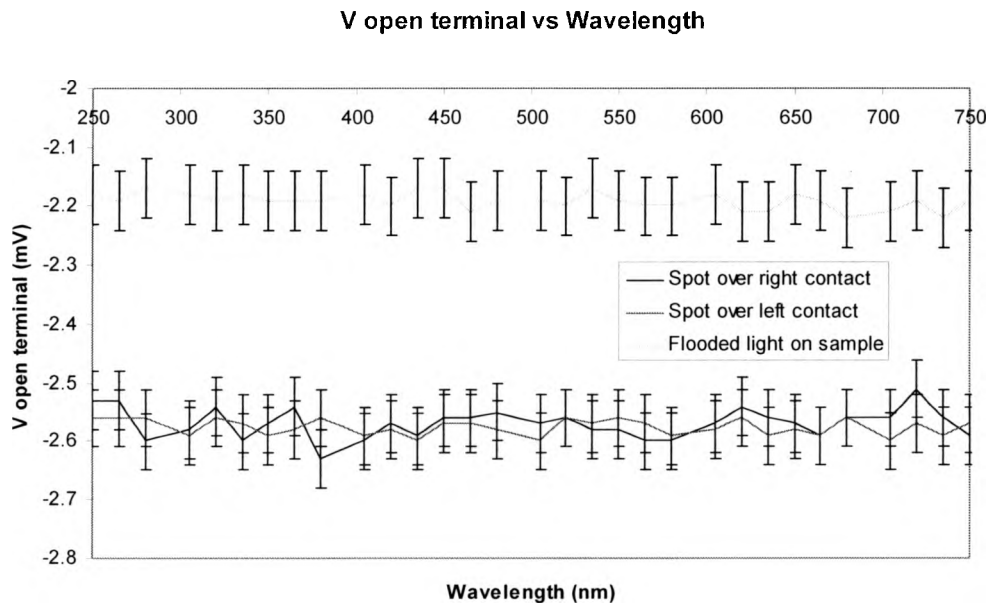


Figure 6 65 Open Terminal Voltage vs Wavelength

By illuminating one of the contacts and measuring the current we would expect two effects: one, photovoltaic current by creating charge carriers in the depletion region of the p-n junction between the contact and the sample and two, a Seebeck effect by the temperature difference between the two contacts. For the photocurrent, the illuminated contact acts as a photocell and the second contact acts as a diode (consequence of the Schottkey barrier) or also as the circuit load. These measurements were examined at different wavelengths. Since the photocurrent is expected to be both energy dependant and intensity dependant we measured over a long range of wavelengths from 200 nm to 1000 nm (reference figure 5 for intensity versus wavelength). There were no noticeable effects from the picoammeter. For each measurement the result varied between 40pA and 80pA. Although the effect could still exist one possible reason is that the measurable photocurrent was less than the noise current in the ammeter. The voltage burden of the ammeter is on the order of 10 μ volts and the resistance of the sample is approximately 77 M Ω causing the minimum current reading to be in pAmp range. Therefore the photocurrent could still exist below this value.

CHAPTER 7

DISCUSSION AND CONCLUSION

In this thesis we studied from literature previous work on Ilmenite, Ilmenite-Hematite, and Ilmenite-Manganese in bulk, thin films and single crystal. The purpose of this thesis was to determine some electrical transport properties of these materials. There were eight samples of interest for this thesis: three Ilmenite-Manganese bulk ceramic samples, three Pseudobrookite-Manganese(40%) samples including one ceramic, one thin film and one single crystal. The last two samples were thin films: one Ilmenite-Hematite(33%) thin film and one Ilmenite-Manganese(40%) thin film. In this thesis we explored the possibility of photoeffects on the two film samples as a consequence of varying wavelengths on incident light. The samples were prepared at the University of Alabama at Tuscaloosa. A detailed discussion of the sample preparations was discussed in his thesis. Since some of the samples were highly resistive and also since some of the measurements were taken at very low temperatures, the method of electrical characterization was far from trivial and a detailed discussion on equipment and equipment preparation was discussed in this thesis.

The electrical transport properties that were determined included not only the resistivity and temperature dependence on resistivity but also a first approximation on barrier heights, work functions and effective electron masses for the Ilmenite-Manganese

series. An aggressive approach was employed to determine these properties. Although several assumptions were made on the way to these determinations, they were reasonable assumptions that yielded reasonable solutions.

Future work in this area could include a closer examination at lower voltage bias for the modified Norde plot method to insure a minimum exist in the F2 plot. Also an additional modification in the Norde plot method to account for a large parallel resistance in the contact could yield more accurate results.

Also the samples in this thesis not only have non-linear 2pp I-V characteristics but also non-linear 4pp I-V characteristics which could imply a high and low voltage bias dependant resistivity. Although these effects are quite small, they are far from trivial. Future work could include a non-linear van der Pauw approach to solving for non-linear resistivity.

For the PsB-Manganese samples we observed changes in the I-V characteristic as a consequence of an applied magnetic field. Although a field effect did exist, the effect was not noticeable on a macroscopic level. An unorthodox method of subtracting the linear component of the I-V relation exploited not only the non-linear component of the 4pp measurements but also the field dependence of the material. Since these results were obtained from low signal measurements, possible future work could include higher voltage measurements and possible larger field effects.

APPENDIX A

Calculations of two point and four point probe correction factors.

Since the contacts to our sample are not in a nice collinear arrangement and the contacts are not at the edge of the sample we are not able to use correction factors published in literature to determine the sheet resistance from the measured currents and voltages. For this reason we calculated the four point probe (4pp) correction factors using MathCad for all four possible contact configurations. Since the film was much thinner than the contacts and the contact distances we assumed a two dimensional current distribution in the sample and followed an approach similar to reference [4]. The electric potential distribution around a current injecting electrode on an infinite thin film is given by:

$$E(r) = \rho J = \rho \frac{I}{A} = \rho \frac{I}{2\pi r t} = \rho_s \frac{I}{2\pi r} \quad (\text{A-1})$$

Where r is the distance from the electrode, t is the film thickness, ρ is the resistivity, ρ_s is the sheet resistance, and I is the injected current. The electric potential around the electrode is thus:

$$V(r) = -\rho_s \frac{I}{2\pi} \ln(r) \quad (\text{A-2})$$

Writing [A2] in vector coordinates and assuming the electrode is positioned at $\mathbf{r}_a$ we get:

$$V(\vec{r}, \vec{r}_a) = -\rho_s \frac{I}{2\pi} \ln(\vec{r} - \vec{r}_a) \quad (\text{A-3})$$

Assuming now that we have two electrodes on the thin film, i.e. a current source electrode at position $\mathbf{r}_a$ and a current sink electrode at position $\mathbf{r}_b$. The electric potential for an arbitrary position $\mathbf{r}$ in the thin film is the superposition of the electric potential caused by the source and the sink electrodes:

$$V_{\text{sup}}(\vec{r}, \vec{r}_a, \vec{r}_b) = V(\vec{r}, \vec{r}_a) + V(\vec{r}, \vec{r}_b) = -\rho_s \frac{I}{2\pi} \ln \frac{|\vec{r} - \vec{r}_a|}{|\vec{r} - \vec{r}_b|} \quad (\text{A-4})$$

In order to take account of the limited dimensions of the thin film we use the method of images²⁵. Figure A.1 shows the image sources in the vicinity of the sample for the source electrode. Let us first consider the sources in the bold box:

$$V_{bb}(\vec{r}, \vec{r}_a, \vec{r}_b) = V_{\text{sup}}(\vec{r}, \vec{r}_a, \vec{r}_b) + V_{\text{sup}}(\vec{r}, -\vec{r}_a, \vec{r}_b) + V_{\text{sup}}(\vec{r}, \vec{r}_a, -\vec{r}_b) + V_{\text{sup}}(\vec{r}, -\vec{r}_a, -\vec{r}_b) \quad (\text{A-5})$$

Notice that the pattern of image sources outside the bold box is periodic with periodicity $2*s$ where s is the sample size. Assuming that $\mathbf{e}_x$ and $\mathbf{e}_y$ are the unit vectors in the x and y direction, the electric potential can be approximated by summing over image sources in the vicinity of the sample:

$$V_{\text{corrected}}(\vec{r}, \vec{r}_a, \vec{r}_b) = \sum_{m=-N}^N \sum_{k=-N}^N V_{bb}(\vec{r}, \vec{r}_a + m2s\vec{e}_x, \vec{r}_b + k2s\vec{e}_y) \quad (\text{A-6})$$

The larger N the more accurate the approximation. In our calculations we used $N=6$.

Assuming that the voltage electrodes are at position $\mathbf{r}_c$ and $\mathbf{r}_d$, the measured electric potential difference is given by:

$$\Delta V(\vec{r}_c, \vec{r}_d, \vec{r}_a, \vec{r}_b) = V_{\text{corrected}}(\vec{r}_c, \vec{r}_a, \vec{r}_b) - V_{\text{corrected}}(\vec{r}_d, \vec{r}_a, \vec{r}_b) \quad (\text{A-7})$$

The correction factor can now be calculated from:

$$RCF = \frac{I \rho_s}{\Delta V(\vec{r}_c, \vec{r}_d, \vec{r}_a, \vec{r}_b)} \quad (\text{A-8})$$

Since ΔV is proportional to I and ρ_s , this expression is independent of the current and sheet resistance and only depends on the geometry of the sample. This expression does assume that the contacts have an infinite small size. Up to now we have not made any correction for the finite size of the contacts.

We used expression (A-8) to calculate the correction factors for all 4pp combinations using the geometry data of table A.1. The results are given in table A.2 and are used to estimate the sheet resistance of the sample.

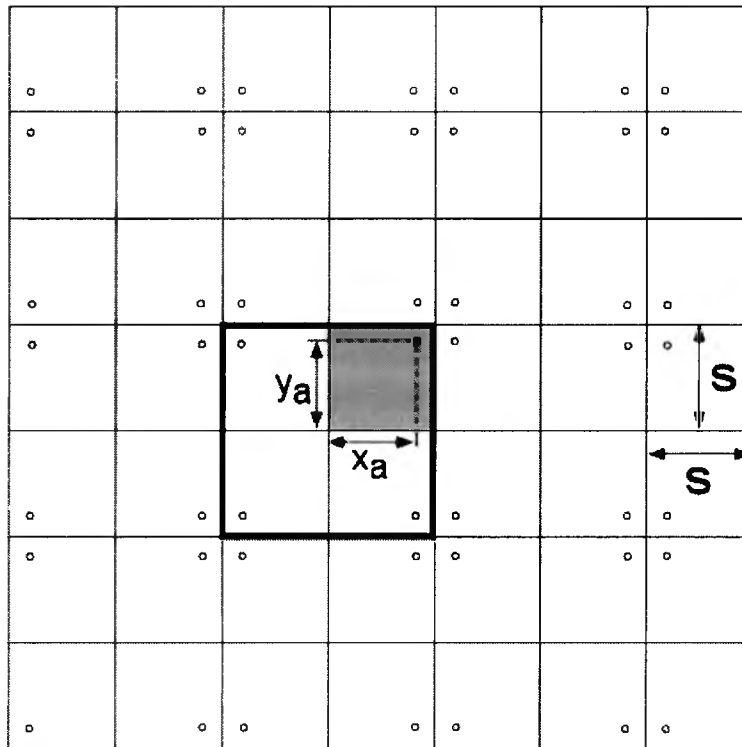
We also used equation (A-8) to estimate the correction factors for 2pp measurements. For these calculations we assumed the current electrodes to be positioned at the center of the contacts involved and the voltage electrodes to be positioned at the edge of the contacts on a line that connects the center of both contacts. The results are summarized in table A.3 and are used to calculate the series resistance of the thin film.

Table A 1 Calculated correction factors for 4pp

Ia	Ib	Vc	Vd	RCF
2	6	7	5	3.451
2	7	5	6	52.8
2	5	7	6	3.692
7	5	2	6	3.451
7	6	2	5	3.692
5	6	2	7	52.8

Table A 2 Calculated correction factors for 2pp

Ia/Vc	Ib/Vd	RCF
2	7	2.408
5	7	2.661
5	6	1.594
6	7	1.579
2	6	0.809
2	5	1.042



-  Sample of size $s \times s$
-  Current Source or Current Sink at position (x_a, y_a)
-  Image Source or Image Sink
-  Repeated pattern of Sources or Sinks (periodicity is $2s$)

Figure A.1 Image Sources

Mathcad file to calculate correction factors given sample dimensions and contact positions for 2D cylindrical—thin films

Chris O'Brien, Wim Geerts
Spring 2007
Calculation of Correction Factor for 4pp
all configurations

Current in at x_a, y_a
Current out at x_b, y_b , sample size $s1 \times s2$, i.e. rectangular sample
thin film sample line source through sample thickness

$I = 0.00001$ Calculation is independent of I , but included I for clarity in equations (current)

$s1 = 0.01$ Length in the x -direction

$s2 = 0.01$ Length in the y -direction

$t = 9.2 \cdot 10^{-9}$ Thickness of the sample in meters

Position of the Contacts IHF33

$x2 = 0.002767$ $x5 = 0.001594$ $x6 = 0.001406$ $x7 = 0.005066$

$y2 = 0.005054$ $y5 = 0.004636$ $y6 = 0.001126$ $y7 = 0.004704$

Voltage distribution in the thin film:

$V_{ps}(R) = - \left(\frac{I}{2\pi} \ln(R) \right)$ Electric potential distribution caused by line current source at distance R away from source normalized to ρ/t where t is film thickness and ρ is resistivity

Electric potential caused by sources and image sources in bold square (V_{Ia} is the current source and V_{Ib} is the current sink)

$$V_{Ia}(x, y, x_a, y_a) = V_{ps} \left[\sqrt{(x - x_a)^2 + (y - y_a)^2} \right] + V_{ps} \left[\sqrt{(x + x_a)^2 + (y - y_a)^2} \right] + V_{ps} \left[\sqrt{(x - x_a)^2 + (y + y_a)^2} \right] + V_{ps} \left[\sqrt{(x + x_a)^2 + (y + y_a)^2} \right]$$

$$V_{Ib}(x, y, x_b, y_b) = V_{ps} \left[\sqrt{(x - x_b)^2 + (y - y_b)^2} \right] + V_{ps} \left[\sqrt{(x + x_b)^2 + (y - y_b)^2} \right] + V_{ps} \left[\sqrt{(x - x_b)^2 + (y + y_b)^2} \right] + V_{ps} \left[\sqrt{(x + x_b)^2 + (y + y_b)^2} \right]$$

Including image sources near the sample

$$Vlb_ps(x, y, xb, yb) = \sum_{m=-6}^6 \sum_{k=-6}^6 Vlb(x-2k s1, y-2m s2, xb, yb) \quad \dots \dots \dots$$

$$Vla_ps(x, y, xa, ya) = \sum_{m=-6}^6 \sum_{k=-6}^6 Vla(x-2k s1, y-2m s2, xa, ya)$$

$$Vmeasured_ps(xc, yc, xd, yd, xa, ya, xb, yb) = (Vla_ps(xc, yc, xa, ya) - Vlb_ps(xc, yc, xb, yb)) - (Vla_ps(xd, yd, xa, ya) - Vlb_ps(xd, yd, xb, yb))$$

Calculated correction factors for 4pp measurements:

$$I2I6/V7V5: \quad RCF = \frac{I}{Vmeasured_ps(x7, y7, x5, y5, x2, y2, x6, y6)} \quad RCF = 3.451$$

$$I2I7/V5V6 \quad RCF = \frac{I}{Vmeasured_ps(x6, y6, x5, y5, x2, y2, x7, y7)} \quad RCF = 52.349$$

$$I2I5/V7V6: \quad RCF = \frac{I}{Vmeasured_ps(x7, y7, x6, y6, x2, y2, x5, y5)} \quad RCF = 3.692$$

$$I7I5/V2V6: \quad RCF = \frac{I}{Vmeasured_ps(x2, y2, x6, y6, x7, y7, x5, y5)} \quad RCF = 3.451$$

$$I7I6/V2V5: \quad RCF = \frac{I}{Vmeasured_ps(x2, y2, x5, y5, x7, y7, x6, y6)} \quad RCF = 3.692$$

$$I5I6/V2V7: \quad RCF = \frac{I}{Vmeasured_ps(x2, y2, x7, y7, x6, y6, x5, y5)} \quad RCF = 52.249$$

Mathcad file to calculate correction factors given sample dimensions and contact positions for 3D semi-spherical—bulk sample.

Chris O'Brien, Wim Geerts
 Spring 2007
 Calculation of Correction Factor for 4pp
 all configurations 3 dimensional current distribution

Current in at x_a, y_a
 Current out at (x_b, y_b) , sample size $s1 \times s2$
 thin film sample point source at surface of sample

$I = 0.00001$ Calculation is independent of I , but included I for clarity in equations (current)

$s1 = 0.01$ Length of the sample in the x -direction

$s2 = 0.01$ Length of the sample in the y -direction

$t = 0.01$ Thickness of the sample in meters

Position of the Contacts IHF33

$x2 = 0.002767$ $x5 = 0.001594$ $x6 = 0.001406$ $x7 = 0.005000$

$y2 = 0.005054$ $y5 = 0.004636$ $y6 = 0.001126$ $y7 = 0.004704$

Voltage distribution in the thin film

$V_{\rho}(P) = \left(\frac{I}{2\pi} \frac{1}{P} \right)$ Electric potential distribution caused by point current source at distance P away from source normalized to ρ/t where t is film thickness and ρ is resistivity

Electric potential caused by sources and image sources in bold square (Ia is the current source and $-Ib$ is the current sink)

$$V_{Ia}(x, y, xa, ya, za) = V_{\rho} \left[\sqrt{(x - xa)^2 + (y - ya)^2 + za^2} \right] + V_{\rho} \left[\sqrt{(x + xa)^2 + (y - ya)^2 + za^2} \right] + V_{\rho} \left[\sqrt{(x - xa)^2 + (y + ya)^2 + za^2} \right] + V_{\rho} \left[\sqrt{(x + xa)^2 + (y + ya)^2 + za^2} \right]$$

$$V_{Ib}(x, y, xb, yb, zb) = V_{\rho} \left[\sqrt{(x - xb)^2 + (y - yb)^2 + zb^2} \right] + V_{\rho} \left[\sqrt{(x + xb)^2 + (y - yb)^2 + zb^2} \right] + V_{\rho} \left[\sqrt{(x - xb)^2 + (y + yb)^2 + zb^2} \right] + V_{\rho} \left[\sqrt{(x + xb)^2 + (y + yb)^2 + zb^2} \right]$$

Including image sources near the sample

$$V_{Ib_A}(x, y, x_b, y_b) = \sum_{q=-50}^{50} \sum_{m=-6}^6 \sum_{k=-6}^6 V_{Ib}(x, y, x_b - 2k s_1, y_b - 2m s_2, 2q t) + \dots$$

$$V_{Ia_A}(x, y, x_a, y_a) = \sum_{q=-50}^{50} \sum_{m=-6}^6 \sum_{k=-6}^6 V_{Ia}(x, y, x_a - 2k s_1, y_a - 2m s_2, 2q t)$$

$$V_{measured_A}(x_c, y_c, x_d, y_d, x_a, y_a, x_b, y_b) = (V_{Ia_A}(x_c, y_c, x_a, y_a) - V_{Ib_A}(x_c, y_c, x_b, y_b)) - (V_{Ia_A}(x_d, y_d, x_a, y_a) - V_{Ib_A}(x_d, y_d, x_b, y_b))$$

Calculated correction factors for 4pp measurements:

I2I6/V7V5:	$RCF = \frac{I}{V_{measured_A}(x_7, y_7, x_5, y_5, x_2, y_2, x_6, y_6) t}$	RCF = 1.616
I2I7/V5V6	$RCF = \frac{I}{V_{measured_A}(x_6, y_6, x_5, y_5, x_2, y_2, x_7, y_7) t}$	RCF = 12.019
I2I5/V7V6:	$RCF = \frac{I}{V_{measured_A}(x_7, y_7, x_6, y_6, x_2, y_2, x_5, y_5) t}$	RCF = 1.867
I7I5/V2V6:	$RCF = \frac{I}{V_{measured_A}(x_2, y_2, x_6, y_6, x_7, y_7, x_5, y_5) t}$	RCF = 1.616
I7I6/V2V5:	$RCF = \frac{I}{(V_{measured_A}(x_2, y_2, x_5, y_5, x_7, y_7, x_6, y_6) t)}$	RCF = 1.867
I5I6/V2V7:	$RCF = \frac{I}{V_{measured_A}(x_2, y_2, x_7, y_7, x_6, y_6, x_5, y_5) t}$	RCF = 12.019

MathCad file for IV Diode and Diode plus parallel resistor

Influence Shunt Resistance
 Wim Geerts, Chris O'Brien
 June 2007, TxState University

slope := 5.25 Found from the high bias slope of contact #1

$$T := 300 \quad q := 1.6 \cdot 10^{-19} \quad k := 1.38 \cdot 10^{-23} \quad n := \frac{q}{\text{slope} \cdot k \cdot T}$$

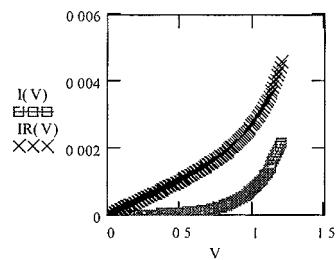
n = 7.361 ideality constant

$$I_0 := 4 \cdot 10^{-6} \quad R := 500$$

V := 0, 0.01, 1, 2 Bias Range

$$I(V) := I_0 \left(e^{\frac{q \cdot V}{k \cdot T \cdot n}} - 1 \right) \quad \text{diode equation}$$

$$IR(V) := \frac{V}{R} + I(V) \quad \text{diode equation plus parallel resistor}$$



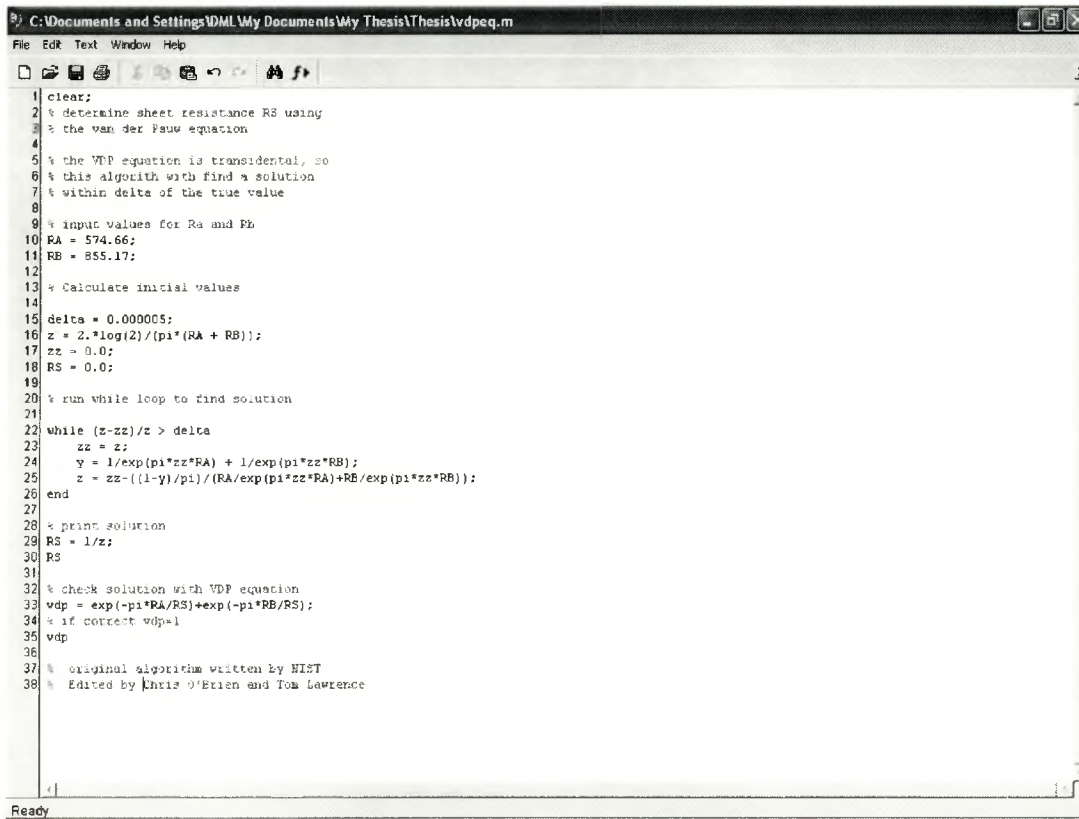
derivatives evaluated at zero

$$\text{derI}(V) = \frac{d}{dV} I(V) \quad \text{derI}(0) = 2.1 \cdot 10^{-5}$$

$$\text{derIR}(V) = \frac{d}{dV} IR(V) \quad \text{derIR}(0) = 2.021 \cdot 10^{-3}$$

APPENDIX B

MatLab program to solve the transcendental van der Pauw equation for resistivity.



```

1 clear;
2 % determine sheet resistance RS using
3 % the van der Pauw equation
4
5 % the VDP equation is transcendental, so
6 % this algorithm will find a solution
7 % within delta of the true value
8
9 % input values for Ra and Rb
10 RA = 574.66;
11 RB = 855.17;
12
13 % Calculate initial values
14
15 delta = 0.000005;
16 z = 2.*log(2)/(pi*(RA + RB));
17 zz = 0.0;
18 RS = 0.0;
19
20 % run while loop to find solution
21
22 while (z-zz)/z > delta
23     zz = z;
24     y = 1/exp(pi*zz*RA) + 1/exp(pi*zz*RB);
25     z = zz-((1-y)/pi)/(RA/exp(pi*zz*RA)+RB/exp(pi*zz*RB));
26 end
27
28 % print solution
29 RS = 1/z;
30 RS
31
32 % check solution with VDP equation
33 vdp = exp(-pi*RA/RS)+exp(-pi*RB/RS);
34 % if correct vdp=1
35 vdp
36
37 % original algorithm written by H1ST
38 % Edited by Chris O'Brien and Tom Lawrence

```

Figure B 1 MatLab Program to solve VDP Equation

APPENDIX C

LabView VI Program List and Main GUI

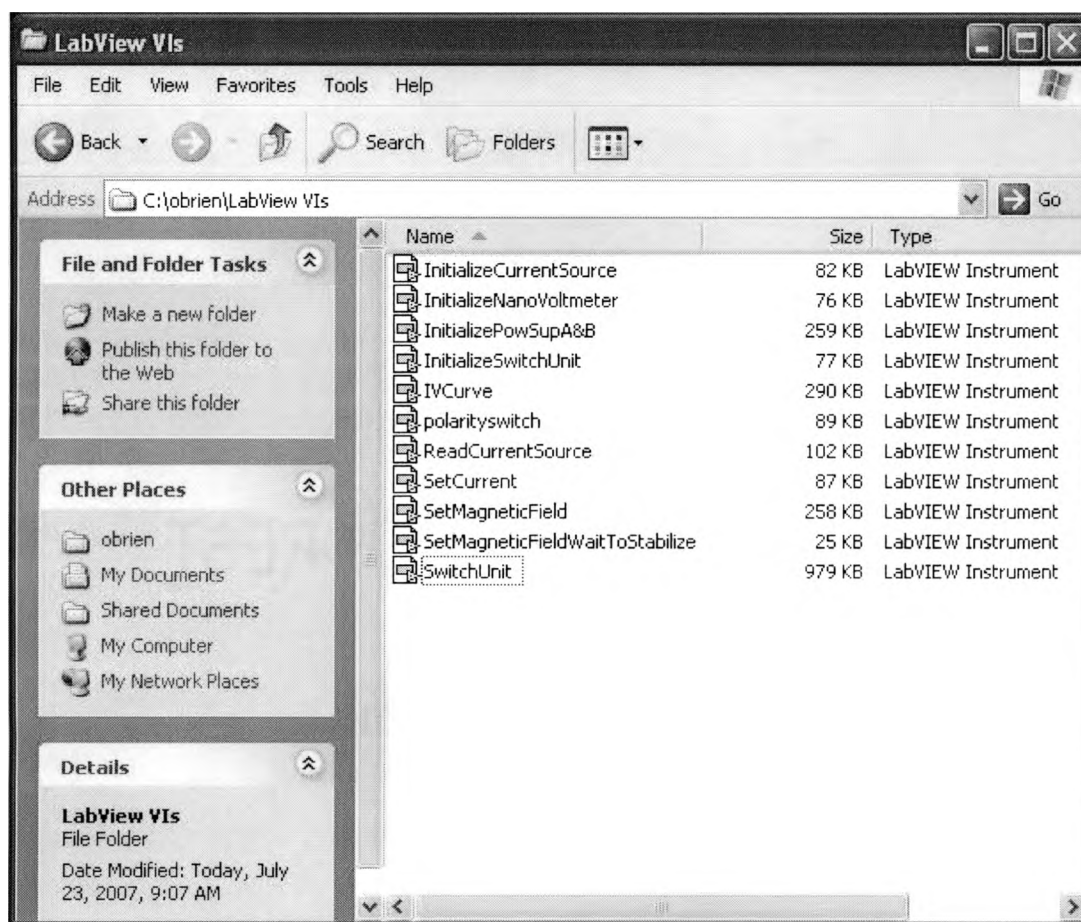


Figure C.1 LabView VI Program List

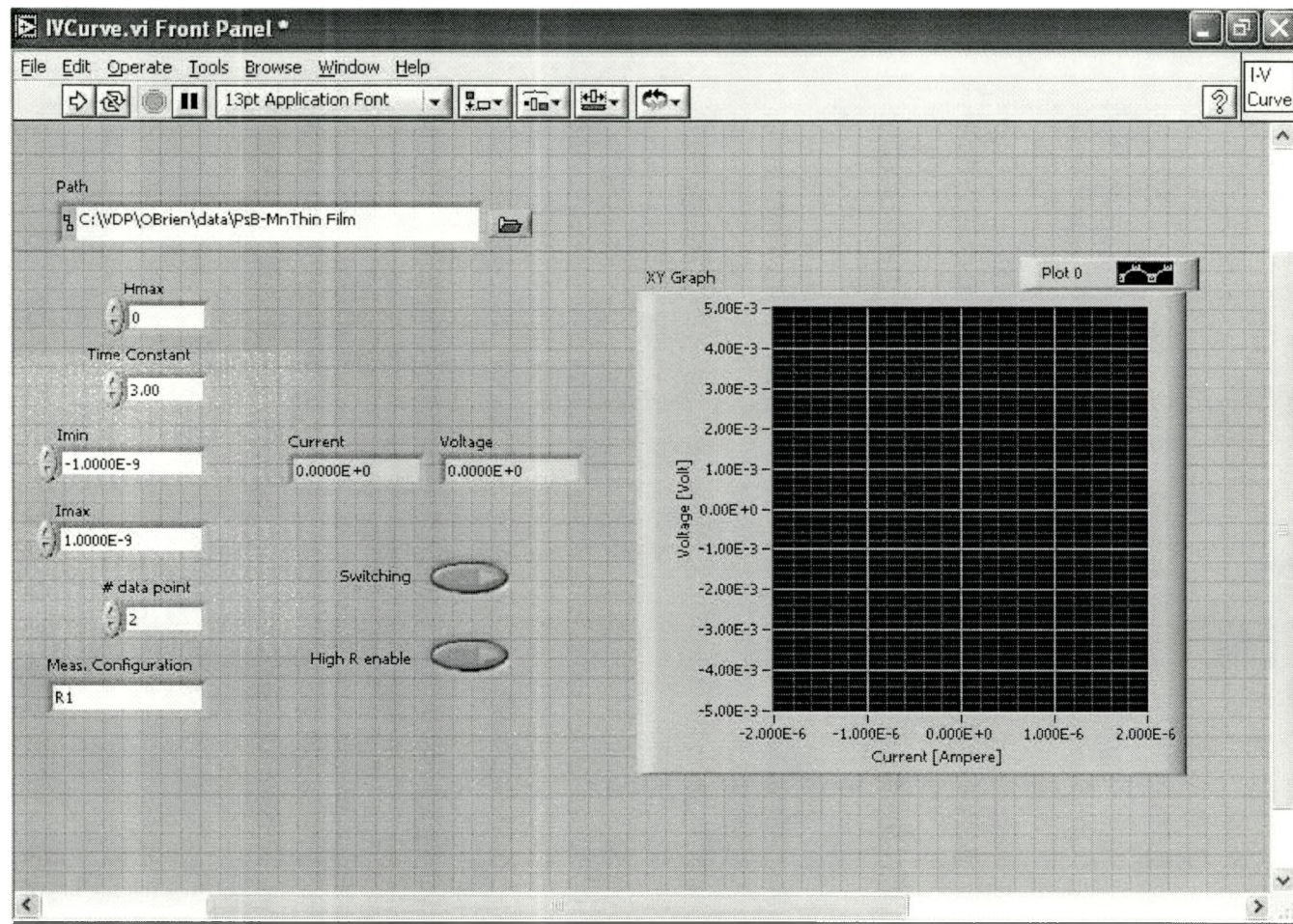


Figure C 2 LabView GUI

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VITA

Chris B. O'Brien was born in Victoria, Texas, on March 9th, 1972. After completing his work at Calallen High School in Corpus Christi, Texas in 1990, he attended Del Mar College before attending Texas State University-San Marcos where he completed his Bachelor of Science in Physics (*cum laude*) in August 2005. In the fall of 2005 he entered the Graduate College at Texas State to pursue his Master of Science. During his graduate studies, he was employed as a research assistant and an instructional assistant and was co-author in three professional publications. He completed his Master of Science in Physics in August 2007 with a 3.9 grade point average.

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This thesis was typed by Chris B. O'Brien.

