

Thermal evaporative growth of high-quality bismuth thin films

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In an attempt to create high quality bismuth thin films, we have developed a technique for producing large bismuth grains. A thin layer of germanium (~200 angstroms) is grown on glass substrates (both at room temperature and heated to 150 °C), followed by the evaporation of the bismuth thin film (~10 μ m). The substrates are then individually placed in a tube furnace and annealed in an N₂ environment at various temperatures, both above and below the melting point of bismuth. The films are characterized through direct current resistance and magnetoresistance measurements. Although the quality of the films produced to date is not comparable with films previously created by other methods, we believe that further investigation will yield higher quality films. Additionally, the research conducted has provided much insight into the nature of bismuth and bismuth thin films, and presents suggestions for further experimentation.

1. Introduction

Elemental bismuth is an unusual semi-metal that exhibits some very interesting properties that could have profound applications. Particularly, metallic single-crystal bismuth has an extremely high magnetoresistance (where the electrical resistance has been known to increase by a factor of 10⁵ in a magnetic field of 7 T), giving rise to the potential for creating very good magnetic field sensors. Such metallic forms of bismuth will typically demonstrate a resistance that decreases by two orders of magnitude when cooled to liquid helium temperatures (~5 K). The growth of high-quality metallic thin films of bismuth, however, has proven to be very difficult. Usage of molecular beam epitaxy (MBE) on BaF₂ substrates has had some success, but is an expensive and slow fabrication technique [1]; and more conventional production methods such as thermal evaporation have generally resulted in the growth of polycrystalline bismuth, exhibiting a non-metallic resistance that increases with decreasing temperature.

Although the mechanism is not entirely understood, it is believed that this non-metallic behavior is due to the small grain sizes in such films. A current in a typical metal will travel due to diffusive electron scattering; in bismuth, however, it appears that the electrons actually follow ballistic trajectories within a single crystal grain. Bismuth has an exceptionally low electronic carrier density ($3 \times 10^{17} \text{ cm}^{-3}$) for a metal, yet will behave metallically because this effect is compensated by a long mean-free-path ($\sim 100 \text{ }\mu\text{m}$). In polycrystalline thin films, however, the bismuth crystals are much smaller than the mean-free path, causing strong diffusive electron scattering at the grain boundaries and effectively reducing the scattering time (i.e., the average length of time between electron collisions). Furthermore, since the magnetoresistance is proportional to the scattering time, this effect might also account for the low magnetoresistance in such samples.

Theoretically, by melting the bismuth in these films and then allowing it to cool, large grain size crystals should form as the bismuth re-freezes, thereby resulting in the desired metallic characteristics. Some work to this effect has already been completed. F.Y. Yang *et al.* [1] have grown single-crystal bismuth thin films by electrodeposition on pre-deposited gold substrates followed by suitable annealing, and have observed magnetoresistances up to 250% at 300 K and 380,000% at 5 K as well as clean Shubnikov-de Haas oscillations (a periodic magnetotransport phenomenon that occurs in metals in an intense magnetic field). However, Yang *et al.* failed to discuss what role the pre-deposited layer of gold played in their experiment. The greatest difficulty with melting thin film bismuth is that it has a high tendency to “ball up,” losing any pre-deposited shape or pattern above its melting temperature (271°C). We believe that the gold in Yang *et al.*’s experiment played a very crucial role in the creation of the films—

diffusing into the bismuth and creating a Bi-Au alloy with a eutectic temperature lower than the melting point of pure bismuth, thereby allowing the film to be melted without balling up. By thermally evaporating bismuth onto pre-deposited gold thin films followed by a post-annealing process, Du and Hebard [2] have been able to grow bismuth thin films with quality comparable to those grown by electrodeposition. In their study, they have tested the quality of their films due to different methods of preparation to determine what growth and annealing conditions produce the best films.

The scope of the present project was to conduct a similar study on the effects that a thin layer of pre-deposited germanium, in place of gold, would have on the quality of bismuth thin films, to determine what growth and annealing conditions produce the highest quality films (i.e., the greatest decrease in resistance with decreasing temperature and the greatest magnetoresistance at 5 K). Germanium, unlike gold, actually increases the eutectic temperature of the bismuth alloy, and therefore operates under a different mechanism. Instead of diffusing into the bismuth and allowing the alloy to melt at lower temperatures, the germanium effectively “wets” the substrate, preventing the melted bismuth film from balling up, much like a thin layer of water on glass will prevent drops from forming. With this technique, the bismuth can be annealed at much higher temperatures. The bismuth grains will then try to align with each other, and as the bismuth cools the films will recrystallize and form larger grains. Because this technique has never been tested before, the purpose of this experiment was twofold: A) to attempt to create bismuth thin films with quality comparable to that of single crystal bismuth; and B) to analyze the results, whether successful or not, in order to better understand the

peculiar electronic and magnetic transport properties of bismuth and to discern in what direction further studies should be directed.

2. Procedure

2.1 Thermal Evaporation.

The first step in the growth process of bismuth films is the preparation of the substrates on which the film will be deposited. Because they are so thin, any impurities on a dirty substrate will potentially have significant effects on the electrical or magnetic properties of the films. Therefore, Fisher Scientific Premium microscope slides, 1mm thick, are cut with a diamond knife into 1cm x 1cm squares and handled with tweezers to place them in a plastic substrate holder which prevents them from being scratched during cleaning. The substrate holder is placed in a glass beaker, which is filled with a series of cleaning agents and placed in a Branson 1210 sonicator for 20 min each step. First, alconox detergent is mixed with deionized water to wash the substrates, and is then rinsed out with deionized water alone. Next, the beaker is filled with acetone, then isopropanol, and finally methanol. The substrates are removed individually from the methanol with tweezers, and immediately blown dry with high pressure N₂ gas.

Once a substrate has been properly cleaned, a shadow mask, which was cleaned along with the substrates, is affixed to its surface by applying a small dot of rubber cement to one corner. The shadow mask is used to form a four-terminal measurement pattern on the substrate (Fig. 1). The substrates are then applied to a steel puck and placed in the vacuum deposition chamber. The chamber is sealed and the pressure reduced to approximately 2×10^{-6} torr by a diffusion pump. An 85-amp current is then passed

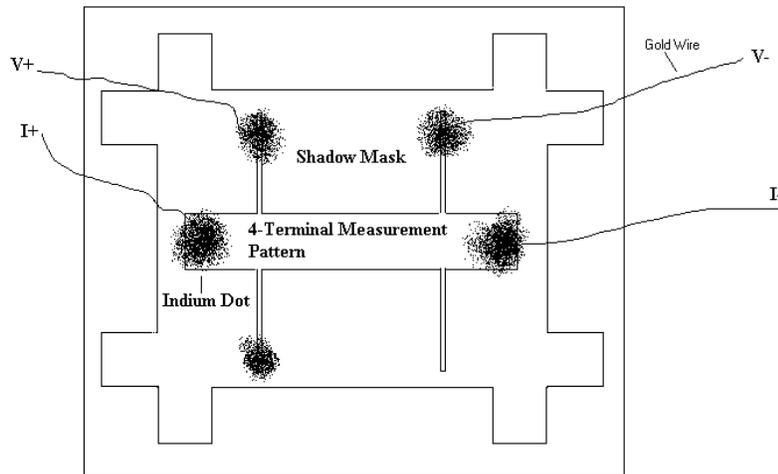


Figure 1. Sample substrate.

through a tungsten boat containing germanium powder, causing the germanium to heat up and evaporate. As the evaporated molecules come into contact with the relatively cold substrate, they immediately condense, forming the thin film. Once deposition is complete, the system is allowed to cool down and pump out any molecules remaining in the atmosphere; and, using 75 instead of 85 amps, the process is repeated for the bismuth. The growth rates for both the germanium and the bismuth can be observed using an Inficom XTC crystal monitor, allowing us to precisely grow a 200-angstrom-thick layer of germanium followed by $1\mu\text{m}$ of bismuth.

A variation on this method of growth was to heat the substrates during the bismuth deposition. In such cases, silver paint is used instead of rubber cement to affix the shadow masks to the substrates, and then to attach the substrates to a small heater of the same diameter as the steel puck used previously. The heater is then attached to a variac, and a 5V potential is applied to the heater to raise the temperature of the substrates to 150°C for the bismuth deposition (the temperature being monitored by a j-type thermocouple attached to the heater).

2.2 Annealing.

Once a bismuth film has been created, it is prepared for the annealing process. The substrate is fastened to an aluminum block by a steel screw, and the block is placed in a Lindberg Oven tube furnace. The tube itself is attached to a turbo-pump on one end and is sealed by a feed-through on the other. When steel blades are spun at turbo speeds, the turbo-pump reduces the pressure within the tube to approximately 5×10^{-5} torr; a valve on the feed-through is then opened, allowing the evacuated tube to be filled with N_2 gas (Fig. 2). The pump is turned on again and the process repeated, purging the environment of any oxygen or other reactive chemicals in the atmosphere. N_2 itself is non-reactive, and the presence of the gas in the tube ensures thermal uniformity. The temperature of the sample is monitored by a k-type thermocouple attached to the aluminum block.

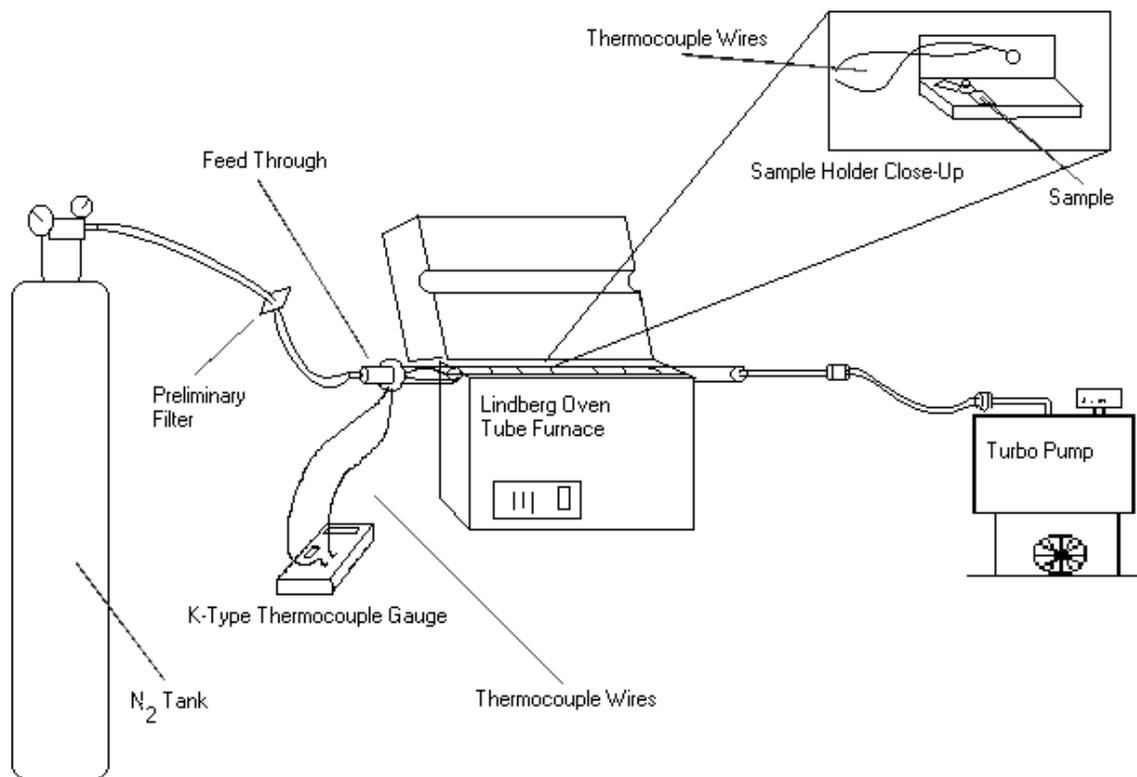


Figure 2. Experimental setup for the anneal process.

Furthermore, to ensure thermal accuracy, a small piece of bismuth is placed on a glass substrate next to the sample, and the observed melting point is calibrated against the theoretical 271°C. In all experiments, the measured temperature was accurate to within 2°C.

By using a variety of annealing temperatures and methods, four categories of samples were prepared:

- I. Samples grown at room temperature heated to 258°C, 273°C, 285°C, 294°C, or 305°C, where the oven was immediately turned off, allowing the samples to cool slowly within the oven's residual heat. Because bismuth melts at 271°C, these temperatures will therefore provide data points below, near, and above the melting point, allowing us to examine any trends from bismuth films that have not been melted, partially melted, or melted significantly.
- II. Samples with bismuth grown at 150°C heated to 287°C, 294°C, or 305°C, where the oven was immediately turned off, allowing the samples to cool slowly. Similar to category I, these data points will allow us to examine any trends developing for the samples grown under heat, and any differences these samples have from those of the first category.
- III. Samples grown at room temperature and annealed at 285°C by various methods, allowing us to compare annealing techniques. These methods include a) heating the sample to the desired temperature and immediately turning off the oven to allow the samples to cool slowly in the oven (the method used in the previous two categories); b) heating the samples to the desired temperature and using a fast cool method, where the oven is turned off and the lid opened as soon as the sample

reaches 285°C; c) heating the sample to 285°C and allowing it to sit for 2 hours before turning off the oven; and d) heating the samples to the desired temperature and allowing the sample to sit for two hours at 285°C, ramping the furnace temperature down manually to well below the melting point of bismuth (~260°C) at 1°C / 5min.

- IV. Unannealed samples grown at either 150°C or room temperature, providing a reference point.

2.2 Measurement.

Once a sample has cooled to room temperature from the annealing process, it is removed from the furnace, and indium dots are placed on the film to provide contacts for a four-terminal resistance measurement. Although not within the scope of this project, a fifth contact is made for a measurement of the Hall effect, a primary interest for further experimentation. The sample is then placed on a specially designed sample puck, from which gold wires lead to the indium contacts, and the puck is inserted into the Quantum Design Physical Properties Measurement System (PPMS). The PPMS consists of a liquid helium dewar with LN₂ jacket, in which lies the equipment necessary for establishing precise thermal and magnetic environments. Wires connect the sample puck inside the dewar to an external Linear Research Inc LR700 AC resistance bridge, which acquires four-wire resistance measurements for a range of temperatures (5 K to 300 K) at 0 T magnetic field, as well as for a range of magnetic field strengths (-7 T to 7 T) at 5 K (the magnetic field is oriented perpendicular to the films with positive field in the direction from germanium to bismuth, and resistance measurements are taken for both

increasing and decreasing field). Data from the bridge are sent electronically to be collected by a computer.

3. Results and Discussion

3.1 Category I.

Despite the thinness of the films, both the germanium and the bismuth on the samples grown at room temperature are visible to the naked eye. On top, the film appears to be a very smooth, reflective, silver metal, characteristic of bulk bismuth; through the glass substrate reflects the blue tint of germanium. Whether melted or not, the films look the same even after being annealed. On the surface of the melted films, however, there appears a series of lines branching off from each other at 60° angles visible under a microscope—perhaps the boundaries of large bismuth grains.

By examining the resistance vs. temperature curves (Fig. 3) for various annealing temperatures for the samples grown at room temperature, we notice immediately that, up to a certain point, the more the bismuth is heated during the anneal process, the more metallic its behavior. More specifically, at anneal temperatures lower than the bismuth's melting point (271°C) the samples are completely non-metallic (i.e., the resistance greatly increases with decreasing temperature). In fact, ignoring any relative shift in resistance (which for the most part is due to impurities, scratches, or placement of the contacts rather than the nature of the metal itself), the two samples (unannealed and 258°C) are almost identical, their resistance going as approximately $1/T$ from 75 to 300 K. Below 75 K, the films exhibit an interesting saturation effect, a peculiar quality of bismuth very uncommon in ordinary non-metals. Of course, as long as the grains have not melted we

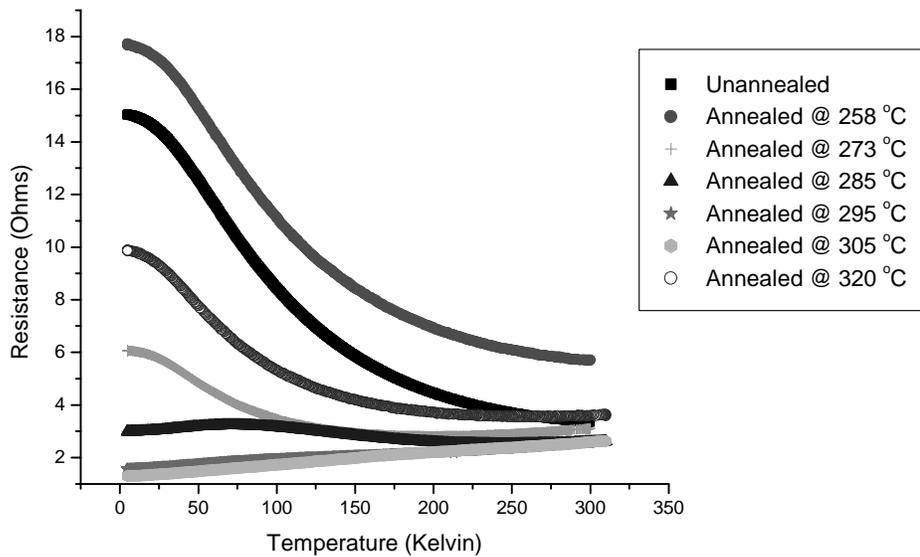


Figure 3. Resistance vs temperature for samples grown at room temperature.

would not expect any major differences. As the bismuth melts, however, the behavior begins to change dramatically. For the samples annealed near the melting point, the films will be only partially melted, and the resistance displays both metallic and non-metallic properties. At still higher anneal temperatures, the resistance becomes linear in temperature, dropping by approximately a factor of two between room temperature and 5 K for the 305°C sample. Once the sample becomes too hot, the bismuth begins to ball up, creating grains that are large but rather discontinuous, thereby depressing electrical conductivity

We might expect to see a correspondence between the metallic nature of the temperature dependent resistance of a film and its magnetoresistance. For unannealed samples, for example, which have not been melted and exhibit an increasing resistance with decreasing temperature, we might expect to have a relatively low magnetoresistance as compared with the highly metallic samples annealed at 295°C or 305°C. This trend,

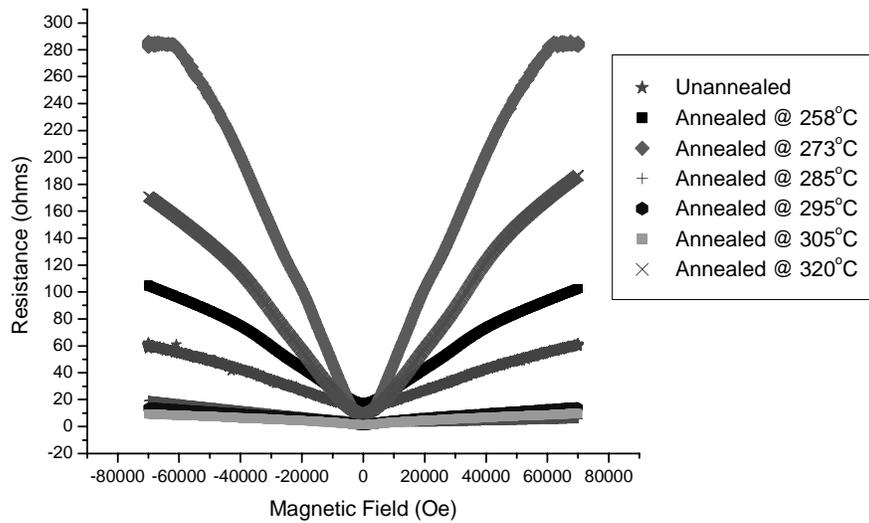


Figure 4. Resistance vs magnetic field for samples grown at room temperature.

however, is not very clear. Figure 4 provides an idea how the samples respond to magnetic fields, but, because magnetoresistance is a relative effect (magnetoresistance is defined as $[R(B) - R(0)] / R(0)$, where $R(B)$ is the resistance at high magnetic field strength, in this case 7 T, and $R(0)$ is the resistance at zero field), we must consult the table of magnetoresistances (Table I) to accurately compare.

TABLE I. Magnetoresistance vs anneal temperature for samples grown at room temperature.

<u>Anneal Temperature (°C)</u>	<u>Magnetoresistance</u>
Unannealed	3.2
258	4.8
273	46.9
285	5
295	13.1
305	8.7
320	18

Although it's not uniform, there seems to be a trend towards higher magnetoresistances at higher annealing temperatures. The 320°C sample, which was showing

non-metallic character because the high annealing temperature was causing it to begin balling up, has one of the highest magnetoresistances of all the samples. This might suggest that the bismuth is in fact behaving as a ballistic metal. The higher the annealing temperature, the larger are the grains, and therefore, the greater is the electrical conductivity as well as the magnetoresistance. When the samples become too hot, the bismuth begins separating, diminishing conductivity between the grains, yet the grains themselves will remain large with a high conductivity within each grain. If the bismuth is in fact a ballistic metal, its electrons will travel across the grains and scatter at grain boundaries before scattering at an impurity within the grain. Because magnetoresistance is due to the magnetic induced curvature of electrons within their flight, a large bismuth grain allows a long ballistic trajectory and therefore high curvature, resulting in high magnetoresistance.

However, there is the very prominent anomaly at 273°C (with a magnetoresistance at least three times greater than every other sample) that cannot be overlooked. Such a high magnetoresistance is both exciting and frustrating—it shows that high quality films are possible to create and suggests we can do even better, but it does not seem to fit our picture of grains and grain boundaries. Is there some kind of “sweet spot” right near the melting temperature of bismuth? If so, why is it there?

Perhaps all we can really say about these data is that the method of annealing does work, because the samples that have been melted show much greater magnetoresistances than those that have not. The exception to this is the sample annealed 285°C, but this might be expected because this sample is an exception in another way. The resistance of the 285°C sample is highly asymmetric with respect to the direction of the magnetic field

(Fig. 5). Furthermore, there is no hysteresis, and the data are reproducible. Although this behavior is not understood, it is seen elsewhere (see category II below), and in all cases of asymmetry we find a low magnetoresistance. In any case, even if melting the samples promotes metallic behavior and high magnetoresistance, what method of annealing should be used, and at what temperature? The latter question obviously requires further investigation. The former is addressed in category III below.

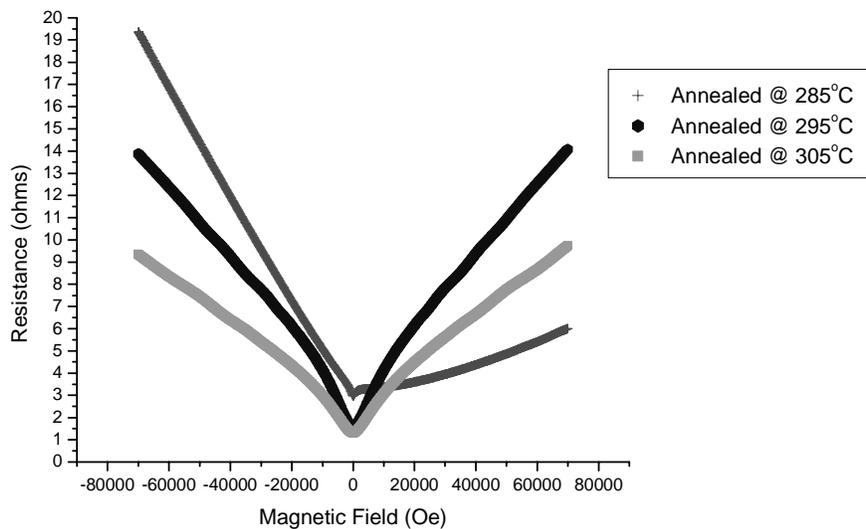


Figure 5. Resistance vs. magnetic field (detail of field asymmetry).

3.2 Category II

Unlike the samples grown at room temperature, the samples grown at 150°C look almost white and are non-reflective, suggesting that the films are very rough and uneven. The idea is not unlikely; during thermal evaporation, the bismuth films are created by individual molecules sticking to nucleation sites—in this case the germanium. With the samples grown at room temperature, the germanium is relatively stable, allowing the bismuth to grow uniformly and smooth out slowly. On a heated substrate, the bismuth atoms are more mobile and diffuse to nucleation sites where they agglomerate to form

large islands. At some critical thickness, these islands merge and the film becomes electrically continuous with a rough topography.

This fact is somewhat apparent in the temperature and magnetic field dependent resistances of these samples (Figs. 6, 7). The unannealed sample is non-metallic, as seen by the dramatic increase in resistance at low temperatures, and this is most likely due to a large number of grain boundaries interacting with traveling electrons. But even once the film has melted, the resistance appears dominated by almost insulating contact between the grains themselves, rather than the metallic dependence expected from the temperature dependant electron phonon scattering within a grain. Despite the shift in relative resistance, all three melted samples exhibit partially metallic behavior in response to decreasing temperature. The bismuth grains are fairly large yet relatively unaffected by electron scattering within the grains—the electrons are able to travel long distances within the grains, but the grains themselves are too far separated to act as a metal.

Samples Heated @ 150°C During Growth

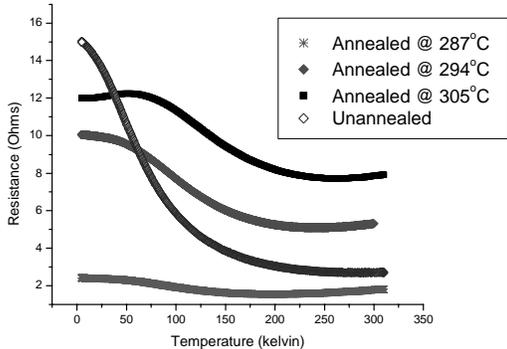


Figure 6. Resistance vs temperature.

Samples Heated @ 150°C During Growth

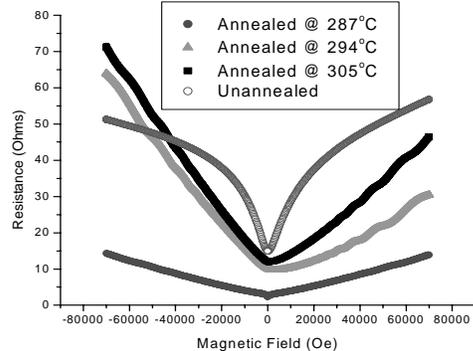


Figure 7. Resistance vs magnetic field.

Similarly, magnetoresistance is not only proportional to the scattering length (i.e., the size of the grain in the ballistic regime), but is dependent on the overall electrical resistance as well. The grains may be large, but if the grains are ineffectually joined the

TABLE II. Magnetoresistance vs anneal temperature for samples heated during growth.

Anneal Temperature (°C)	Magnetoresistance
Unannealed	2.8
287	4.8
294	2
305	2.7

magnetic field will have little effect on the sample's resistance. Table II shows that all samples grown at 150°C have comparable magnetoresistance, whether melted or not. This idea is further enforced by the appearance of strong Shubnikov-de Haas oscillations in the magnetic field dependent resistance of the samples annealed at high temperatures (Fig. 8). The presence of Shubnikov-de Haas oscillations reflects a high quality material with a long mean free path. Therefore, we would expect these oscillations to occur most prominently in samples with large metallic grains, regardless of overall conductivity.

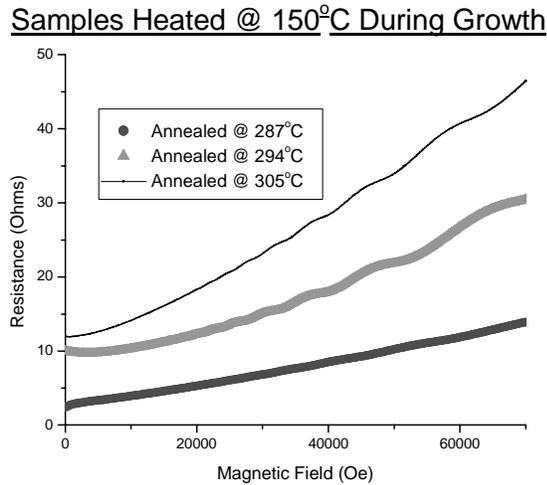


Figure 8. Resistance vs magnetic field (detail of Shubnikov-de Haas oscillations).

So heating the samples during evaporation will cause the growth of large but disconnected grains—an entirely detrimental technique for creating high-quality films. This fact is illustrated by comparing the samples grown at 150°C with those of category I

grown at room temperature. At least in the case of the melted samples, the category I samples exhibit a more metallic temperature dependent resistance (Fig. 9) as well as greater magnetoresistance (Fig 10; also compare Tables I and II).

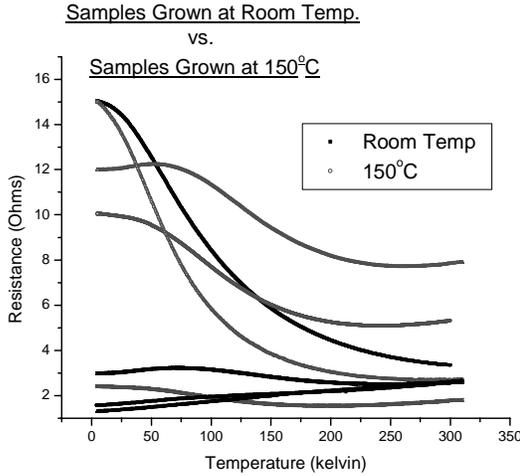


Figure 9. Resistance vs temperature.

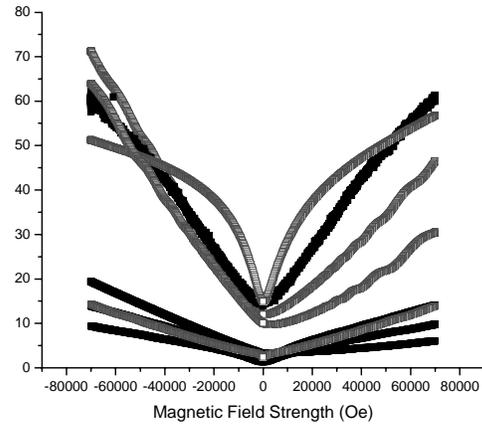


Figure 10. Resistance vs magnetic field.

The 150°C samples do demonstrate some interesting characteristics, however, that are not as pronounced elsewhere. First, these films have very sharp peaks (i.e., large differential magnetoresistance) at low fields; second, there appears for a second time an asymmetry between the effects of positive and negative magnetic fields on the resistance of the 294°C and 305°C samples. These phenomena are not understood and warrant further investigation.

3.3 Category III

In searching for a method of creating the best quality thin films, the question of how to anneal the samples is as important as at what temperature to anneal them. It might even be the case that once a film is melted, regardless of the highest temperature reached, only the method of cooling is relevant. Although we believe that this is not the case, as

we have seen we cannot be absolutely sure of anything, and much more experimentation is required. In any case, we can see a difference in behavior in samples annealed at 285°C by different methods. First, it seems as if the method of annealing we were fortunate enough to have used for the other categories of samples—turning off the oven when the sample has reached the desired temperature and allowing it to cool slowly in the residual heat of the oven—produces the most metallic behavior (Fig. 11). Even so, this method produced only partially metallic behavior. It is possible that 285°C simply is not hot enough to produce metallic samples, but allowing a sample to sit for two hours in this heat causes germanium to diffuse upwards into the material along the grain boundaries, and, because germanium is a semi-conducting material, causes the non-metallic behavior.

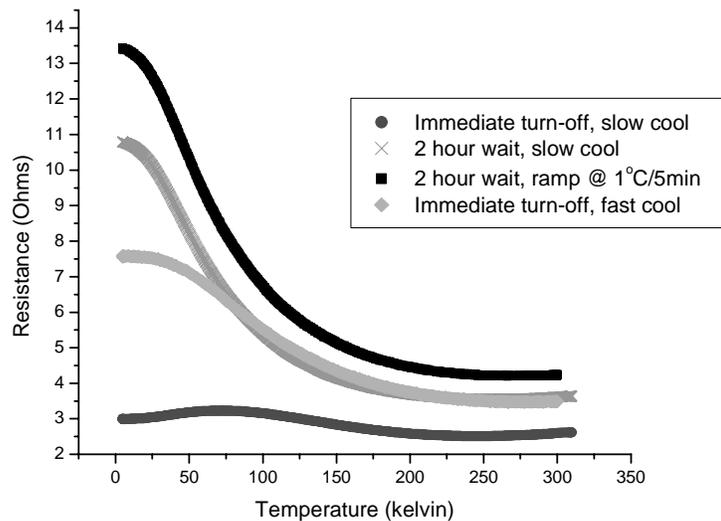


Figure 11. Resistance vs temperature for various annealing methods.

Whether this is true or not, the two samples that sat at 285°C for two hours do exhibit a much greater magnetoresistance than the samples that began cooling immediately (Fig.12, Table III). It may be that even if germanium is diffusing into the bismuth, the extended heat ultimately allows for much larger grains to be created. The

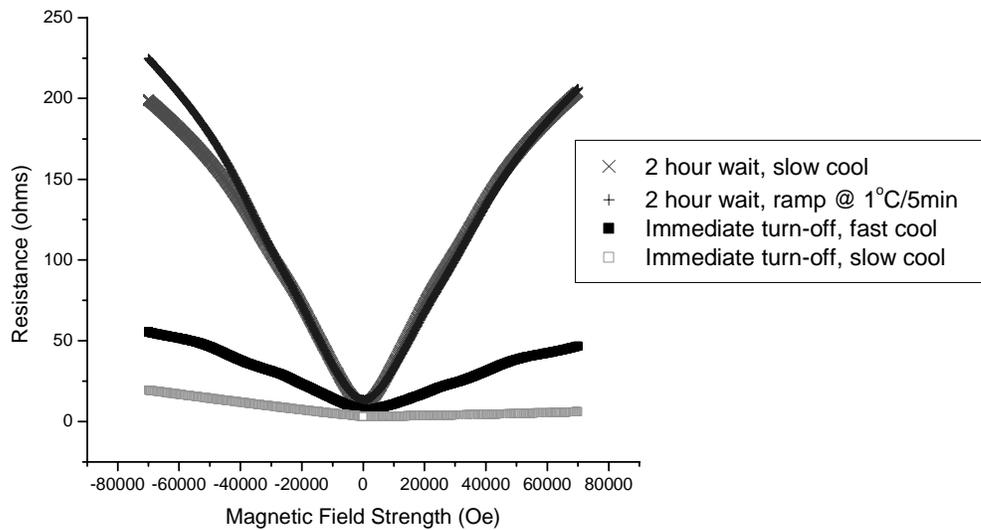


Figure 12. Magnetic field dependent resistance for various anneal techniques. Note the asymmetry.

germanium interferes with electrical conductivity between grains, but does not disturb the long mean free path of the electrons within the grains—in this case a more significant effect. Perhaps if all samples in all categories had been allowed to sit for two hours or even longer before cooling, we could reproduce the high magnetoresistance found in the few anomalous samples.

Table III. Magnetoresistance vs anneal method.

<u>Anneal Method</u>	<u>Magnetoresistance</u>
2 hour wait, slow cool	17.9
2 hour wait, ramp @ 1°C/5min	16.2
Immediate turn-off, fast cool	5.2
Immediate turn-off, slow cool	5.5

4. Conclusion

In general, the technique of using a pre-deposited layer of germanium on our substrates has not reproduced the results shown previously with a pre-deposited layer of

gold. For almost all the samples, the bismuth films demonstrated neither the metallic temperature dependent resistance behavior nor the high magnetoresistance found by using gold. However, in certain cases the magnetoresistance was found to be exceptionally high, providing hope that under certain circumstance the germanium method is a viable means of producing high quality bismuth films. In fact, a sample has been produced that exhibits a magnetoresistance comparable to the pre-deposited gold samples (Fig. 13). This particular sample has a magnetoresistance of 142; unfortunately, an accurate reading of the temperature at which this sample was annealed could not be attained, so the result has not been reproduced. But perhaps there is some “sweet spot” just above the melting point of bismuth that will allow us to recreate these high quality films. Undoubtedly, more experimentation is required.

The fact is, due to the thinness of these films, all results will be highly sensitive to external factors, especially impurities in the films. Fundamentally, the measurements are sample dependent. Although the crystal monitor used to observe and control growth of the films is reasonably precise, there is certainly some variation from batch to batch.

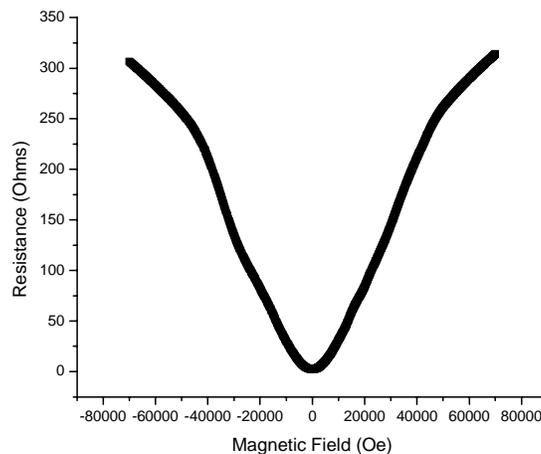


Figure 13. Anomalous data (anneal temperature unknown).

Furthermore, a discrepancy in either germanium or bismuth film thickness between samples, or in film topography, could have profound consequences. An interesting experiment would be to actually grow a range of varying film thickness to see how this variable affects the quality of samples, performing x-ray diffraction or atomic force microscopy to characterize the film's surface. Comparative tests should at least be conducted between samples grown at the same time under the same conditions. Even so, water vapor condensing on a film or oxidization during the annealing procedure, as well as any number of other factors, may introduce differences between samples in a single batch. Thus, further experimentation must not only test for external variables, but must also be able to reliably reproduce results.

Despite the questions concerning sample dependence, this method of growth has produced some very interesting behavior. For one, why do some of these samples exhibit asymmetric responses to positive versus negative magnetic fields? If it is reproducible, this behavior warrants serious investigation. Secondly, why do the non-metallic bismuth films, unlike typical semiconductors, have a resistance that saturates out at low temperatures? Third, a number of the samples display beautiful Shubnikov-de Haas oscillations, and these oscillations are much more prominent than any observed with the pre-deposited gold samples. Further investigation and analysis of this behavior might provide a clue about the intricacies of this peculiar metal. For example, it could help theorists understand the until-now elusive nature of bismuth's Fermi surface. Fourth, understanding the presence of sharp peaks in the magnetic field dependent resistance at low fields could have profound consequences, especially for computer technology. Because most computer hard-drives operate by small magnetic pulses, a high

magnetoresistance in the low field regime could greatly increase sensitivity. Finally, it is interesting to note that, as opposed to the pre-deposited gold samples, a thin layer of germanium on the substrates allows us to fabricate these films by actually annealing the samples *above* the melting point of bismuth. Obviously, there is much left to explore. The important point is that a new mechanism for the creation of bismuth thin films has been developed.

Acknowledgements

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