# RESISTIVITY MEASUREMENTS OF THIN FILMS OF BISMUTH: APPLICATIONS FOR BUILDING BOLOMETRIC DETECTORS

By

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B. Sc. Hons (Physics) University of Regina, 1994

# A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTERS OF SCIENCE

 $_{\mathrm{in}}$ 

THE FACULTY OF GRADUATE STUDIES DEPARTMENT OF PHYSICS AND ASTRONOMY

> We accept this thesis as conforming to the required standard

### THE UNIVERSITY OF BRITISH COLUMBIA

#### Sept 1997

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#### Abstract

The resistivity of thin bismuth films grown on sapphire substrates has been measured as a function of growth rate, thickness, and temperature. Seven different samples were measured. In all cases the resistivity of the films was completely unlike the resistivity of the bulk material, and each sample exhibited a negative temperature coefficient of resistance (TCR). A model is presented which provides a physical interpretation of the shape of the resistivity - temperature curve of thin bismuth films. This model is a new contribution to this field of research, since there appears to be no satisfactory explanation for the anomalous temperature dependence of the resistivity of thin bismuth films published in the literature.

The sheet resistance of the films at 4.2K was found to decrease with increasing thickness. Based on the experimental data, a bismuth film of thickness 200Å should have a sheet resistance of  $188.5\Omega/\Box$  at helium temperatures. The resistance of the thinner films was found to increase as a function of time when exposed to the air, and this seems to be consistent with a layer of insulating  $Bi_2O_3$  forming at the surface of the film. The sheet resistance and resistivity of a 5000Å thick coating of vapor deposited aluminum was measured as a function of temperature in the range 300K - 4.2K. The resistivity was found to be greater than that of the bulk material at all temperatures, and the sheet resistance at 80K was equal to  $R_{\Box} = 0.051\Omega$ .

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## Acknowledgements

I would like to acknowledge several people who have helped me a great deal during my research and writing of this thesis. First, I would like to thank Dr. Mark Halpern of the UBC Experimental Cosmology Lab for many insightful discussions and suggestions. Working under Mark has been a great experience, and I have have found that he is always willing to help, any time of the day or night. Dr. Gregory Tucker has been a great source of knowledge, and has been very helpful thoughout the course of my grad studies. I would also like to thank Dr. Douglas Bonn for reading my thesis so promptly, and for making several very insightful comments. Finally, I would like to thank Colin Borys and Miranda Jackson for their Latex expertise, and for introducing me to new depths of insanity.

### Chapter 1

## Introduction

In this chapter, the basics of bolometer operation will be discussed. In addition, the physics of the transmission line will be discussed, with a focus on its relation to optics and applications for bolometers.

### 1.1 Introducing the Bolometer

The BAM(Balloon Borne Anisotropy Measurement) instrument[4] is a telescope capable of measuring anisotropies in the Cosmic Microwave Background Radiation(CMBR) on the scale of approximately 1 degree. The telescope operates in the following manner. Microwave light enters a two beam Fourier Transform Spectrometer after reflection from an aluminum mirror. After passage through the spectrometer, the light is directed onto two optical detectors called bolometers. These bolometers measure an interference pattern which is proportional to the *difference* in intensity between the two beams. The following discussion is directed towards the elementary physics of bolometer operation.

#### 1.1.1 Basics

A bolometer is a thermal device which measures small temperature changes. There are typically two distinct types of bolometers : composite and monolithic. A composite bolometer consists of three distinct parts:

1) An absorbing layer. This can in principle be any electrically conductive material. Gold and bismuth are common choices for microwave absorbers.

1

2) Substrate. The substrate must be an electrical insulator, be mechanically rigid, and have a very low heat capacity at low temperatures. Typical choices of the substrate are sapphire and diamond.

3) Thermistor. This is a semiconductor device whose resistance is an extremely strong function of temperature, at low temperatures. Neutron Transmutation Doped (NTD) germanium is usually used.

A schematic diagram of a bolometer is drawn in figure 1.1.





A bolometer functions in the following manner. Electro magnetic radiation strikes the absorber, and the energy of the photon is converted to thermal energy. This thermal energy heats the substrate and in turn heats the thermistor, which changes its resistance. This change in resistance can be measured by a high gain amplifier and thus the electrical output of the device is proportional to the bolometeric intensity of the photon source, hence the name "bolometer". For the bolometer to operate effectively it must be operated at low temperatures. The bolometers in the BAM telescope operate at a temperature of approximately 300mK. Another requirement for successful bolometer operation is that the bolometer be in poor thermal contact with its surroundings. If the thermal contact between the bolometer and its environment were good, then any power absorbed by the bolometer would be immediately transmitted to the cryogenic bath, and no change in resistance would be measured.

The basic thermodynamics of bolometer operation are easily derived from first principles. We consider a body with heat capacity C in weak thermal contact with a cryogenic bath at temperature  $T_0$ . The thermal conductance, G, of the link is defined in the following way,

$$G(T) = -\frac{k(T)A}{\Delta x} \tag{1.1}$$

where k(T) is the thermal conductivity of the link, A is the cross-sectional area, and  $\Delta x$ is the length of the link. We consider only thermal conduction as contributing to the transport of heat. If the body, initially at temperature  $T_0$ , is subjected to some external source of heat W, then the physics of the system can be described by the following differential equation,

$$C\frac{d\Delta T}{dt} + G(T)\Delta T = W$$
(1.2)

where t is the time, and  $\Delta T$  is the change in temperature. The solution of equation 1.2 is,

$$\Delta T = \frac{W}{G} \left[1 - e^{-\frac{t}{\tau}}\right] \tag{1.3}$$

where  $\tau = C/G$ , and is called the thermal time constant. In general,  $\tau$  is a function of temperature since both the heat capacity of the body and the thermal conductance of the link are functions of temperature. Equation 1.3 shows that the temperature of the body will rise in an exponential fashion to an asymptotic value of T = W/G, in a characteristic time  $\tau$ .

One can see from equation 1.3 that if the heat capacity of the body is high, then the time constant will be large, and the body will respond slowly to any input of heat. Thus, one would like to minimize the heat capacity of the body in order to get a device with reasonably quick response. When designing a bolometer, one must consider the magnitudes of the heat capacity of both the absorber and the substrate, since these have a direct effect on the performance of the device. The specific heats of some common materials are listed in table 1.1.

Material	$c(\mu J/mol K)$	Debye Temperature $\Theta_D(K)$
aluminum	405	428
copper	200	343
gold	165	165
bismuth	40	119
sapphire	0.05	1034

Table 1.1: The specific heats of some materials at a temperature of 0.3K. The values are computed from the Debye equation, which provides excellent agreement with experiment.

#### **1.2 Transmission Line Analogy**

The physics of the transmission line will be developed in the following sections. The transmission line is directly analogous to many optical systems of interest. A detailed analysis of the transmission line is useful because it provides an intuitive physical picture which can be extended exactly to many optical problems.

#### 1.3 What is a transmission line?

A transmission line consists of 2 conductors in a parallel orientation, separated by an insulator[5]. Transmission lines are very common in electronics; a regular bnc cable is an example. To understand the physics of the transmission line, consider two parallel ideal

conductors (no internal resistance) as shown in figure 1.2. These conductors are connected by a resistive load  $Z_L$ , and the circuit is driven by an AC signal. For simplicity assume that  $Z_L = 0$ , and that the conductors are oriented along the z axis. The conductors, because of their proximity, are coupled by their mutual capacitance and their mutual inductance, and this gives rise to some interesting effects. Assume the conductors have mutual capacitance equal to C per unit length and mutual inductance equal to L per unit length. A thin slice dz through the conductors will have capacitance Cdz and inductance Ldz. The counter emf produced as a result of the changing current is proportional to the inductance, such that



Figure 1.2: Two parallel conductors with an ac voltage applied across the leads is all there is to a transmission line. The mutual capacitance and inductance between the two wires create some interesting effects.

$$dV = \frac{\partial V}{\partial z}dz = -Ldz\frac{\partial I}{\partial t}$$
(1.4)

The conductors are also coupled through their mutual capacitance, and the counter emf, dV, produces a current, dI, which is given by

÷ .

$$dI = \frac{\partial I}{\partial z} dz = -C dz \frac{\partial V}{\partial t}.$$
(1.5)

Eliminating dz from these equations leaves two coupled differential equations 1.6 and 1.7.

$$\frac{\partial V}{\partial z} = -L\frac{\partial I}{\partial t} \tag{1.6}$$

$$\frac{\partial I}{\partial z} = -C \frac{\partial V}{\partial t} \tag{1.7}$$

Differentiating 1.6 with respect to z and differentiating 1.7 with respect to t yields the following:

$$\frac{\partial^2 V}{\partial z^2} = -L \frac{\partial^2 I}{\partial t \partial z} \tag{1.8}$$

$$\frac{\partial^2 I}{\partial z \partial t} = -C \frac{\partial^2 V}{\partial t^2} \tag{1.9}$$

Direct substitution of equation 1.9 into 1.8 yields the following second order partial differential equation for the voltage:

$$\frac{\partial^2 V}{\partial z^2} = LC \frac{\partial^2 V}{\partial t^2} = \frac{1}{v^2} \frac{\partial^2 V}{\partial t^2}.$$
(1.10)

Equation 1.10 is readily recognized as the one dimensional wave equation. It describes the propagation of the voltage in space and time down the transmission line. A similar equation may be derived for the current:

$$\frac{\partial^2 I}{\partial z^2} = LC \frac{\partial^2 I}{\partial t^2} = \frac{1}{v^2} \frac{\partial^2 I}{\partial t^2}$$
(1.11)

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From equations 1.10 and 1.11 we see that the voltage and the current propagate down the transmission line with speed  $v = 1/\sqrt{LC}$ . For two conductors in a coaxial configuration one may derive the capacitance per unit length C to be

$$C = \frac{2\pi\epsilon}{\ln(b/a)} \tag{1.12}$$

where b is the radius of the outer conductor, a is the radius of the inner conductor, and  $\epsilon$  is the dielectric constant of the insulating material separating the conductors.

The inductance per unit length, L, is

$$L = \frac{\mu}{2\pi} ln(b/a) \tag{1.13}$$

where  $\mu$  is the magnetic permeability of the insulating material.

The speed of propagation, v, is from 1.12 and 1.13,

$$v = \frac{1}{\sqrt{LC}} = \frac{1}{\sqrt{\mu\epsilon}} \tag{1.14}$$

Equation 1.14 shows that if the conductors are in vacuum and separated only by free space, such that  $\mu = \mu_0$  and  $\epsilon = \epsilon_0$ , then the speed of propagation will be  $v = 1/\sqrt{\mu_0\epsilon_0}$ , which is equal to the speed of light.

The solution of equation 1.10 is composed of two traveling waves, one moving to the left and one moving to the right. The solution is of the following form:

$$V(z,t) = W_1(t - z/v) + W_2(t + z/v)$$
(1.15)

Differentiating 1.15 with respect to z yields

$$\frac{\partial V}{\partial z} = -\frac{1}{v}W_1'(t-z/v) + \frac{1}{v}W_2'(t+z/v) = -L\frac{\partial I}{\partial t}$$
(1.16)

Integrating 1.16 with respect to time yields the following equation for the current

$$I(z,t) = \frac{1}{vL}(W_1 - W_2) + constant$$
(1.17)

where the constant comes from the integration and is not of interest for the traveling wave solution. The impedance of the transmission line can be derived by taking the ratio of V to I for either of the traveling waves. One ends up with the so called "characteristic impedance" of the line, which is defined by the following equation,

$$Z_{line} = vL = \sqrt{\frac{L}{C}} \tag{1.18}$$

Equation 1.18 shows that the impedance of an ideal transmission line whose ends are shorted  $(Z_L = 0)$  depends only on the mutual capacitance and mutual inductance between the conductors. The current and voltage are waves which travel at speed v along the transmission line in the positive and negative z directions.

#### 1.4 Transmission Line with a Resistive Load

In this section we will consider an ideal transmission line with a resistive load attached between the outputs. We will develop expressions for the transmission, and reflection of waves through a resistive boundary, as well as developing expressions for the power transmitted to and reflected from the load. These equations are identical to their optical counterparts. Referring to figure 1.2, the load,  $Z_L$ , is attached at z = 0, and the AC generator is attached at the inputs which are located at z = -l. As before the transmission line is ideal and has characteristic impedance  $Z_{line}$ . The traveling wave solution developed in section 1.2 consists of a wave moving to the right, and a wave moving to the left. The voltage across the load resistor will be given by the sum of the two traveling waves,

$$V(0,t) = W_1(t) + W_2(t) = V_{load}.$$
(1.19)

The current through the load must be the sum of currents entering and leaving the load and is given by

$$I(0,t) = \frac{1}{Z_{line}} (W_1(t) - W_2(t)) = I_{load} = \frac{V_{load}}{Z_{load}}.$$
 (1.20)

In these equations,  $W_1$  refers to the transmitted wave and  $W_2$  refers to the reflected wave. We may calculate the *reflection coefficient*,  $\rho$ , from 1.19 and 1.20 by taking the ratio  $W_2(t)$  to  $W_1(t)$  as follows:

$$\rho = \frac{W_2}{W_1} = \frac{Z_{load} - Z_{line}}{Z_{load} + Z_{line}}.$$
 (1.21)

The transmission coefficient,  $\tau$ , can be calculated by taking the ratio of the load voltage,  $V_{load}$ , to the transmitted wave  $W_1$ ,

$$\tau = \frac{V_{load}}{W_1} = \frac{2Z_{load}}{Z_{load} + Z_{line}}.$$
(1.22)

From equations 1.21 and 1.22 we can see that if  $Z_{load} = Z_{line}$ ,  $\rho = 0$  and  $\tau = 1$ . This corresponds to no reflected wave, and the load impedance,  $Z_{load}$ , is said to be *impedance* matched to the transmission line. If  $Z_{load} = \infty$ , as would be the case for an open circuit,

$$\lim_{Z_{load} \to \infty} \rho = \frac{1 - Z_{line}/Z_{load}}{1 + Z_{line}/Z_{load}} = 1, \qquad (1.23)$$

and we see that there is only reflection from the boundary and no transmission. In the case of a short circuit,  $Z_{load} = 0$ ,  $\rho = -1$ , and again there is only reflection.

The power in the transmitted component of the wave is  $P_+ = I_+W_+ = W_+^2/Z_{line}$ , while the power in the reflected component of the wave is  $P_- = W_-^2/Z_{line}$ . The fractional reflected power,  $P_{ref}$ , is the ratio of  $P_-$  to  $P_+$ , which is

$$P_{ref} = \frac{P_{-}}{P_{+}} = \rho^2. \tag{1.24}$$

From conservation of energy, the power transmitted to the load resistor must be,

$$P_{trans} = 1 - P_{ref} = 1 - \rho^2. \tag{1.25}$$

### 1.5 Sinusoidal Input Signal

Thus far the results obtained have been in general applicable to any type of AC input signal. Special consideration of the case where the input signal is sinusoidal in nature warrants some attention, since the sinusoidal driving voltage is so commonplace. In particular, let us consider the case where the voltage applied to the transmission line varies according to the following equation,

$$V(-l,t) = V\cos(\omega t). \tag{1.26}$$

The voltage on the line will again be the sum of two traveling waves. In phasor notation the voltage V(z,t) on the transmission line will be,

$$V(z,t) = W_1 e^{-i\beta z} + W_2 e^{i\beta z}$$
(1.27)

where  $W_1 = |W_1|$  and  $W_2 = |W_2|e^{i\theta_p}$ , and  $\beta = \omega/v$ . The phase shift,  $\theta_p$ , could be applied to either  $W_1$  or  $W_2$ . The current on the line will be given by,

$$I(z,t) = \frac{1}{Z_{line}} (W_1 e^{-i\beta z} - W_2 e^{i\beta z}).$$
(1.28)

The transmission and reflection coefficients for this system remain exactly the same as previously derived.

Since we have assumed a definite form for the driving voltage, we may now calculate the input impedance. This is the impedance seen by the generator(located at z = -l) looking down the transmission line at the load(located at z = 0). The impedance at any point on the transmission line can be found by taking the ratio of V(z,t) and I(z,t).

#### Chapter 1. Introduction

Dividing equation 1.27 by equation 1.28 one can obtain,

$$Z(-l,t) = Z_{line} \frac{e^{i\beta l} + \frac{W_2}{W_1} e^{-i\beta l}}{e^{i\beta l} - \frac{W_2}{W_1} e^{-i\beta l}}.$$
(1.29)

The ratio  $W_2/W_1$  is the reflection coefficient,  $\rho$ , from equation 1.21. Substituting for  $\rho$  in equation 1.29 yields the following expression for the input impedance,

$$Z(-l,t) = Z_{line} \frac{Z_{load} \cos(\beta l) + i Z_{line} \sin(\beta l)}{Z_{line} \cos(\beta l) + i Z_{load} \sin(\beta l)}.$$
(1.30)

As a check of the result 1.30, the impedance at z = 0 should be just the load impedance,  $Z_{load}$ . Setting l = 0 in equation 1.30 shows that this is indeed the case. It is worth noting that if  $\omega = 0$ , as for a DC signal, then the input impedance as seen from the generator will just be the load impedance,  $Z_{load}$ . This makes sense since we have assumed that the transmission line is composed of ideal conductors.

One can define a quantity called the *admittance*, Y(z,t), by defining  $Y_{load} = 1/Z_{load}$ , and  $Y_{line} = 1/Z_{line}$ . Then the admittance as seen from the generator is,

$$Y(-l,t) = Y_{line} \frac{Y_{load} cos(\beta l) + iY_{line} sin(\beta l)}{Y_{line} cos(\beta l) + iY_{load} sin(\beta l)}.$$
(1.31)

#### 1.6 Transmission Line With a Resistive Short

Now we consider the situation depicted in figure 1.3.

The transmission line is shorted by a resistive impedance  $Z_L$ . The resistive short and the rest of the line act like impedances in parallel, with equivalent impedance  $Z_{tot} = Z_L Z_{line}/(Z_L + Z_{line})$ . The fractional power delivered to such a load will be given by equation 1.25, and is,

$$P_{trans} = 1 - \left(\frac{Z_{line}}{2Z_L + Z_{line}}\right)^2. \tag{1.32}$$

One can see from equation 1.25 that if  $Z_L = 0$ , the line is shorted, and no power is transmitted to the load. Taking the other extreme, if  $Z_L = \infty$ , the transmission line is no longer shorted, and all the incident power is transmitted to the rest of the line.



Figure 1.3: A transmission line with a resistive impedance connected between the terminals. Consider the transmission line to be of infinite length.

The power dissipated in the resistive short will be  $P_L = W_1^2/Z_L$  and the power dissipated in the rest of the line will be  $P_{line} = W_1^2/Z_{line}$ . Taking the ratio  $P_L$  to  $P_{line}$ , we find,

$$\frac{P_L}{P_{line}} = \frac{Z_{line}}{Z_L}.$$
(1.33)

From equation 1.32, we notice that if  $Z_L = Z_{line}/2$ , then the fractional transmitted power will be 75%, and the fractional reflected power will be 25%. Half as much power will be dissipated in the load impedance as in the line.

### 1.7 Relation to Optics

Thus far we have only considered the transmission line in relation to the analysis of electrical circuits. However, it turns out that many optical problems can be formulated in terms of the transmission line analogy. To see this, we note that Maxwell's equations lead to the following equation for the electric field,

$$\frac{\partial^2 E_x}{\partial z^2} = \mu \epsilon \frac{\partial^2 E_x}{\partial t^2} \tag{1.34}$$

which is the one dimensional wave equation. The solution of this equation is composed of two traveling waves, given by,

$$E_x(z) = E_+ e^{-jkz} + E_- e^{jkz}.$$
(1.35)

Similarly, the magnetic field is composed of traveling wave solutions of the form,

$$H_y = \sqrt{\frac{\epsilon}{\mu}} [E_+ e^{-jkz} - E_- e^{jkz}]$$
(1.36)

Equations 1.35 and 1.36 have the same form as the equations derived previously for the voltage and the current on a transmission line(equations 1.27 and 1.28). In fact, one can transform exactly between the two sets of equations if one makes the following substitutions:  $V = E_x$ ,  $I = H_y$ ,  $L = \mu$ ,  $C = \epsilon$ , and  $\sqrt{\mu/\epsilon} = Z_0$ . The quantity  $\eta = \sqrt{\mu/\epsilon}$  is the ratio of the electric field to the magnetic field, and has units of ohms. It is typically called the characteristic impedance of the medium. For example, the characteristic impedance of free space is  $\eta = \sqrt{\mu_0/\epsilon_0} = 377\Omega$ .

All the equations previously derived for the reflection coefficient, transmission coefficient, admittance, etc. can be used for electro magnetic waves, provided we make the substitutions described above. In particular, the transmission line with a resistive short provides a useful model of a bolometer. Consider light traveling through free space, incident on a resistive short of characteristic impedance  $Z_L$ . This is exactly analogous to the situation described in the previous section, except we make the substitution  $Z_{line} = \eta = 377\Omega$ . Maximum power will be absorbed in the resistive short when  $Z_L = 377\Omega/2 = 188.5\Omega$ , and thus we strive to produce an absorbing layer with sheet resistance  $188.5\Omega/\Box$  at low temperatures.

#### Chapter 2

#### **Electrical Properties of Metals and Thin Films**

#### 2.1 Metals, Insulators, Semiconductors and Semi-metals

The electrical properties of many materials can be analyzed successfully in terms of band theory. In this theory the interactions between the electrons in a material and the crystal lattice cause the energy spectrum of the electrons to be broken up into discrete levels called *bands*. The electrons are only allowed to occupy certain discrete states within these energy bands, and these states correspond to discrete values of the electron wave-vector  $\vec{k}$ . There are no available states in between bands. The gap in energy between these allowed bands is called the *band gap*, and corresponds to forbidden zones.

The number of available states in k space in each energy band can be calculated quite easily[6]. We consider a one dimensional chain of atoms of length L. The spacing between adjacent atoms is a, and this is called the lattice constant. The energy gaps occur for values of  $k = n\pi/a$ , where n is any positive or negative integer, and thus the width of an energy band is  $\pi/a$ . The wave-vector can only take on discrete values inside an energy band. These discrete values are  $|k| = 2\pi n/L$ . The number of available states in an energy band is  $\frac{L}{a}$ , where the negative values of the wave-vector have been accounted for. Allowing for spin degeneracy, since we are allowed to pack 2 electrons into every state k, gives

$$\# \text{ of states} = 2\frac{L}{a} = 2N, \qquad (2.37)$$

where the quantity N is the number of atoms per unit length. The extension to three

dimensions is straightforward, and gives the same result. Equation 2.37 shows that there are two allowed states for every atom in the crystal. This is an important result, since now we can predict the electrical qualities of a material given the number of valence electrons per atom. If a material has two valence electrons, then all available states will be filled. The electrons in a filled band have no empty states in which to move, and an electric field applied to the crystal will produce no net electron flow. Such a material is said to be an *insulator*. On the other hand, if there is only one valence electron per atom, the highest energy band will only be half filled, and the substance will be a *conductor*. This general rule applies very well to most of the elements in the periodic table, however, there are some very important exceptions. Silicon and germanium each have two valence electrons per atom, and should be electrical insulators. At low temperatures this is true for very pure samples. At higher temperatures, however, these substances exhibit a resistivity which is an exponential function of temperature. For this reason, these materials are called semi-conductors.

The behavior of a semiconductor can be understood in terms of band theory. In an insulator, the band gap is large, and there is no way to introduce a transition from a lower energy band to a higher energy band. In a semi-conductor, the band gap is small enough that electrons in the lower energy band can be thermally excited to occupy states in the higher energy band. Thus at higher temperatures, there are available states for the electrons to jump to, and the material is a conductor. The conductivity of a semi-conductor will be governed by the distribution function of the electrons, which varies exponentially with temperature. At low temperatures, the electrons fill the lowest energy band, and since the electrons do not have enough thermal energy to make the transition to the higher band, the material is an insulator.

The conduction in semi-conductors is actually determined by the motion of two types of carriers. When an electron makes the transition from a lower energy band to a higher one, it leaves an unfilled state in the lower energy band. This unfilled state is not very surprisingly called a *hole*. Since the lower band now has an extra state, which other electrons may occupy, the conduction of the material increases. The hole in the lower energy band acts like a particle with a charge opposite to that of the electron, and will move in the opposite direction to an electron if an electric field is applied. Thus, the movement of the hole contributes to the current of the material. The total current will be the sum of the hole current and the electron current,

$$\vec{j} = \vec{j_h} + \vec{j_e} = n_h q_h \vec{v_h} + n_e q_e \vec{v_e}.$$
(2.38)

If we treat the holes as particles which can undergo collisions, the average velocity in response to an electric field will be given by  $v_h = q_h E \tau_h / m_h$ , and we can write

$$\vec{j} = [+n_h \vec{v_h} - n_e \vec{v_e}] e, \qquad (2.39)$$

since the holes and electrons have an opposite charge. The holes and electrons will move in opposite directions, and equation 2.39 can be written in the following way,

$$\vec{j} = \left[\frac{n_h e^2 \tau_h}{m_h} + \frac{n_e e^2 \tau_e}{m_e}\right] \vec{E}.$$
(2.40)

From the Free Electron Theory, one can derive [7] a value of the conductivity of  $\sigma = ne^2\tau/m$ , where  $\tau$  is the average time between collisions, n is the number of electrons, e is the electronic charge, and m is the free electron mass. With this in mind, we see that the terms on the right hand side of equation 2.40 are just the conductivities of the holes and the electrons, respectively. Equation 2.40 is clearer is if we write the conductivity in terms of the *mobility* of the carriers, which is defined as  $\mu = e^2\tau/m$ . Using this definition, equation 2.40 becomes,

$$\vec{j} = [n_h \mu_h + n_e \mu_e] \vec{E}.$$
(2.41)

Thus, the current in the material will be determined by the *number densities* and the *mobilites* of the carriers. The resistivity is found by taking the ratio of the electric field to the current density. Doing this, we find that the conductivity and the resistivity are related in the following way for a two carrier system,

$$\rho = \frac{1}{\sigma} = \frac{1}{n_h \mu_h + n_e \mu_e}.$$
(2.42)

We conclude by stating that the resistivity depends inversely on the number densities and the mobilites of the carriers in the material.

#### 2.2 Semi-metals

A semi-metal is a material which has metallic properties, but is distinguished from other metals by its low conductivity. The semi-metal elements are Bi, As, and Sb. Of the three elements, bismuth has the highest resistivity. The reason the resistivity is so high for these elements is due to a couple of intriguing effects. The crystal structure of these three elements is the same, and is referred to as hexagonal rhombic. The hexagonal rhombic structure can be obtained from the simple cubic structure by making a couple of slight distortions. It is these distortions which are responsible for the strange behavior of semi-metals. If the crystal structure of these materials was simple cubic, the Fermi Surface would be spherical, and these elements would exhibit a much lower resistivity. The slight distortion of the crystal lattice causes the Fermi Surface to become ellipsoidal, and causes the conduction and valence bands to overlap. The resulting Fermi Surface consists of three small pockets of electrons, and one small pocket of holes. This is the fundamental reason why the behavior of semi-metals differs from that of normal metals. The tremendous reduction of the carrier density compared to a good conductor such as aluminum causes the conductivity to be lower in the semi-metals. The conduction in a semi-metal is highly anisotropic with respect to the crystal axes. This is due to the anisotropy of the Fermi Surface. One refers to the *effective mass* of the carriers, which is defined by the following equation[7],

$$m^* = \hbar^2 \left(\frac{\partial^2 E}{\partial k^2}\right)^{-1} \tag{2.43}$$

where E is the energy and k is the wave-vector. The effective mass depends on the second derivative of the energy in the band with respect to the wave-vector. If this derivative is negative, then the effective mass will be negative, and the carrier is no longer an electron, but a hole. The reason the effective mass is a useful quantity is because the carriers in a material, when under the influence of an electric field, move as if they had a mass defined by equation 2.43. In general the effective mass is a tensor quantity given by the following relation,

$$\left(\frac{1}{m^*}\right)_{\mu\nu} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_\mu \partial k_\nu}.$$
(2.44)

The effective masses for the carriers in bismuth have been measured, and are in general quite a bit lower than the mass of the free electron. The values for the effective masses in bismuth are tabulated in table 2.2, in units of the free electron mass  $(m_0)$ .

$m_{11}$	$m_{22}$	$m_{33}$	$m_{23}$
0.00113	0.26	0.00443	-0.0195
0.000521	1.20	0.0204	-0.090

Table 2.2: The effective masses in bismuth, after Smith *et al.* [1]. The top row are the masses at the bottom of the band, while the bottom row are the masses at the Fermi energy,  $\epsilon_F$ .

The effective masses are positive in three directions of the crystal, which correspond to conduction by electrons, and negative in one direction, which corresponds to conduction by holes. The carrier density has also been measured by Smith *et al.*[1], and found to be  $N_{bi} = 2.75 \times 10^{17} cm^{-3}$ , at room temperature. This carrier density is much lower than that

of a normal metal like aluminum, which has a carrier density of  $N_{al} = 18 \times 10^{22} cm^{-3}$ . In general, all the semi-metals have lower carrier densities and lower effective masses than normal metals do.

#### 2.3 Fermi Energy and Fermi Surface

The Fermi Surface is the boundary between occupied and unoccupied states at absolute zero. All the wave-vectors with magnitudes less than or equal to the Fermi wave-vector,  $\vec{k}_F$ , represent occupied states. At absolute zero, all the electrons occupy the ground state. The low carrier densities and the low effective masses in the semi-metals combine to produce materials with very low Fermi Energies. If the Fermi Surface of the material is spherical, the Fermi energy is given by the following equation[7],

$$\epsilon_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right). \tag{2.45}$$

The Fermi energy of a metal is typically quite high, and this is due to the high carrier density. For example, the Fermi energy of aluminum is  $\epsilon_F = 11.3 eV$  (assuming a spherical Fermi energy surface). We may define the Fermi Temperature,  $T_F$ , in the following way,

$$T_F = \frac{\epsilon_F}{k_B} \tag{2.46}$$

where  $k_B$  is Boltzmann's constant. With this formula, the Fermi Temperature of aluminum is  $T_F = 134500K$ . This Fermi Temperature has nothing to do with the actual temperature of the electrons. It basically represents the ground state energy, and equivalent temperature, of the electrons in a material.

In general, the Fermi Surface of most metals and semi-metals is non spherical, and equation 2.45 does not apply. The low carrier densities and low effective masses of the carriers in bismuth combine to give it a very low Fermi energy. The Fermi energy of bismuth has been measured by Smith *et al.*[1], and found to be  $\epsilon_F = 0.027 eV$ . From this, one derives a Fermi Temperature of  $T_F = 320K$ , which is substantially lower than that of aluminum. The low value of the Fermi Energy means that the distribution of carriers can be changed substantially by temperature changes in the range of the Fermi Temperature. Since electrons and holes are fermions, the Fermi-Dirac distribution function applies. The distribution function for fermions is defined as follows,

$$f_e = \frac{1}{exp\left[\frac{\epsilon - \epsilon_F}{k_b T}\right] + 1} \tag{2.47}$$

where  $\epsilon$  is the energy of the fermions, and T is the temperature. This distribution is a step function at absolute zero (T = 0), with the location of the step being at the Fermi Energy. The distribution of the holes created by thermal excitation of electrons in a material must be related to the electron distribution. In fact, the distribution function of holes is given by the following equation, which seems quite intuitive,

$$f_h = 1 - f_e. (2.48)$$

Equation 2.47 shows that the distribution of electrons in a material is a function of the temperature of the system. The distribution functions for electrons and holes in bismuth are plotted in figure 2.4. Figure 2.4 shows that there are a substantial fraction of electrons with energies higher than the Fermi Energy, when the temperature of the system is 50K. With a material like aluminum, which has a very high Fermi Energy, the distribution functions of the carriers are not modified appreciably by changes in the temperature of the system.

The mean free path of the electrons on the Fermi Surface is a quantity of interest. It may be calculated from the following equation, after Kittel[7],

$$\Lambda = \frac{(2m\epsilon_F)^{1/2}}{\rho N e^2}.$$
(2.49)

Approximating the effective mass of bismuth with  $m^* = 0.01m_0$  and using the previously quoted value of the Fermi Energy yields a mean free path of  $\Lambda_{Bi} = 10,900$ Å at room



Figure 2.4: The distribution functions for electrons $(f_e)$  and holes $(f_h)$ , plotted for a material at 50K with a Fermi Energy of 0.027eV. As the temperature tends toward absolute zero, the distributions become step-like in nature.

temperature. A similar calculation for aluminum yields a mean free path of  $\Lambda_{Al} = 143$ Å. The long mean free path of the carriers in bismuth as compared to the carriers in aluminum is due to the tremendous differences (a factor of  $10^5$ !) in the carrier concentrations.

#### 2.4 Quantum Size Effect

The quantum size effect (QSE) was first worked out by Sandomirskii[8] in 1967. The argument is as follows. When the dimensions of a material become comparable to the effective wavelength of the carriers at the Fermi Surface, the energy levels in the material will be modified. The energy spectrum, which in the bulk material consists of discrete bands, will be further quantized by the reduction in sample thickness. This quantization will modify the density of states on the Fermi Surface, and will have an effect on the mobility of the carriers. From equation 2.41, we see that the conductivity of a material depends on the carrier density of holes and electrons, and on the mobility of each carrier. So, the QSE will have an effect on the conductivity of the material, and will affect all quantities which depend on the mobility of the charge carriers.

The QSE is only observable in thin films, since the dimensions of the film may be comparable to the wavelength of the carriers at the Fermi Surface. In normal metals, the carrier wavelength is very short. For example, the carrier wavelength of aluminum is,

$$\lambda = \frac{2\pi}{k} = 2\pi \sqrt{\frac{\hbar^2}{2m\epsilon_F}} = 3.6\mathring{A}$$
(2.50)

where the value of  $\epsilon_F = 11.3 eV$  has been used. The calculation shows that quantum size effects will be observable in aluminum films when the film thickness is on the order of 3 - 4Å. In practice, however, observation of QSE in a film of this thickness would be impossible, since a film of this thickness would certainly be discontinuous, and the QSE would be masked by other effects. The situation is different for the semi-metals, which have a low Fermi Energy, and thus a longer carrier wavelength. The carrier wavelength for bismuth can be estimated from equation 2.50, using  $\epsilon_F = 0.027 eV$ , with the result that  $\lambda = 740$ Å. A bismuth film of this thickness will be continuous, and in theory, the QSE will be readily observable.

The QSE model has some special predictions in the case of a semi-metal. In the bulk material, the conduction and valence bands overlap by an amount  $\delta$ . The QSE causes the conduction and valence bands to break up into discrete sub-bands. Consider a 3D system with dimensions  $t \times L_y \times L_z$ . The dimensions in the y and z directions are to be considered infinite. The energy states of such a system are given by the following,

$$E_{s,k_y,k_z} = \epsilon_n s^2 + \hbar^2 (k_y^2 + k_z^2)/2m_n \tag{2.51}$$

where the subscript on the mass,  $m_n$ , refers to the electron mass, and s is a positive integer. The wave-vectors in the z and y directions are  $k_y = 2\pi s_y/L_y$  and  $k_z = 2\pi s_z/L_z$ ,  $s_y = s_z = 0, +-1, +-2, ...$ , and  $L_y$  and  $L_z$  are the lengths of the sides of the normalization rectangle. The quantity  $\epsilon_n$  in equation 2.51 is the quantized energy due to the QSE, and is given by

$$\epsilon_n = \frac{\hbar^2 \pi^2}{2m_n t^2} \tag{2.52}$$

where t is the thickness of the film. The energy states of the holes can be obtained from equation 2.51 by replacing the electron mass,  $m_n$ , by the mass of the hole,  $m_p$ . The QSE affects the energy states of the system in only one component of the wave-vector.

The band overlap,  $\delta$ , is equal to the sum of the Fermi Energies of the electrons and the holes,

$$\delta = \epsilon_n + \epsilon_p. \tag{2.53}$$

A very intriguing prediction of the QSE model is the so-called semi-metal to semiconductor (SMSC) transition. The band overlap,  $\delta$ , is a function of the thickness of the film, and decreases as the film thickness decreases. This is due to the movement of the electron band upwards and the hole band downwards. At some critical thickness,  $t \leq a$ , the electron and hole bands will no longer overlap. The result is a band gap of magnitude  $\epsilon_g = \delta(a^2/t^2 - 1)$ , and the material is no longer a semi-metal, but is a *semiconductor*. This transition will occur at a critical thickness which is equal to  $a = \pi \hbar/\sqrt{2M\delta}$ , where  $M = m_n m_p/(m_n + m_p)$ . This critical thickness is approximately 400Å for bismuth. Films thinner than this are expected to exhibit semiconductor properties, while films thicker than this maintain an overlap in energy, and are semi-metals.

The QSE model makes several other quantitative predictions. According to the theory, the electrical conductivity of thin semi-metal films will be an oscillatory function of the thickness. These oscillations have been reported by several groups[9][10][11]. The conductivity is found to oscillate with a period of approximately 400Å, which is in good agreement with the theory[8]. The Hall coefficient and the magneto-resistance coefficient should also display oscillatory behavior, and these have been observed by the same groups.

#### 2.5 Surface Scattering

The Fuchs-Sondhiemer model attributes the higher resistivity in thin films as compared to the bulk material to the scattering of the electrons off of the surfaces of the film. The Fuchs formula is obtained by solving the Boltzmann transport equation using the relaxation time approximation[12]. The result is the following equation,

$$\frac{\sigma}{\sigma_{\infty}} = 1 - \frac{3}{8k}(1-p).$$
 (2.54)

The conductivity  $\sigma_{\infty}$  is the conductivity of the bulk material with the same defect density as the film, and  $k = t/\lambda_{\infty}$ , where  $\lambda_{\infty}$  is the mean free path in the bulk material and t is the thickness of the film. The quantity p is called the specularity parameter, and is defined as the ratio of the number of electrons reflected at angle  $\theta$  to the number of
electrons incident at angle  $\theta$ . Equation 2.54 is valid for values of k which are greater than one, which means for thick films. It has been shown, however, that equation 2.54 applies fairly well for all values of k[12]. Writing equation 2.54 in terms of the resistivities, and using the binomial expansion formula and keeping only first order terms, we find

$$\rho = \rho_{\infty} \left[ 1 + \frac{3}{8k} (1-p) \right] = \rho_{\infty} \left[ 1 + \frac{3\lambda_{\infty}}{8t} (1-p) \right].$$
 (2.55)

Multiplying both sides of equation 2.55 by the thickness, t yields

$$\rho t = \rho_{\infty} t + \frac{3\lambda_{\infty}\rho_{\infty}}{8}(1-p).$$
(2.56)

A plot of  $\rho t$  vs t should yield a straight line of slope  $m = \rho_{\infty}$  and intercept  $b = \frac{3\lambda_{\infty}\rho_{\infty}}{8}(1-p)$ . This formula has been applied to the data appearing in chapters 4 and 5 of this thesis.

# 2.6 Grain Boundary Scattering

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The grain boundary scattering model of Mayadas and Shatzkes [13] attributes the increase in resistivity of a thin film as compared to the bulk material to scattering of electrons off of the grain boundaries. The model represents the grain boundaries as N parallel, partially reflecting planes, randomly distributed throughout the material. The average distance between the planes is d, and this can be taken as the average grain diameter. The Boltzmann transport equation was solved with the assumption that the average time between collisions can be represented by a relaxation time,  $\tau$ . It is assumed that grain boundary scattering obeys Matthiessen's rule, and that the following equation holds;

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_{grains}},\tag{2.57}$$

where  $\tau_0$  is the average time between collisions for the normal processes which give rise to the resistivity of a metal. With these assumptions the ratio of the conductivity of the film to the conductivity of the bulk material depends on the following equation,

$$\frac{\sigma_g}{\sigma_0} = 3\left[\frac{1}{3} - \frac{1}{2}\alpha + \alpha^2 - \alpha^3 ln\left(1 + \frac{1}{\alpha}\right)\right].$$
(2.58)

The parameter  $\alpha$  in equation 2.58 is defined in the following manner,

$$\alpha = \frac{\lambda_0}{d} \frac{R}{1-R} \tag{2.59}$$

where R is the grain boundary reflection coefficient, and  $\lambda_0$  is the mean free path in the bulk material. In terms of the resistivities, equation 2.58 becomes,

$$\frac{\rho_g}{\rho_0} = \frac{1}{3\left[\frac{1}{3} - \frac{1}{2}\alpha + \alpha^2 - \alpha^3 ln\left(1 + \frac{1}{\alpha}\right)\right]} = \frac{1}{f(\alpha)}.$$
(2.60)

A considerable simplification of this result was noticed by De Vries[14]. For values of  $\alpha \geq 3.5$ , the following formula provides only 5% deviation from the original function:

$$f(\alpha) = \frac{1}{1.39\alpha + 1}.$$
 (2.61)

The ratios of the resistivities can now be written as,

$$\frac{\rho_g}{\rho_0} = \frac{1}{f(\alpha)} = 1.39\alpha + 1,$$
(2.62)

which should apply for larger values of  $\alpha$ . The contribution of grain boundary scattering to the resistivity depends on three independent parameters,  $\lambda_0$ , R, and d. Variations in any of the three parameters can cause a higher resistivity than that observed in the bulk.

# 2.7 Concluding Remarks

The Fermi Temperature of metals is in general quite high due to the high carrier concentration. The physical result of this is that the energy distribution of the carriers is not changing appreciably with temperature, in the temperature range 300K - 4.2K. Mathematically this can be stated as follows:  $\epsilon_F >> kT$ . Thus, the conductivity of a metal in this temperature range is governed almost exclusively by changes in the mobilites of the carriers. The mobilites of the carriers in the bulk material are affected by thermal distortions of the lattice (lattice vibrations), scattering off of crystal dislocations, scattering off of lattice imperfections, and scattering off of impurities. The motion of the atoms in the crystal lattice is due to thermal excitation, and the contribution to the scattering will be *temperature dependent*. The other scattering processes are *temperature independent*. Matthiessens's rule states that the total resistivity of the material will be the sum of the scattering contributions of both these terms, such that

$$\rho = \rho_i(T) + \rho_0. \tag{2.63}$$

In general, the temperature independent term,  $\rho_0$ , dominates at low temperatures while the temperature dependent term,  $\rho_i$ , is an approximately linear function of T from room temperature to 77K, then in general varies as  $T^5$  at low temperatures. As the dimensions of the material become comparable to the mean free path of the carriers on the Fermi Surface, additional scattering effects can contribute to the resistivity. In particular, scattering from the surfaces of the film and scattering from the boundaries of the grains in the film will increase the resistivity of the film compared to that of the bulk. These effects never change the character of the resistivity - temperature profile, meaning that the temperature dependent part of the resistivity is not affected by these additional scattering contributions. This can be seen from the data for vapor deposited aluminum, which appears in chapter 5. The bulk data and thin film data essentially differ only by a constant offset on the y axis. This indicates that these additional scattering processes are not temperature dependent for metals.

The situation for semi-metals is different. The resistivity of a semi-metal is higher than that of a normal metal, and this is due to the lower carrier concentration. Experimentally, the temperature dependence of the resistivity of bulk bismuth is well described

# Chapter 2. Electrical Properties of Metals and Thin Films

by Matthiessens's rule, and the temperature dependent part of the resistivity decreases nearly linearly with decreasing temperature. This is the same behavior as observed in metals, and indicates that the dominant scattering process at higher temperatures in bulk bismuth is electron-phonon scattering. However, the temperature dependence of the resistivity of thin films of bismuth is completely unlike that of the bulk material. In particular, the resistivity of a thin bismuth film increases as the temperature decreases, and becomes approximately constant at lower temperatures. Anticipating our conclusions somewhat, which are developed more fully in chapter four, we surmise that this anomalous behavior may be due to a combination of scattering of the carriers off of grain boundaries, and changes in the energy distribution of the carriers as a function of temperature. Further discussion of this effect is deferred until chapter four, where the experimental data is interpreted in terms of this model.

# Chapter 3

# Growth of Thin Films

## 3.1 Equipment

A major part of this thesis involved the growth of bismuth films on sapphire substrates. There are several different ways to grow a thin film on a substrate, but the films produced in the present work were made by thermal evaporation. The method for producing the films will be discussed, and the theory of thin film growth will be briefly touched upon in this chapter.

## **3.1.1** Thermal Evaporation

Thermal evaporation is a common and inexpensive technique for producing thin films. The substance to be evaporated is placed in a resistance heater inside a vacuum chamber and heated until melting. Vapor atoms of the condensate collect on the surface of the substrate with a speed depending on the location of the substrate in relation to the resistance heater, and the temperature of the resistance heater. Evaporation may be stopped immediately by use of a mechanical shutter which may be moved in front of the substrate. The speed of deposition and deposition thickness are often measured using a commercially available crystal thickness monitor. This device measures the fundamental frequency of oscillation of a quartz crystal, which changes slightly with the amount of material deposited on it. The crystal monitor is placed as close to the substrate as possible during evaporation to accurately measure the thickness of the deposited film. Precision of a few angstroms is easily attainable with such a device. The substrate is cleaned inside the chamber during pump down by a device called a glow discharge. This is a high voltage rod which discharges electrically inside the chamber during pump down, ionizing all the remaining air in the chamber. This ionized air pulverizes everything in the chamber and removes excess material from the surface of the substrate. The thermal evaporator is typically operated at pressures of  $1 - 2 \times 10^{-6}$  torr. This pressure is easily attainable with the use of a diffusion pump and a liquid nitrogen cooled cold trap.

The substance to be evaporated is placed in a tungsten boat, which is then placed between two poles of a transformer. Passing current through the boat causes it to heat up, which in turn heats the material inside the boat. Tungsten is used because of its high melting temperature (3653K). If the substance to be evaporated is in the form of solid pellets, like bismuth or indium, a tungsten boat or crucible may be used. The advantage of the crucible over the boat is that the evaporate is kept at a more uniform temperature. If the substance to be evaporated is in the form of a wire, such as gold, then it may be twisted around a wire filament. When current is passed through the filament the evaporate melts and covers the entire length of the filament, thereby increasing the effective surface area of the evaporating material.

The speed of deposition is controlled by the amount of current passing though the boat or filament. It is often not necessary to work out how much power is needed to bring a sample up to its melting temperature. By slowly increasing the amount of current passing through the sample holder and watching the thickness monitor, the deposition speed can be controlled with some precision.

# 3.2 Properties of Thin Films

The physical properties of a thin film often depend heavily upon the procedure used to produce the film. Films produced by MBE are usually highly ordered and low defect in nature - those produced by thermal evaporation can be highly disordered with many defects. The deposition rate, substrate temperature, cleanliness of the substrate, purity of the evaporate, and quality of the vacuum can all have a major effect on the physical properties of the thin film. In this section the theory of thin film growth will be briefly discussed.

#### 3.2.1 Thin Film Growth

Electron microscopy has been done in situ during the growth of a thin film by a number of investigators (see the book by Chopra[15] for a comprehensive review). These experiments have revealed that thin film growth proceeds in a number of distinct steps. Atoms arriving on the surface of the substrate from the vapor phase are usually quite hot, as they have more or less the same temperature as the source from whence they came. When they encounter the surface of the substrate, which is presumably at a lower temperature than that of the atom source, they do not immediately lose all their energy. They are free to roam around on the surface of the substrate for a short time and if they do not lose any energy in that time, then they will re-evaporate and rejoin their companions in the vapor phase. The probability that an atom will re-evaporate is given by [12]

$$W = \nu exp^{\frac{-Q_{ad}}{kT}} \tag{3.64}$$

where  $\nu$  is the vibrational frequency of the atom and  $Q_{ad}$  is the energy of adsorption. The atom will lose energy if it collides with any point defects or crystal dislocations on the substrate, and SEM pictures reveal that it is these locations where thin film growth begins. Atoms will also lose energy in colliding with other atoms on the surface, and this begins the next stage of film growth. The atoms coalesce into small nuclei called "islands". These islands smatter the surface of the substrate and provide further growth centers for incoming atoms. The size of these islands is something that is specific to each material being evaporated, and depends on a number of things e.g. the surface energy of the substrate and the energy of the incoming atoms. These islands grow larger and larger until a critical radius is reached. Islands larger than this radius will break up into two or more islands of smaller radius, and the process will begin again. The islands will eventually become so numerous that contact between two or more islands will be inevitable. The islands do not join together in a contiguous manner, but jam together in random orientations. This gives rise to the notion of a grain - the boundaries of the grains are simply the edges of all the other islands around it. In this way, the surface of the substrate will eventually be covered to give a continuous thin film.

Several factors can have an effect on the growth of a thin film. If the rate of incoming atoms is quite high, then an atom will have less time to roam the surface of the substrate before it meets another atom. Island formation will occur sooner, and this process will generally result in a film with a large number of small-sized grains. A film with a slower growth rate has more of an opportunity to form large grains, and we expect to see fewer but larger grains in a slowly deposited thin film. The substrate temperature can have a large effect on the properties of the film. A striking example is shown by Komnik et. al[16]. Thin films of bismuth were grown on substrates at 4 K. Such a procedure is known as quenching the substrate. One expects that nearly every atom which strikes the surface will stick, and will produce a film with very small grains. The result was a super-conducting film, with a critical temperatures in the range  $T_c = 4 - 8K$ . This is quite striking indeed, since bulk bismuth is not super-conducting above temperatures of 10mk[17]. If the lattice constants of the substrate and those of the material being evaporated match quite closely (typically within 1 percent), then epitaxial growth may occur. The temperature of the substrate plays an important role in this process, as epitaxy is usually poor or non-existent if the temperature is too low. This critical temperature is different for every pair of materials, and is determined largely by trial and error. It is known that bismuth grows epitaxially on mica, but only if the substrate is held at a constant temperature of 100 C[3][10].

Pictures of a bismuth film taken with a Scanning Electron Microscope (SEM) reveal the grain structure of the film quite nicely, and this is shown in figures 3.5 and 3.6. The film in these pictures has a thickness of 2000Å, and was grown at a rate of  $1\text{\AA}/s$ . The substrate is sapphire. The temperature of the substrate was not controlled during the deposition. SEM photos of a very thin bismuth film were also taken, and these are shown in figure 3.7. The thickness of this film was  $15\text{\AA}$ . The photo shows some small, bright dots smattering the surface of the substrate. These spots are presumably insulating in nature, since the brightness is due to the accumulation of charge at those points. These may be due to oxidation of the film. Also visible are small clumps, which seem to be bismuth islands in the early stages of growth.



Figure 3.5: An SEM photo of a 2000Å bismuth film grown on a sapphire substrate. The magnification in this image is 10 000 times. The tick marks on the bottom right indicate the scale of the photo.



Figure 3.6: An SEM photo of a 2000Å bismuth film magnified 30 000 times. The crystallites are clearly visible, and the disordered nature of the film is apparent.



Figure 3.7: A picture of a discontinuous bismuth film. The dark clumps are bismuth islands in the early stages of growth. The bright dots may be due to the formation of an oxide.

The longest dimension of the crystallites in figure 3.6 were measured, and the average was found to be  $x = 188 \pm 50 nm$ . This seems consistent with the data of other investigators, whose results show that the average size of the grains in bismuth scales roughly with the thickness of the film[10]. These photos clearly show the disordered structure of the film.

It is not known if bismuth grows epitaxially on sapphire. The crystal structures of the two materials are both hexagonal rhombic, although the space groups are not identical. The space group (SG) of bismuth is  $R\overline{3}m(166)$  while the space group of sapphire(corundum) is  $R\overline{3}c(167)$ . The lattice constants match pretty closely, as shown in the following table:

Substance	$a_0$	$b_0$	$c_0$
Bi	4.5459	4.5459	11.8622
$Al_2O_3$	4.7591	4.7591	12.9894

Figure 3.8: A comparison between the lattice constants of sapphire and bismuth.

The greatest mismatch is between the lattice constants in the c direction, which amounts to 8.7%. If the film is grown in the a-b plane of the substrate, then the lattice mismatch is 4%. This may be too great of a mismatch for epitaxial growth.

## **3.3** Effect of Pressure on Growth

The ambient pressure in the vacuum chamber has a large effect on the growth of the film. This was discovered somewhat accidentally, as a film was deposited in an ambient pressure of  $1.7 \times 10^{-4} Torr$ . The ambient pressure was high because one of the electrical feedthroughs used in the experiment developed a vacuum leak during pump down. When the ambient pressure is around  $1.0 \times 10^{-6} Torr$ , there is a mono-layer per second of air molecules striking the surface of the substrate. One can usually observe the pressure

rising in the bell jar when the evaporation is begun, which indicates that the evaporate source is heating up and outgassing inside the chamber. When the quality of the vacuum is low, the film will be subject to a large amount of impurities, and these impurities may adversely effect the electrical properties of the film. The effect of poor vacuum is shown in figure 3.9. The straight vertical line at t=0 hrs results from the use of the Hewlett-Packard digital multi-meter used to measure the resistance of the sample. When the meter is on the setting "4 wire resistance", and the sense leads are not connected, the reading on the multi-meter is  $0.004\Omega$ . As the evaporation proceeds, the sense leads become connected, and the multi-meter starts measuring the resistance of the evaporated film. The resistance of another sample was measured during and after deposition for an



Figure 3.9: The resistance of a bismuth film was measured during and after deposition. The ambient pressure in the bell jar was  $1.7 \times 10^{-4} Torr$ . The film is oxidizing inside the chamber, and thus its resistance is increasing with time.

ambient pressure of  $3.4 \times 10^{-6}$  Torr. This data is shown in figure 3.10. The resistance decreases with time, and this is due to the cooling of the film. From this data we can state a general rule of thumb : better films are grown in lower ambient pressures. From the data in figure 3.10, it is evident that successful growth can be carried out at a pressure of  $3.4 \times 10^{-6}$  Torr. This pressure is not extremely low, and certainly nowhere near the limiting pressure for an oil pumped chamber of  $2 \times 10^{-7}$  Torr.



Figure 3.10: The resistance of a bismuth film during and after deposition. The actual evaporation only lasted for 1 minute. The ambient pressure in the bell jar was  $3.4 \times 10^{-6}$  torr. The decrease in resistance with time is due to cooling of the film.

# 3.4 Cohesion and Robustness

In principle any substance can be evaporated onto any other substance to give a thin film. However, the cohesion between the two substances may be an issue. If the cohesive forces are primarily Van Der Walls in nature, which is a weak binding force, then the cohesion between the two substances will be poor. The result will be a film which can be easily scratched off. In general, a layer of oxide between the two substances will improve cohesion enormously[15]. Such a layer is called a sticking layer, or adhesion layer. An example of two substances with poor cohesion is gold and sapphire. This problem was directly encountered while preparing samples to measure the resistance of bismuth films for this thesis. The cohesion can be greatly increased if a sticking layer of chromium is deposited between the gold layer and the sapphire.

The robustness of a film can be quantified by applying a couple of simple tests. The first test is innocuously named "the scratch test", in which the surface of the film is scratched lightly with a hard object. Visible flaking off of the film constitutes a fail. If the film is undamaged from the scratch test, the imaginative "scotch tape test" is the next step. True to its name, a piece of 3M clear scotch tape is placed on the surface of the film, sticky side down. The tape is pressed down using light pressure (as from your finger) and quickly removed. In an effort to quantify this procedure somewhat, NASA spec. ASTM# specifies 3M 810 tape with 10 oz applied pressure. If nearly all the film is removed by the sticky tape, this constitutes a fail. If a film passes both tests, the cohesion is quite good, and the film is said to be "robust".

The growth rate of the two layers was also found to have a large effect on the cohesion between gold and sapphire. If the chromium and gold layers were grown at rates which exceeded  $10 \text{\AA}/s$ , the cohesion between the layers was poor, and the gold film failed both the scratch test and the scotch tape test miserably. If the growth rate was kept at or below  $1 \text{\AA}/s$ , the resulting films were extremely robust, and passed both the scratch test and the scotch tape test with flying colors.

### 3.5 Substrate Cleanliness

The cleanliness of the substrate has an effect on the cohesion of the film. All samples were cleaned using trichloroethelyne, acetone, and methanol in an ultrasonic cleaner. Samples which weren't cleaned using the ultrasonic cleaner showed poor cohesion. This seemed to be a necessary step in the production of usable films.

## 3.6 Sample Preparation

The substrate used for these experiments was a rectangular piece of  $Al_2O_3$  (sapphire) of dimensions  $0.5 \times 0.25 \times 0.010$  inches. This was bonded to an aluminum chip of dimensions  $2.36 \times 0.4 \times 0.125$  inches using Stycast 2850FT epoxy, set with Catalyst #9. The dimensions of the aluminum chip were chosen for easy insertion into a liquid helium storage dewar. Before bonding the sapphire to the aluminum chip, the sapphire was cleaned according to the following procedure:

5 mins in hot trichloroethelyne bath and ultrasonic cleaner

5 mins in hot acetone bath, and ultrasonic cleaner

5 mins in hot methanol bath, and ultrasonic cleaner

Rinse with distilled water

Blow dry sample in dry nitrogen atmosphere

During cleaning the sample was handled by the edges only, using tweezers.

The electrical leads consist of 4 individual strips of gold deposited by thermal evaporation lengthwise along the chip. The deposition of these electrical leads deserves some discussion. In an earlier attempt to measure the resistance of the film, a mask was constructed which allowed deposition of four gold circles in a row near the edge of the substrate. The thought was to then deposit bismuth over the entire surface of the sapphire, and measure the resistance of the film using a four wire measurement. Although such a procedure will certainly measure the resistance of the film, this configuration does not allow easy estimation of the important quantity  $\Omega/\Box$ . A sketch of the equipotential lines in the film shows this more clearly. The conduction path in such an arrangement is complex as the electric field lines are perpendicular at every point to the equipotential lines. This situation is resolved by depositing conductive leads lengthwise along the sapphire chip. The equipotential lines are then lines parallel to the edge of the chip, and the electric field points perpendicular to these lines, so that the conductive path is perpendicular to the electrical leads. The estimation of the quantity  $\Omega/\Box$  is then trivial; if the film is rectangular in shape and has dimensions  $N \times M$ , where N is the width of the sample and M is the sensing lead separation, then the sheet resistance is given by the following:

$$\Omega/\Box = \frac{RN}{M}$$

where R is the measured resistance.

To improve the cohesion between the sapphire substrate and the gold layer, a thin (50 angstrom) layer of chromium is deposited before the gold layer. The thickness of the gold layer is not critical, and a thickness of approximately 1000 angstroms was used successfully. Both these layers are grown fairly slowly, with deposition rates never exceeding 1 angstrom/second. It was found that depositing either layer more quickly resulted in a film that would easily flake off if scratched. The films produced by slower deposition were extremely robust, and showed very good cohesion to the sapphire surface. The films easily resisted the so-called "scotch tape test", where a piece of scotch tape is placed on the surface of the film, sticky side down, and then quickly removed.

The electrical connections to the gold strips were made by bonding 0.005 inch copper wires to them with EpoTek silver epoxy. The other ends of these wires were bonded to a TO5 8 pin header, again using silver epoxy. Ultrasonic wire bonding was investigated as a method to make the electrical connections, but it was found that the thin (0.001") gold wires would usually break when the sample was heated from room temperature to 270 degrees Celsius. This was most likely due to the thermal expansion of the Stycast. Availability of the ultrasonic bonder was also an issue, since our laboratory did not own one.

The end result is shown in figure 3.11.



Figure 3.11: A diagram of the sample used to measure the resistance of bismuth films. The finished sample is placed inside a thermal evaporator and bismuth is deposited over the entire sapphire surface.

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## Chapter 4

#### Results

In this chapter the results of the resistivity measurements on thin films of bismuth will be presented. A number of interesting features are evident in the data, and a separate section has been devoted to each.

#### 4.1 Temperature Dependence of The Resistivity

The most intriguing feature evident in the data is the anomalous temperature dependence of the resistivity. The resistivity of 6 thin films of bismuth has been characterized as a function of temperature in the range 295K to 4.2K. The resistivity at all temperatures was higher than that of the bulk material for every sample. The resistivity of each sample is observed to *increase with decreasing temperature* for thicknesses ranging from 87 - 3005Å. This behavior is markedly different than that of the bulk resistivity, which decreases with temperature over the same temperature range. The data for the temperature dependence of the resistivity is shown in figure 4.12. The films were prepared by thermal evaporation in a diffusion-pumped bell jar. The growth rate and thickness of each film, and the ambient pressure in the bell jar at the time of evaporation are summarized in table 4.3. The resistivity-temperature data for sample F is not plotted in figure 4.12 for reasons given in section three of this chapter. The films were all prepared under relatively poor vacuum conditions, and this is a result of the vacuum system used. A pressure of approximately  $3.8 \times 10^{-6}$  Torr was reached after 20 hours of pumping, and a further 28 hours of pumping did not lower the pressure any further. The inside of the jar was meticulously cleaned with methanol, and most of the components inside the jar were replaced, but this had no effect on the final pressure. The presence of a leak was suspected, and the system was checked throughly using a helium spectrometer, but no leak was found. This lead to the conclusion that the limiting pressure of the bell jar used

Sample Label	$\operatorname{Thickness}(\check{A})$	$Pressure \times 10^{-6} (Torr)$	Growth $\operatorname{Rate}(\check{A}/s)$
A	85	3.8	0.25
В	87	4.2	30
С	103	3.8	0.33
D	146	4.0	1.2
E	500	4.0	0.33
F	3000	4.4	1.0
G	3005	4.4	17.0

Table 4.3: The thickness, growth rate, and pressure in the bell jar just before evaporation. The ambient pressure was the pressure reached after approximately 20 hours of pumping.

in these experiments was approximately  $3.8 \times 10^{-6}$  Torr. The pressure at evaporation of each film was kept approximately constant, and as such each film is subject to the same amount of impurities present in the bell jar.

The temperature is measured with a diode in good thermal contact with the sample. For a constant current, the voltage across the diode varies linearly with temperature in the range 295-40K. Below 40K the diode is no longer a good thermometer, and it is not used to infer the temperature below this limit. The points at 4.2K are measured after contact with the liquid helium bath had been established. No data is measured between 40K and 4.2K. The data for samples A, B, and C is interpolated with a straight line between these points. The data for samples D, E, and G is not interpolated in this region. The results of other investigators indicate that the resistivity becomes constant at low temperatures, and the temperature at which the resistivity becomes constant is a function of the film thickness[11]. If we compare the data for samples D, E and G, it is evident that the resistivity of sample D is beginning gradually to plateau at 40K, while the

Chapter 4. Results



Figure 4.12: Resistivity versus temperature for bismuth films. The thicknesses are: A -  $85\mathring{A}$ ; B -  $87\mathring{A}$ ; C - 103  $\mathring{A}$ ; D -  $146\mathring{A}$ ; E -  $500\mathring{A}$ ; G -  $3005\mathring{A}$ . The resistivities of samples A, B, and C has been interpolated with straight lines in the region between the data points.

resistivities of samples E and G clearly has not. This agrees with other measurements in the literature[3], which find that the resistivity plateaus at lower temperatures for thicker films. A feature that is evident in all the data for samples A, B, and C is a maximum in the resistivity at a temperature of approximately 65K, followed by a monotonic decrease with temperature thereafter. The maximum is more pronounced in the data for sample A (t = 85Å) than for samples B(t = 87Å) or C(t = 103Å). This feature is not found in the data for the thicker films. This observation agrees with published data in the literature, which find that the resistivity maximum occurs only in thin films[11].

The anomalous character of the temperature dependence of the resistivity of thin bismuth films has received much attention in the literature. In most metals it is observed that the temperature dependent part of the resistivity of a metallic thin film is identical to the temperature dependent part of the resistivity of a bulk material[14]. The thin films always show a higher resistivity than the bulk, and this can be successfully interpreted in terms of the Fuchs-Sondhiemer model and the grain boundary scattering model presented earlier. However, the situation for thin film bismuth is different. In what follows, we will systematically apply each of the three models presented in chapter two to the resistivity - temperature data. We state at the outset that each model fails to adequately explain the temperature dependence of the resistivity of thin bismuth films.

# 4.1.1 Surface Scattering

The Fuchs-Sondhiemer model attributes the higher resistivity of the film (compared to the bulk material) to the scattering of electrons off of the surfaces of the film. Plotting  $\rho t$  against t should yield a straight line. The data has been plotted for three different temperatures: 295K, 60K, and 4.2K. The data is well described by a linear relation for all three temperatures, and the slope and y-intercept of each line has been computed. These parameters appear in table 4.4.

Temperature(K)	$ ho_{bulk}(\mu\Omega cm)$	$ ho_{\infty}(\mu\Omega cm)$	$(1-p)\lambda_{\infty}(A)$
295	116	109.6	126
60	19.0	389.9	-32.3
4.2	5.8	576.53	-52.8

Table 4.4: Parameters derived from analyzing the data in terms of the Fuchs-Sondhiemer model. Notice that the specularity parameter must be greater than one to reproduce the values in the last column of the table.

The resistivity of a bulk sample with the same defect density as the film  $(\rho_{\infty})$  is seen to increase as the temperature decreases. This is an anomalous result, since the resistivity of bulk bismuth decreases as the temperature decreases. Another anomaly in the data are the y-intercepts for the fits to the 4.2K and 60K data. The specularity parameter, p, must take on values greater than one to explain the negative values of the y-intercepts at low temperatures. A value of p > 1 indicates that more electrons are bouncing off the surfaces of the film than were incident in the first place, and this can't be accounted for in terms of the Fuchs - Sondhiemer model. These results indicate that the anomalous temperature dependence of the resistivity of thin bismuth films cannot be explained by non-specular reflection of the carriers from the film surfaces.

#### 4.1.2 Grain Boundary Scattering

We can analyze the resistivity-temperature data in terms of the grain boundary scattering model presented earlier. In this model, the mobility of the carriers is impeded by scattering off of the grain boundaries. If we assume that the average grain diameter has some relation to the film thickness, which seems to be true in general[10], then we can analyze the data at 295K in terms of the grain boundary scattering model. If we plot the ratio of film resistance to bulk resistance  $\rho_f/\rho_0$  against the thickness t, we find that a marginal fit to the data is obtained if  $\alpha$  is equal to the following,

$$\alpha = \frac{35.0}{t} \tag{4.65}$$

and thus

$$\lambda_0 \frac{R}{1-R} = 35.0 \text{\AA}.$$
 (4.66)

Using the value  $\lambda_0 = 10\,900$ Å, we find a reflection coefficient equal to R = 0.0032. This indicates that 99.68% of the particles incident on a grain boundary are transmitted through the boundary, which indicates that grain boundary scattering is a weak process in these films at room temperature. This data is plotted in figure 4.13. The model fails when we try to apply it to the data for the resistivities at 4.2K. The ratio of film resistivity to bulk resistivity at 4.2K increases as a function of thickness, and this can't be explained solely in terms of grain boundary scattering. It would require a negative value of the reflection coefficient, which doesn't have an interpretation in terms of the grain boundary scattering model. The grain boundary scattering model doesn't account for the temperature dependence of the resistivity of thin bismuth films.

#### 4.1.3 Quantum Size Effect

A quantitative prediction of the QSE model is that the low temperature resistivity of a semi-metal film will oscillate as a function of thickness, with a period of about 400Å. The data presented in this thesis show no such oscillations. This is not conclusive, however, since the thicknesses of the films grown here were not varied at regular intervals to search for such oscillations.

Another quantitative prediction of the QSE model is that the SMSC transition will be observed in bismuth for film thicknesses of about 400Å. Films thinner than this are predicted to have an energy gap, since the splitting due to the small film thickness has erased the band overlap. A semi-conducting material has a resistivity which is given by the following equation,

$$\rho = Aexp(W_g/2kT) \tag{4.67}$$



Figure 4.13: The grain boundary scattering applied to the data. A marginal fit is obtained for the room temperature resistivity data.

where  $W_g$  is the band overlap. A plot of  $\log \rho$  vs 1/T should yield a straight line with intercept  $b = \log(A)$  and slope  $m = W_g/2k$ . A plot of this for any of the data presented here fails to yield this type of relation. Another fact which should be noted is that the resistivity-temperature curves for thick samples ( $t = 500, 3005 \text{\AA}$ ) has more or less the same shape as that of the thinner samples. According to the QSE model, films thicker than  $400 \text{\AA}$  are still semi-metals. This poses a problem, since the temperature dependence of the resistivity of a semi-metal and a semi-conductor are not the same. No experimental group has claimed to observe the SMSC, and this may be evidence that the SMSC in bismuth is being masked by other effects[18]. We conclude that the QSE model is not able to explain the temperature dependence of the resistivity observed in thin bismuth

# 4.1.4 A New Model

films.

So far, we have seen that the surface scattering model, the grain boundary scattering model, and the quantum size effect can't explain the temperature dependence of the resistivity of thin bismuth films. It is expected that these effects do play a role in determining the resistivity, but by themselves or in combination they can't explain why the resistivity increases with temperature, then plateaus to a constant value. In what follows, we will explain the general features of a model which successfully explains many features in the data presented here, and many features in the data of other investigators. We note that although many groups have published data on the temperature dependence of thin bismuth films, no group has satisfactorily explained the physical mechanism responsible for such behavior. We provide a physical explanation for the temperature dependence of the resistivity and we have come up with a phenomenological fit to the data based on our physical interpretation.

Looking at figure 4.12, one is tempted to analyze the data in terms of the mean free

path of the carriers in the material. However, this may lead to erroneous results. The resistivity of a material is determined by two important factors : the *mobility and the number density* of the carriers. Changes in either one of these variables will cause changes in the resistivity of the material. Since the resistivity is affected by both variables, one cannot make general statements concerning the mobility of the carriers by only analyzing the resistivity curves.

Many investigators who are interested in the temperature dependence of thin bismuth films measure the Hall coefficient, and the magneto-resistance coefficient. The Hall effect occurs when a magnetic field is applied perpendicular to the current flowing in a conductor. The resulting Lorentz Force causes an accumulation of charge on the sides of the conductor, which leads to a transverse voltage known as the Hall Voltage. For a system with only one type of carrier, the Hall coefficient is given by,

$$R_H = \frac{1}{ne} \tag{4.68}$$

where e is the charge on the electron, and n is the carrier concentration. Measuring the Hall coefficient for such a system provides direct information about the carrier density, and the charge of the carriers(since the Hall Coefficient can be negative or positive). For a two component system, the formula (for isotropic carrier motion with respect to the crystal axes) is

$$R_H = \frac{n_h \mu_h^2 - n_e \mu_e^2}{e(n_h \mu_h^2 + n_e \mu_e^2)}.$$
(4.69)

So, for a two component system, the Hall coefficient probes the number density and mobility of the carriers. The sign of the Hall coefficient indicates which carrier is playing the more dominant role. Experimental results reported in the literature often give conflicting results for the Hall coefficient in thin bismuth films. This indicates that the conditions under which the film is grown have a noticeable effect on the electrical characteristics of the film. The size of the grains in bismuth films has been shown by Jin *et al.*[2] to have a remarkable effect on the resistivity. In particular, they found that annealing thick epitaxial films  $(t = 1\mu m)$  according to different schedules could completely change the character of the resistivity - temperature curve, even turning the temperature coefficient of resistance (TCR) from negative to positive. A plot of their data appears in figure 4.14. The result of this change in sign of the TCR is that the resistivity of the film is observed to decrease with decreasing temperature, which is the same behavior observed in the bulk. The size of the grains in an unannealed sample of thickness  $1\mu m$  was measured (by Jin *et al.*) and was found to range from  $0.5 - 5\mu m$ . The size of the grains in an annealed sample of the same thickness was found to range from  $10 - 30\mu m$ , which is approximately a factor of 20 larger than the grains in an unannealed sample. The conclusion reached from this work is that the mean free path of the carriers in bismuth can be increased by annealing the film at a temperature close to the melting temperature (271*C*) of bismuth.

In light of the data in figure 4.14 from Jin *et al.*, the size of the grains in bismuth films has an enormous effect on the resistivity at all temperatures. From the analysis presented earlier, grain boundary scattering can not explain the anomalous temperature dependence of the resistivity. However, an implicit assumption in the derivation by Mayadas and Shatkes[13] of equation 2.60 is that the carrier density is constant, which is a valid assumption for materials with large Fermi Energies, namely metals. As shown in chapter two, the energy distribution of the carriers in bismuth is a function of temperature, and this is a result of the low Fermi Energy of bismuth. The anomalous temperature dependence of the resistivity can be explained as a result of the temperature dependence of the carrier energies, and scattering of the carriers off of grain boundaries in the film. If we model the grain boundary as a potential barrier of height  $U_0$  and width L, the transmission coefficient is given by the following equations[19],



Figure 4.14: Resistivity versus temperature for bismuth films of  $1\mu m$  thickness. The data is from Jin *et al.*[2]. It is interesting to note that the resistivity of the bottom curve is actually lower than that of the bulk, for temperatures greater than 100K. This fact was not noted by Jin *et al.*, and indeed is hard to explain.

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$$T = \frac{4\epsilon(U_0 - \epsilon)}{4\epsilon(U_0 - \epsilon) + U_0^2 sinh^2(\eta L)}, \ \epsilon < U_0$$
(4.70)

$$T = \frac{4\epsilon(\epsilon - U_0)}{4\epsilon(\epsilon - U_0) + U_0^2 sin^2(kL)}, \epsilon > U_0$$
(4.71)

where  $\eta = \sqrt{U_0 - \epsilon}$  and  $k = \sqrt{\epsilon - U_0}$ . This represents the probability that a particle with energy  $\epsilon$  will be transmitted through the barrier. The transmission coefficient is plotted in figure 4.15. One can see that if  $\epsilon \ll U_0$ , the transmission coefficient is essentially constant, and is small. When  $\epsilon \sim U_0$ , the transmission probability increases quite quickly, and the particle can pass through the barrier without too much trouble. If the height of this potential barrier is comparable to the Fermi Energy of the carriers in bismuth, the number of particles able to pass through the barrier easily will be a function of temperature. To see this, imagine that the Fermi Energy is less than the height of the potential barrier. At absolute zero, the Fermi-Dirac distribution will be a step function, and the number of particles that can pass through the barrier easily will be a constant. As the temperature increases, the number of particles with energies greater than  $\epsilon_F$ increases. However, if  $\epsilon_F \ll U_0$ , most of the particles will have energies  $\epsilon \ll U_0$ , and the number of particles passing through the barrier will be essentially unchanged, since the transmission coefficient is small. As the temperature increases further, a significant fraction of the particles may have energies which are comparable to the height of the barrier. As a result, the number of particles passing through the barrier will suddenly increase, since the transmission coefficient rises steeply when  $\epsilon \sim U_0$ . The Fermi-Dirac distribution is plotted on the same graph as the transmission coefficient (see figure 4.15). In terms of the resistivity of such a material, this model predicts a constant resistivity at low temperatures, followed by a sudden decrease when the temperature exceeds some critical value. This model reproduces many of the features seen in the data if we postulate that the height of the barrier has some dependence on the size of the grains in the film. If the barrier height decreases as the thickness of the film increases, then the temperature at which the resistivity becomes constant will occur at a higher temperature for thinner films than for thicker films. This behavior is evident from the experimental data in figure 4.12.

Finally, we note that the resistivity-temperature curves can be fit approximately with the following function,

$$\rho = \rho_0 + R \frac{T/\tau}{e^{T/\tau} - 1} \tag{4.73}$$

where T is the temperature,  $\rho_0$  is the bulk resistivity, and R and  $\tau$  are constants. This function has been applied to the data of Baba *et al.* [3], Jin *et al.*[2], and the data for sample D, and this appears in figure 4.16. In computing the fit for each curve, data from the annealed sample of Jin *et al.* has been used as the bulk resistivity,  $\rho_0$ . This data is shown as the bottom curve in figure 4.16. The parameters for the fits are listed in table 4.5.

Film 'Thickness $\AA$	$R(\mu\Omega cm)$	$\tau(K)$
146	325	140
300	1450	210
10000	180	48

Table 4.5: The parameters for the fits shown in figure 4.16. The fits are computed from equation 4.73.

From figure 4.16 we see that the resistivity values for sample D(and in fact for all the samples in this thesis) are in disagreement with the data of Baba *et al.*, and Jin *et al.*. As can be seen from figure 4.12, the low temperature resistivity of the samples measured in this work increases as the thickness increases, and this is the opposite trend to that observed by Baba *et al.*, and Jin *et al.*. Explanation of this is deferred until the next



Figure 4.15: The transmission coefficient and the Fermi Dirac distribution for a material at 200K are plotted on the same graph. The Fermi-Dirac distribution at absolute zero is also shown. As the temperature increases, more particles will be able to tunnel through the barrier, and the resistivity will decrease.

section in this chapter.

The function in equation 4.73 is a phenomenological fit to the data. We note that the fit does not exactly reproduce all the data points, however, it seems to describe the general shape of each curve. Equation 4.73 has two free parameters, R and  $\tau$ . Rcorresponds to the low temperature resistivity of the film, and  $\tau$  roughly corresponds to the temperature at which the resistivity starts to plateau. From table 4.5, we see that for the data of Baba *et al.* and Jin *et al.*, the value of  $\tau$  for thinner films is higher than the value of  $\tau$  for thicker films. The data for the samples measured in this thesis show this same general trend.

In summary, the anomalous temperature dependence of the resistivity of thin bismuth films is mainly due to the fact that bismuth is a semi-metal, and as such has a low Fermi Energy. The energy distribution of the carriers is a function of temperature, for temperature variations in the range 300 - 4.2K. Scattering of the carriers from the grain boundaries causes the resistivity to become nearly constant at low temperatures. As the temperature increases, so does the number of particles which are able to tunnel easily through the grains, and thus the resistivity drops as the temperature increases. The effect of annealing the film is to increase the average crystallite size, which increases the mean free path of the carriers in the film.

# 4.2 Low Temperature Resistivity

The resistivity at 4.2K is found to increase as the thickness increases. The data is plotted in figure 4.17. A data table appears in table 4.7. This same behavior has been observed by Chu *et al.*[20], but not by Baba *et al.*[3], or Jin *et al.*[2]. Referring to figure 4.16, which shows data from Baba *et al.*, Jin *et al.*, and data for sample D, we note that the data presented in this thesis show a different dependence on the film thickness than that



Figure 4.16: The data from Jin *et al.*, Baba *et al.*, and sample D from this thesis. The solid lines through the top 3 curves are fits computed from equation 4.73, and the parameters are listed in table 4.5. Note that the fits do not exactly reproduce the data points, but seem to describe the general shapes of the curves quite well.

observed by Baba et al. . The low temperature resistivity of the films in figure 4.12 increases with increasing film thickness, while the data of Baba et al. decreases with increasing film thickness. The reason for the disagreement is not known, however, the effect may have something to do with the quantum size effect (QSE). As the thickness of the film becomes comparable to the mean free path of the charge carriers, some interesting effects should begin to show themselves. At absolute zero, the Fermi-Dirac distribution shows that all energy levels with energies higher than the Fermi energy  $(\epsilon_F)$  are empty, while all those below are filled. As the film thickness decreases, it may occur that the only occupied levels for electrons and holes are those which correspond to zero longitudinal energies. If this is the case, the motion of the charge carriers may be considered to have become two dimensional. Such a transition depends on the direction of motion in relation to the crystal axes. Chu et al. [20] calculate that the 2D-3D transition will be observed for the following film thicknesses:  $t = 255 \text{\AA}$ , perpendicular to trigonal axis;  $t = 137 \text{\AA}$ , perpendicular to binary axis; t = 134Å, perpendicular to bisectrix axis. The orientation of the films grown in this thesis is not known, but the thicknesses of the films A, B, and Care all less than the values listed above. The motion of the charge carriers in these films may very well be two dimensional, and this could account for the lower resistivities at low temperatures. If scattering off of the surfaces of the film is important in determining the mobility of the charge carriers, the resistivity of a thicker film could be higher than the resistivity of a thinner film. This behavior would manifest itself at low temperatures since the states of lowest energy would be filled at low temperature.

Another fact which may be important is that the films of Baba *et al.* were prepared on mica substrates, held at a temperature of 100C during evaporation. These films were epitaxial, as shown clearly by X-ray diffraction studies[3]. The films presented here are most likely not epitaxial, judging by the large (8%) difference in the lattice constants in the c direction between bismuth and sapphire. Perhaps the oriented nature of an
epitaxial film gives rise to the disagreement between the data sets.

# 4.3 Effect of Growth Rate on Resistivity

The growth rate of the films was found to have an effect on the resistivity. In four of the samples, the thickness was kept constant while the growth rate of the film was varied. Samples A and B are very similar in thickness, but differ noticeably in resistivity over the entire temperature range shown(see figure 4.12). Sample A was grown very slowly, with a growth rate of  $0.1 \text{\AA}/s$ , while sample B was grown 300 times faster. The data for sample B shows a resistivity which is higher at all temperatures than the resistivity of sample A, and this is presumably due to the tremendous difference in growth rate. One expects a rapidly grown film to have smaller, more numerous grains than a film which is grown slowly. If the transport properties of the charge carriers are affected by scattering off of these grain boundaries, a rapidly grown film would have more grains to scatter off of, and would presumably have a higher resistivity than a film of similar thickness but slower growth rate.

The data for sample F seem to be in disagreement with that of sample G. The resistivity data for all the samples is tabulated in table 4.6. The thicknesses of samples F and G are nearly identical, yet the resistivities do not agree at any temperature. The growth rate of sample F was  $1\text{\AA}/s$ , and the evaporation took nearly 50 minutes. The resistivity was measured as a function of thickness for this sample, and this is plotted in figure 4.19.

The data show that the resistivity reached a minimum value at a thickness of 800Å, then began to increase monotonically as the thickness decreased. The reason for this increase is unknown, but oxidization is suspected. Heating of the film may have been a factor as well, since the temperature of the substrate was not controlled during the



Figure 4.17: The resistivity at 4.2K increases as the film thickness increases. This data disagrees with that of Baba *et al.*[3].

experiment. The tungsten boat can get quite hot during an evaporation, and the substrate may have been heated radiatively. For this reason, the resistivity-temperature data for this sample has not been plotted along with the other samples in figure 4.12. This data indicates that slow growth of a thick film may be a bad idea, since heating of the substrate and a higher concentration of impurities may lead to a film with a higher resistivity than a film of comparable thickness but faster growth rate.

## 4.4 Resistivity Ratio

The resistivity ratio,  $\Gamma$ , is defined as follows,

$$\Gamma = \frac{\rho_{4.2}}{\rho_{295}} \tag{4.74}$$

where  $\rho_{4.2}$  is the resistivity at 4.2K, and  $\rho_{295}$  is the resistivity at 295K. The resistivity ratios have been computed for seven samples, and the data appears in figure 4.6. The

Sample label	Thickness(Å)	$ ho_{295}(\mu\Omega cm)$	$ ho_{4.2}(\mu\Omega cm)$	Γ
A	85	151.5	211.4	1.395
B	87	163.2	246.6	1.511
C	103	165.8	255.3	1.540
D	146	152.3	314.4	2.064
E	500	123.0	519.8	4.228
F	3000	168.8	637.4	3.776
G	3005	111.2	566.3	5.093

Table 4.6: The data for the resistivity ratio,  $\Gamma$ , for films of various thicknesses. The data is plotted in figure 4.18.

data from table 4.6 are plotted in figure 4.18. The general appearance of the data in figure 4.18 is similar to that of other investigators[3]. The data points show that the resistivity ratio is a function of thickness. The data point for sample F has been included in this plot, and it disagrees significantly with the other data. The reason for the large discrepancy has been discussed in section 3 in this chapter. A solid line has been drawn

#### Chapter 4. Results

in a "connect the dots" style between the remaining data points. There is no theoretical framework from which to interpret this data, and thus no effort has been made to fit the data with a model. The usefulness of an exact fit is questionable as well in light of the data from Baba *et al.* [3]. They have observed that films with identical thicknesses grown simultaneously on mica substrates exhibit a scatter in their resistivity ratios. Apparently, small differences in the cleaving and the cleanliness of the substrate can have an effect on the electrical properties on the film.

#### 4.5 Effect of Substrate

The resistivity was measured as a function of thickness for bismuth films grown on sapphire and on glass. The thickness of the film, measured by a crystal thickness monitor located as close as possible to the substrate, was controlled by opening and closing a mechanical shutter. After each deposition the shutter was closed and the film was left to equilibrate for a period of about 1 minute before taking data. The resistance of the film grown on the glass substrate was measured with a two lead technique. The leads, which were brass wires, were bonded to gold pads on the substrate using Epo-Tek silver epoxy, and fed through a vacuum feed-through to a digital multi-meter. It was realized later that the contact resistance of the leads may not have been negligible. Contact resistances of approximately 20 $\Omega$  have been observed for leads improperly bonded to gold surfaces. The contact resistance was not measured for this sample, and thus the raw data appears in figure 4.19. The correction to the resistivity is expected to be small since the film resistance ranged from  $1000\Omega$  to  $400\Omega$ , which should be much larger than the contact resistance of the leads. In light of this, however, the resistivity could have been measured much more accurately, and the data for the resistivity of bismuth grown on glass should be viewed as approximate only. The resistance of the film grown on the sapphire



Figure 4.18: The resistivity ratios of the bismuth films increase as the thickness increases. The data point for sample F disagrees with the other data.

substrate was measured with a four lead dc technique, and the contact resistance in this arrangement is not problematic since negligable current flows through the sensing leads.

The resistivity is measured to be higher at all thicknesses for the film grown on the glass substrate than for the film grown on the sapphire substrate. This could be due to the amorphous crystal structure of glass, but certainly the lead resistance is a factor. The data is plotted in figure 4.19. Most of the data points for each substrate seem to follow a straight line with identical slope but unequal intercept in these coordinates, which indicates a power law dependence on the thickness. The data is well described by the following two functions, which represent linear least squares fits:

$$\rho = 414.0 \left[\frac{1}{t}\right]^{0.19} \mu \Omega cm, \text{ sapphire substrate}$$
(4.75)

$$\rho = 1096.0 \left[\frac{1}{t}\right]^{0.19} \mu \Omega cm, \text{ glass substrate}$$
(4.76)

(4.77)

From figure 4.19 we see that the data points for sample F do not agree with the other data points for bismuth grown on a sapphire substrate. The reason for this is explained in section 3 of this chapter. The data point for sample G lies below the bulk value of the resistivity. This gives an estimate of the systematic uncertainty present in these experiments, since the resistivity of the thin film will never be lower than that of the bulk material. The data points for the film grown on the glass substrate are seen to deviate significantly from the fit at small thicknesses. The reason for this is most likely that the film was not given enough time to equilibrate between data points. Testing done since this run indicates that the resistance of the film is still dropping slowly up to 10 hours after the evaporation is completed. This indicates that the film cools very slowly in vacuum, and 1 minute in between data points is not sufficient to allow the film to come to thermal equilibrium with its surroundings.



Figure 4.19: The resistivity of bismuth films grown on sapphire and glass, plotted as a function of inverse thickness. The solid lines are fits to the data, and the dashed line is the bulk resistivity at 295K. The values for the room temperature resistivity from table 4.6 are plotted as well. The filled squares are data for sample F, which were taken during evaporation. It is evident that sample F behaves differently than the other samples, and radiative heating of the substrate during evaporation may have been a factor.

The resistivity is found to be different for bismuth films grown on glass and sapphire substrates. This may have implications for the procedure used to produce low temperature bolometers. In the BAM experiment[4], the absorbing material is a thin coating of bismuth, which is deposited on a sapphire substrate. The resistance of the film is usually monitored in situ using a glass witness slide, and the evaporation is terminated when the desired sheet resistance is reached. According to the results presented here, bismuth films grow differently on glass and sapphire substrates. This means that using a glass witness slide to monitor the sheet resistance may lead to an improperly thick coating of bismuth. This problem can be rectified by using a sapphire witness slide to monitor the sheet resistance, and/or using a thickness monitor to control the thickness of the evaporation.

## 4.6 Room Temperature Resistivity

The room temperature resistivity shows some anomalous characteristics. The resistivity is a function of thickness, but not a monotonic one. The data for the room temperature resistivity is tabulated in figure 4.6. The resistivity increases with thickness for the thinner films, i.e. films with thicknesses below  $146 \text{\AA}$ , but then decreases with increasing thickness for films thicker than  $146 \text{\AA}$ . The reason for this behavior is not understood. It may be indicative of a transition in terms of the mobility of the carriers inside the film. If the mobility of the carriers is affected by the potential at the surface of the film, then the thickness beyond which the mobility of the carriers is no longer as sensitive to the potential at the surface of the film. This may explain why the resistivity drops as the thickness increases for film thicknesses which are greater that  $146 \text{\AA}$ .

### 4.7 The Sheet Resistance at 4.2 K

The surface resistivity of the bismuth films at low temperatures is of interest because this is the relevant parameter for microwave absorption. It is important for our lab to ensure that the surface resistivity of the films is  $188.5\Omega/\Box$  at low temperatures, since the bolometeric detectors in the BAM experiment[4] rely on this thin coating to absorb microwaves. It has been possible to come up with an empirical model to predict the surface resistivity at 4.2K given the thickness of the film. The sheet resistance of the films was measured at 4.2K as a function of film thickness, and this data appears in table 4.7. The relationship between the sheet resistance and the film thickness is clearer when

Film Thickness( $\mathring{A}$ )	$ ho_{4.2}(\mu\Omega cm)$	$R_{\Box}(\Omega)$
85	211.4	248.7
87	239.4	279.8
103	247.8	240.6
146	317.4	217.4
500	519.8	104.0
3005	566.3	18.9

Table 4.7: Data showing the sheet resistance and the resistivity at 4.2K for the bismuth films prepared in this thesis. The sheet resistance clearly decreases as the thickness increases.

we plot the logarithm of  $R_{\Box}$  against the logarithm of the inverse thickness. The data is plotted in figure 4.20. A quadratic fit gives an acceptable fit to the data, as evidenced by a plot of the residuals in figure 4.21, although the sheet resistance of the thinnest films seems to be scattered considerably. No improvement to the fit is observed for fitting the data to higher order polynomials. The equation of the fit plotted in figure 4.20 is,

$$log(R_{\Box}) = 1.907 - 0.771 log\left(\frac{1}{t}\right) - 0.279 \left[log\left(\frac{1}{t}\right)\right]^2$$
(4.78)

where the thickness of the film, t, is in angstroms. A calculation using equation 4.78 shows that a film with a thickness of 198Å will have a sheet resistance of  $188.5\Omega/\Box$  at

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4.2K. This is shown on the graph as the intersection between the vertical and horizontal lines.

## 4.8 Oxidization of Bismuth Films

The resistance of two of the samples, E and C, was measured as a function of time at room temperature. The films were left sitting on the bench, exposed to the air, for a period of 8 days. The resistance of each sample was measured at the same time each day. The data is plotted in figure 4.22. The resistance of sample E is found to stay approximately constant over this time period, while the resistance of sample C is found to increase with time. The reason for this increase could be due to the growth of an insulating layer of  $Bi_2O_3$  on the surface of the film. Cohn and Uher[21]have observed growth of this type of layer on thin  $(t \leq 90\text{ Å})$  bismuth films as a function of time, and found that the sheet resistance increases with time. The growth of this insulating layer would tend to increase the resistivity, since the effective film thickness decreases. This provides a plausible explanation for the data in figure 4.22. The resistance of the thicker film is fairly insensitive to small changes in the thickness caused by growth of the insulating layer, and thus stays basically constant over short time scales. The thinner film changes resistance quickly, and this is due to the reduction of the effective film thickness as a function of time.

#### 4.9 Conclusions About Thin Films of Bismuth

The main motivation for investigating the electrical characteristics of thin bismuth films, for our laboratory, is the production of bolometeric detectors. The bolometers used in the BAM experiment consist of small rectangular pieces of sapphire with a thermistor



Figure 4.20: The sheet resistance at 4.2K as a function of the film thickness. The solid line is a fit to the data, computed from equation 4.78. The lines drawn in show that a 198Å film should have a sheet resistance of  $188.5\Omega/\Box$  at 4.2K.



Figure 4.21: The residuals for the fit from figure 4.20. There is considerable scatter in the sheet resistance of the thinnest films.



Figure 4.22: The resistivity was measured as a function of time for two samples. The thicknesses are E - 500Å; C - 103Å.

attached. A thin film absorbing layer, which in principle could be any conductive material, is deposited on the surface of the sapphire. Maximum power will be dissipated in the absorber when the sheet resistance of the thin film is equal to  $188.5\Omega/\Box$ . A primary result of this thesis is a method to consistently produce bismuth films with a sheet resistance of  $188.5\Omega/\Box$  at low temperatures. The method is summarized as follows:

1)Cleanliness of the substrate is important. A cleaning schedule similar to the one quoted in chapter three should be applied. Any other cleaning schedule may produce significantly different results than those obtained in this thesis.

2) The thickness of the film should be approximately 200Å. Reproducibility of the measurements has proved to be a problem, since small differences in the cleanliness or cleaving of the substrate cause noticeable fluctuations in the resistivity. Thus, one is likely to get films of slightly different sheet resistances even though the thicknesses may be the same.

3) The growth rate is important. Slow growth, i.e. a rate which is less than 1Å per second, should be avoided. The reason is most likely due to a combination of radiative heating of the substrate inside the vacuum chamber, and buildup of oxides and other impurities. This has been observed to affect the resistivity of the film unpredictably. An extremely fast growth rate, i.e. 30Å per second, was found to produce a film with higher resistance than a film of similar thickness but with a growth rate of 0.1Å per second. With an extremely fast growth rate, it is hard to consistently produce films of the required thickness. Therefore, it is recommended that the films be grown with a moderate growth rate, in the range 1-5Å per second. With such a growth rate, radiative heating of the substrate is not a problem, since the temperature of the boat is not too high. Consistency of film thickness is easily attainable with the moderate growth rate.

4)Films grown on glass and sapphire substrates with the same thickness were measured to have different resistivities. This indicates that the use of a glass witness slide to monitor the resistance of the film during evaporation is poor practice. A sapphire witness slide should be used.

5)The resistance of the films was measured to increase as a function of time, due to exposure to the air. This was observed to increase the resistivity of a thin film more than that of a thicker film. This increase in resistance might be stopped by coating the bismuth film with a SiO overlayer.

The method above differs significantly from the current method employed to produce absorbing layers for bolometers. The main practical contribution of the results presented here is that the absorbing films may be produced by monitoring the thickness of the film, instead of using a witness slide to monitor the sheet resistance. This is a time saving step, since one is no longer required to produce a witness slide, which involves vacuum evaporation of gold leads on a glass substrate. A crystal thickness monitor can be used instead, and such a device is usually standard equipment in a thermal evaporator.

Perhaps the most important result of this work is a physical interpretation of the temperature dependence of the resistivity of thin bismuth films. This is an important contribution, since there seems to be no model in the literature which successfully accounts for the shape of the resistivity - temperature curves in thin film bismuth. We have seen that the application of the standard models one invokes to explain the resistivity of a thin film all fail when applied to bismuth films. The anomalous temperature dependence of the resistivity of bismuth films arises primarily because bismuth is a semi-metal. Semi-metals are characterized by low Fermi Energies, and a low carrier concentration. In such a material, the energy distribution of the carriers is a function of temperature, fewer and fewer electrons and holes are able to tunnel through the grain boundaries easily, and the resistivity increases. The resistivity becomes approximately constant at low temperatures because most of the carriers have energies which are comparable to

the Fermi Energy  $\epsilon_F$ , and are not energetic enough to tunnel through the grains easily. The reason this anomalous temperature dependence of the resistivity is not seen in the bulk material is because the grains in the bulk material are larger than the mean free path of the carriers, and grain boundary scattering makes a negligible contribution to the resistivity. This is shown conclusively by the data of Jin *et al.* [2], who observe that the character of the resistivity-temperature curve can be completely changed by increasing the size of the grains in the film by annealing it at a temperature close to its melting temperature. Properties like those of the bulk are observed in films with grain sizes larger than the mean free path of the carriers in bismuth, and this seems to indicate that grain boundary scattering makes a large contribution to the resistivity of thin bismuth films.

A final note; the grain size in bismuth films has been shown by Hoffman et al.[10]to be practically independent of film thickness for thicknesses of 2000Å and greater, and decreases with decreasing thickness for films thinner than 2000Å. The original motivation for this thesis was to change the temperature dependence of the resistivity of a thin bismuth film by annealing it at a temperature near its melting temperature, as shown by Jin et al.(figure 4.14). If one could arrange it so that the sheet resistance of the film at low temperatures was equal to or lower than the sheet resistance at room temperature. then one could build a bolometer which has less bismuth and consequently, a lower heat capacity. Such a device would have a faster response than bolometers that are currently built. Several experiments were attempted to reproduce the results of Jin et al. for films of approximately  $180\Omega/\Box$  at low temperatures. These experiments all failed due to the following reason : the grain size can not reasonably exceed the thickness of the film, for a film thinner than 2000Å. Thus, trying to anneal a bismuth film that is thinner than 2000Å doesn't increase the grain size, since it is fundamentally limited by the thickness of the film. When one chooses to use thin films of bismuth as an absorbing layer for a bolometer, one is in some sense stuck with the anomalous temperature dependence of Chapter 4. Results

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the resistivity. Annealing such a thin film unfortunately doesn't change the temperature dependence of the resistivity.

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#### Chapter 5

### **Resistance of Composite Aluminum**

### 5.1 MAP Mirror

The Microwave Anisotropy Probe(MAP) is a satellite slated to fly in the year 2000. Its goal is to measure the temperature anisotropies in the entire microwave sky over a broad range of angular scales. MAP's microwave receivers are High Electron Mobility Transistors (HEMT's) which are illuminated by 2 gregorian type mirrors. In order to reduce the payload weight, these mirrors have been fashioned out of a carbon fiber composite material, specifically SF-70A-75/RS-3 spread fabric. The reflectivity of this material by itself is poor, and to make up for this shortfall a 5000Å thick coating of aluminum has been vapor deposited on the surface. The emissivity of the mirror will depend largely on the sheet resistance of the aluminum surface. The sheet resistance of the aluminum coating has been measured at 80K, and the resistivity of the sample has been characterized as a function of temperature over the temperature range 300K-4.2K.

## 5.2 Experiment

The sample is cut to a rectangular shape with dimensions  $1.52'' \times 0.075''$ . The sample is then glued onto the surface of an aluminum chip using Miller Stevenson 907 Epoxy. This epoxy is an excellent electrical insulator, and electrically isolates the sample from the aluminum chip. Electrical leads are bonded to the sample in a four wire measurement configuration using EpoTek silver epoxy. The distance between the sensing leads is ÷

1.1780 inches. The room temperature resistance of this sample is 1.375 ohms. With such a low value of resistance, the contact resistance between the electrical leads and the sample surface produced noticeable effects when the connectivity was checked with a two wire resistance measurement. This is not problematic, however, since the four wire resistance measurement is insensitive to the resistance of the measurement leads. This is confirmed by measuring a V-I curve of the sample at room temperature. This is plotted in figure 5.23.



Figure 5.23: A voltage versus current curve for the MAP mirror sample at room temperature. The material shows ohmic behavior over the range of current shown. The error bars on each point are the same size as the plotting symbols. The slope derived from this graph is  $1.376 + 0.005\Omega$  which is in excellent agreement with measurements made using a four wire resistance technique.

## Chapter 5. Resistance of Composite Aluminum

The temperature of the sample is measured with a diode which is bonded to the backside of the sample holder. The diode is the load for a constant current source of 50 micro-amps, and as the temperature decreases, the diode voltage increases in a linear fashion. The sample is loaded into a cryogenic probe which is designed to fit inside the neck of a liquid helium storage dewar. The probe is evacuated with a mechanical vacuum pump and then backfilled with helium gas prior to cooling. The temperature of the sample is changed by moving the probe to different vertical positions inside the neck of the dewar. The probe is initially positioned near the top of the dewar, and is lowered slowly into the liquid helium bath. After each movement the probe is held stationary for a period of twenty minutes to allow the diode voltage to stabilize. Once the probe is submerged in the liquid helium, the process is reversed using the same procedure. The total length of the experiment was 3 hours.

#### 5.3 Results

The temperature and the resistance of the sample were each measured at five second intervals. The resistivity has the following relation to the measured resistance:

$$\rho = R_{meas} \frac{0.075''}{1.1780''} \times 500 \times 10^{-9} m, \tag{5.79}$$

which gives the result in units of  $\Omega m$ . A graph of the resistivity for the temperature range 300K - 4.2K appears in figure 5.24. No appreciable hysteresis was noticed between the cooling and warming data, and this indicates that the sample and the diode were in good thermal equilibrium during the experiment. The data points shown on the graph are the raw data for both the cooling and warming data sets. The diode is not an accurate temperature sensor for temperatures below 40 K, and was not used to infer the temperature below this limit. The data point at 4.2 K was obtained after contact

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with the liquid helium bath had been established. The accuracy in the temperature is approximately +-0.5 K.

Also shown in figure 5.24 is data for bulk aluminum from the American Institute of Physics Handbook.

## 5.4 Conclusions

### 5.4.1 Vapor Deposited Aluminum

At all temperatures measured, the resistivity of the VDA coating is higher than that of the bulk material. Comparing the measured data to the bulk data shows that the sample has some of the same characteristics as the bulk material, most notably a general decrease in resistance with decreasing temperature and the existence of a temperature independent component of resistivity. The temperature independent part of the resistivity begins to dominate at a temperature of approximately 40K in both the VDA sample and the bulk material. One can see that the shapes of the curves for the VDA sample and the bulk material are quite similar, and seem to differ only by a constant offset on the y axis. This indicates that the temperature dependent parts of the resistivity of the thin film and the bulk material are about equal, but that the temperature independent parts of the resistivities are not.

If we analyze the data in terms of the models presented in chapter 2, we find some surprising results. At 295K, the values of resistivity derived from the graph are,  $\rho_{film} =$  $4.3\mu\Omega cm$  and  $\rho_{bulk} = 2.74\mu\Omega cm$ . Applying equation 2.54 given in chapter 2, we find a value for the specularity parameter of p = -33.6, where we have used the value of  $\lambda =$ 144Å for the mean free path of the electrons in bulk aluminum at room temperature. This negative value of the specularity parameter has no interpretation in terms of the Fuchs-Sondheimer model, and indicates that surface scattering is not the only contribution to



Figure 5.24: The resistivity of vapor deposited aluminum (VDA) versus temperature. The open squares are data taken while cooling the sample, and the filled squares are data taken while warming the sample.

the resistivity.

We can make a lot more progress if we analyze the data in terms of the grain boundary scattering model. Using the simplification noticed by De Vries[14], equation 2.61, we get the following equation for  $\alpha$ :

$$\alpha = \frac{\frac{\rho_{film}}{\rho_0} - 1}{1.39}.$$
 (5.80)

Using the values for the resistivities of the sample and the bulk material at 295K gives a value of  $\alpha = 0.409$ . We don't know the grain size of the grains in the VDA sample. However, if we make an educated guess of approximately 2000Å, which comes from the grain size evident in the SEM pictures taken of bismuth (see chapter 3), the value of the reflection coefficient turns out to be R = 0.85. This value is only an estimate, however, it indicates that grain boundary scattering is a more dominant process than surface scattering in determining the resistivity of the VDA sample.

The relevant parameter for microwave absorption in this material is the sheet resistance. The sheet resistance of the VDA sample at a temperature of 80K is,

$$R_{\Box}(80K) = 0.051\Omega/\Box.$$
(5.81)

The impedance of free space is  $\eta = 377\Omega$ , and the ratio  $R_{\Box}/\eta = 1.35 \times 10^{-4}$ , which is quite small. For a plane wave traveling through free space normally incident on such a conductor, we can calculate the reflected power from the following equation:

$$|\rho|^2 = 1 - \frac{4R_{\Box}}{\eta},\tag{5.82}$$

which yields a value for the percentage of reflected power of  $|\rho|^2 = 99.946\%$ . Thus the percentage of power absorbed in this conductor will be  $1 - |\rho|^2 = 0.054\%$ .

Scanning electron microscopy (SEM) of a cross section of the sample has been done by Dr. Liquin Wang of the Materials Engineering Branch of the Goddard Space Flight Center. The SEM photos appear here with permission from Mr. Tim Van Sant of the Materials Engineering Branch of the Goddard Space Flight Center. These pictures appear in figures 5.25 and 5.26. These pictures clearly show the thread structure of the carbon fiber composite. The surface of the carbon fiber fabric was grit blasted prior to deposition of the aluminum, and this has resulted in a rough aluminum surface. This is quite evident in figure 5.26.



Figure 5.25: SEM micrograph of cross-section of VDA coated SF-70A-75 Spread Fabric/YLA RS-12D. The VDA is the bright irregular line running horizontally through the middle of the micrograph. The magnification is 300 times.



Figure 5.26: The same sample as in the previous figure, magnified 4000 times. The VDA is the bright irregular line running through the middle of the micrograph. The irregular surface of the VDA is evident from this picture. This is due to grit blasting of the carbon fiber spread before deposition of the VDA.

# 5.4.2 General Conclusions

Considerable progress has been made in understanding the temperature dependence of resistivity of thin films of bismuth in this work. We have come up with a plausible model which explains the shape of the resistivity-temperature curve for thin bismuth films, and a phenomenological fit which describes the general shape of the curves. The resistivity of the bismuth films can be explained in terms of the semi-metal nature of bismuth, and a strong dependence on grain boundary scattering. The model presented here is unique, in that no satisfactory explanation of the temperature dependence of the resistivity of thin film bismuth has been published in the literature. We acknowledge that some of the details of this model have not been worked out in full mathematical rigor, however, due to the sensitive nature of the electrical properties of thin bismuth films to the conditions under which they are grown, a mathematical model predicting the exact resistivity at a certain temperature is likely to find limited use at best.

We have also found that a bismuth film of thickness 200Å has a sheet resistivity of approximately  $188.5\Omega/\Box$  at helium temperatures, and this is useful for building bolometeric detectors. The grain size of the grains in films thinner than 2000Å cannot reasonably exceed the thickness of the film, and thus annealing a thin film of bismuth is unlikely to increase the grain size. This means that the character of the temperature dependence of the resistivity of a thin bismuth film cannot be changed by annealing the film, and an improvement in detector performance is not realized by such a strategy.

The resistivity of vapor deposited aluminum has been characterized as a function of temperature, and was found to be higher at all temperatures than that of bulk aluminum. We have found that this can be successfully interpreted in terms of scattering of carriers off of grain boundaries in the film. The sheet resistance of the VDA has been measured at 80K, and found to be a factor of 10 larger than a sample of equivalent thickness, but

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with resistivity equal to that of the bulk. The power absorbed by the VDA has been calculated to be approximately 0.054%, which is quite a small fraction of the incident power. Despite having a resistivity which is higher than the bulk resistivity, the VDA coating will likely make a suitable coating for the carbon fiber mirrors on the MAP sattelite.

### Bibliography

- [1] G.E. Smith, G.A. Baraff, and J.M. Rowell. Effective g factor of electrons and holes in bismuth. *Phys. Rev. A*, (135):A1118, 1964.
- [2] B.Y. Jin, H.K. Wong, G.K. Wong, J.B. Ketterson, and Y. Eckstein. Effect of annealing on the transport properties of an epitaxial film of bismuth. *Thin Solid Films*, (110):29 - 36, 1983.
- [3] Akira Kinbara Shigeru Baba, Hideaki Sugawara. Electrical resistivity of thin bismuth films. *Thin Solid Films*, 31:329 – 335, 1976.
- [4] Gregory S. Tucker, Herb P. Gush, Mark Halpern, Ichiro Shinkoda, and Bill Towlson. Anisotropy in the microwave sky: Results from the first flight of the balloon-borne anisotropy measurement (bam). Astrophysical Journal, 475:L73-76, February 1997.
- [5] Simon Ramo, John R. Whinnery, and Theodore Van Duzer. Fields and Waves in Communication Electronics, Second Edition. John Wiley and Sons, 1965.
- [6] L. Solymar and D. Walsh. Lectures on the Electrical Properties of Materials. Oxford University Press, 1979.
- [7] Charles Kittel. Introduction to Solid State Physics. John Wiley and Sons, Inc., 1953.
- [8] V.B. Sandomirskii. Quantum size effect in a semimetal film. Soviet Physics JETP, 25(1):101 - 106, July 1967.
- [9] V.P. Duggal, Raj Rup, and P. Tripathi. Quantum size effect in thin bismuth films. Applied Physics Letters, 9(8):293 - 295, 1 September 1966.
- [10] R.A. Hoffman and D.R. Frankl. Electrical properties of thin bismuth films. *Physical Review B*, 3(6):1825 1833, 15 March 1971.
- [11] Yu. F. Komnik et. al. Features of temperature dependence of the resistance of thin bismuth films. *Soviet Physics JETP*, 33(2):364-373, August 1971.
- [12] T. J. Coutts. Electrical Conduction in Thin Metal Films. Elsevier Scientific Publishing Company, 1974.

- [13] A.F. Mayadas, M. Shatzkes, and J.F.Janak. Electrical resistivity model for polycrystalline films: The case of specular reflection at external surfaces. *Applied Physics Letters*, 14(11):345 - 347, 1 June 1969.
- [14] J.W.C De Vries. Temperature and thickness dependence of the resistivity of thin polycrystalline aluminum, cobalt, nickel, palladium, silver and gold films. *Thin Solid Films*, (167):25 - 32, 1988.
- [15] Kasturi L. Chopra. Thin Film Phenomena. McGraw Hill Book Company, 1969.
- [16] Yu F. Komnik and B.I. Belevtsev. Temperature dependence of the electrical resistance of amorphous bismuth films. Soviet Journal of Low Temperature Physics, 6(10):629 - 635, October 1980.
- [17] C. Uher and W.P. Pratt Jr. High precision, ultra-low temperature resistivity measurements on bismuth. *Physical Review Letters*, 39(8):491-494, 22 August 1977.
- [18] Mei Lu et. al. Low temperature electrical transport properties of single crystal bismuth films under pressure. *Physical Review B*, 53(3):1609 – 1615, 15 January 1996.
- [19] Albert Messiah. Quantum Mechanics, Volume 1. John Wiley and Sons, New York, 1958.
- [20] H.T. Chu, P.N. Henriksen, and J. Alexander. Resistivity and transverse magnetoresistance in ultrathin films of pure bismuth. *Physical Review B*, 37(8):3900 - 3905, 15 March 1988.
- [21] J.L. Cohn and C. Uher. Electrical resistance and the time-dependent oxidation of semicontinuous bismuth films. Journal of Applied Physics, 66(5):2045 - 2048, 1 September 1989.