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# THEMOELECTRIC PROPERTIES OF BISMUTH-ANTIMONY THIN FILMS

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NOTICE

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# THERMOELECTRIC PROPERTIES OF BISMUTH-ANTIMONY THIN FILMS

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## Introduction

Thermoelectrics have a wide range of potential applications in the temperature range of 0° to 100°C. In the area of power generation, there are a variety of low-grade heat sources (such as ocean thermal gradients, geothermal sources, and industrial waste heat) that can be exploited to generate electric power using thermoelectrics.[1] In the area of cooling, there is a growing market for industrial air conditioning, cooling of microcircuitry, and refrigeration down to cryogenic temperatures. Many of these applications can be realized if thermoelectric converters, given the situation of limited efficiency, can be made inexpensive. Present-day technology uses expensive materials and, more importantly, uses very expensive manufacturing techniques. Materials used in the temperature range of 0° to 100°C are quaternary alloys of bismuth, antimony, selenium, and tellurium. Processes used for device fabrication are elaborate with hundreds of n and p elements arranged individually and connected in series, resulting in excessive labor costs.

In an effort to enhance the feasibility of thermoelectrics, we have begun investigation of potentially cheaper materials and cheaper techniques for thermoelectrics. Two features of bismuth and antimony have influenced our work. First, Horst and Williams[2] have reported quite respectable figure of merit values in bulk single crystals of bismuth-antimony, up to 2.5 × $10^{-3}$ at room temperature. Second, bismuth and antimony are an order of magnitude cheaper in cost compared to selenium and tellurium, making this binary alloy a natural candidate to reduce the cost of thermoelectric devices. Our avenue of approach involves a simplification of the fabrication process using an established technique of solid-state electronics: thin-film deposition. We have recently begun to investigate the extent to which the favorable properties of bulk Bi-Sb are preserved in thin films. This paper reports some of the preliminary data coming out of this ongoing investigation.

## Sample Preparation and Characterization

Our samples are prepared by simultaneous evaporation from heated crucibles containing pure bismuth and pure antimony respectively. The simultaneous evaporation from separate crucibles causes a range of alloy compositions to deposit along the substrate. In our studies so far, we used 25-micron-thick mylar substrates held at room temperature for convenience. The films adhere well, generally have a smooth, uniform appearance, and can be handled easily. They have not shown any change in properties on exposure to atmosphere. Our film thicknesses to date have been on the order of 1 micron and have required evaporation times of about 20 minutes/micron at a starting pressure of 2 × $10^{-5}$ torr. Copper contact strips, for use in the electrical measurements, are deposited beforehand along the longitudinal edges of the substrate.

Following the deposition, we slice the film into transverse strips, each of approximately uniform composition, numbered consecutively from the antimony-rich to the bismuth-rich end. The odd-numbered strips are set aside for thickness measurements using a precision stylus gauge. Portions of these strips can be pulled from the substrate with adhesive tape. The heights of several of the steps thus formed, as measured by the stylus gauge, are averaged to determine the thickness of each strip to ± 5%.

The even-numbered strips are preserved for the electrical measurements. Their thicknesses are inferred by interpolation of the odd-numbered strip data. Finally, after the electrical properties have been determined, the compositions of the even-numbered strips are ascertained by X-ray fluorescence.

## Experimental

Measurements of the Seebeck coefficient $\alpha$ and of the electrical resistance R were carried out at temperatures ranging from -100°C to over +100°C. For all of the measurements, the samples were clamped between two copper blocks that were indi-

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vidually equipped with heaters and thermocouples. The latter were in electrical as well as thermal contact with the copper blocks. The heaters were used to establish temperature differences across the samples, typically 2° to 5°C as measured by the thermocouples. The Seebeck coefficients of the samples relative to those of the thermocouple materials (copper, Constantan, and/or Chromel) were then determined by measuring the voltages induced across the appropriate thermocouple leads. All of the results were corrected to absolute values using standard tables. The coefficients deduced from measurements relative to the several thermocouple materials generally agreed with one another to within 1 μV/°C.

In a similar manner, the resistances of the films were determined from two-lead resistance measurements across the thermocouples, after subtracting the resistance of the thermocouple wires.

Three separate assemblies of the type just described were used to cover the temperature range of interest. For measurements below room temperature, one assembly was situated in a vacuum chamber above a liquid nitrogen bath. For the high-temperature measurements, a second set-up was located in a sealed furnace. These measurements, at elevated temperatures, are usually carried out in an atmosphere of dry nitrogen or helium. Finally, for work near room temperature, a third assembly was simply exposed to air during the measurements.

The use of three different apparatuses, each of which provided several quasi-independent Seebeck coefficients and resistance measurements, provided an ongoing cross-check of the results.

## Results and Conclusion

The Seebeck coefficients of a series of three bismuth-rich films are displayed as a function of temperature in Fig. 1. In comparison, several results by previous authors on bulk, single-crystal alloys are shown as well. The important aspect of the figure, and a principal result of this preliminary investigation, is that the Seebeck coefficients of evaporated alloy films are comparable to those which have been seen in well-prepared single crystals. This suggests that economical device development using these materials may well be based on film technology rather than on bulk materials processing.

The relatively large degree of scatter in our data may be due to difficulties in the clamping arrangements we used. Improved, positive thermal and electrical contact, through conductive paints, soft metal pads, or the like, should result in future data that are smooth on the scale of our instrumental resolution--i.e., ± 1 μV/°C. However, our main point (that the Seebeck coefficients are comparable to those of bulk samples) is unaffected by this problem.

For increasing concentrations of antimony (increasing from Sample 1 to Sample 3), the Seebeck coefficient and electrical conductivity decreases. This behavior is similar to bulk material and could be explained by the model Horst and Williams have proposed. Preliminary annealing studies on these films show a marked increase in Seebeck coefficient and electrical conductivity around 200°C. The exact compositions of these films are being determined by X-ray fluorescence technique and will be reported.

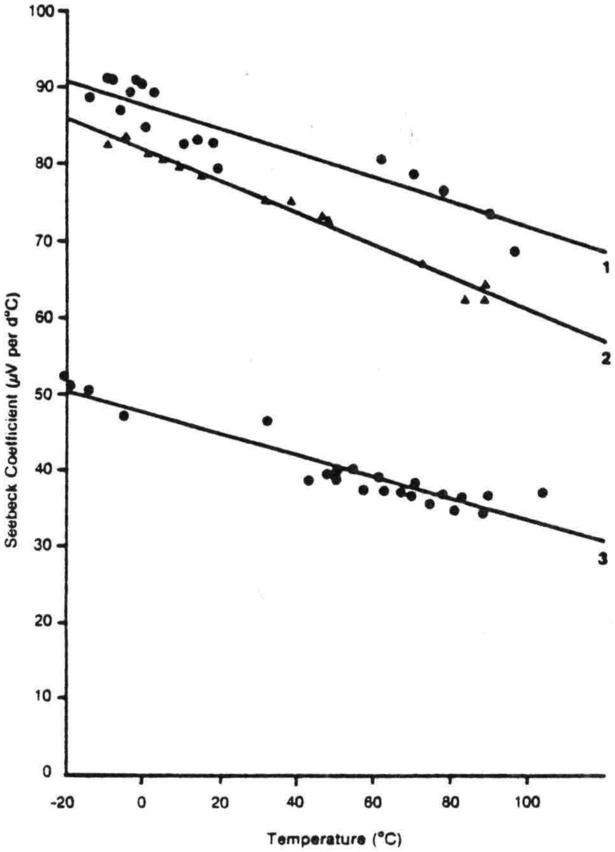

**Figure 1. Plot of Seebeck Coefficient versus Temperature in Bismuth-Antimony Thin Films. (Antimony Concentration Increases from 1 to 3.)**

Our preliminary data indicate that thin films of bismuth-antimony, prepared by very simple means of thermal evaporation onto plastic substrates, are quite interesting from the point of view of inexpensive thermoelectric generator development. Values of Seebeck coefficients are similar to that of the bulk single crystals, but the electrical conductivities are somewhat lower. However, the physical processes (due to the structure of thin films) that decrease the electrical conductivity also decrease the electronic part of thermal conductivity. Therefore, the decrease in figure of merit of thin films as compared to bulk may not be as serious as the $\alpha^2\sigma$ product (Fig. 3) would indicate. Further investigations are progressing in the study of thermoelectric properties of these films using thicker samples (a few microns in thickness). We are also studying the effect of annealing, doping, and substrate temperature on thermoelectric properties, which are known to produce significant improvement in these properties[2] in the bulk and in bismuth telluride thin films.[3] The results of these investigations will be published later.

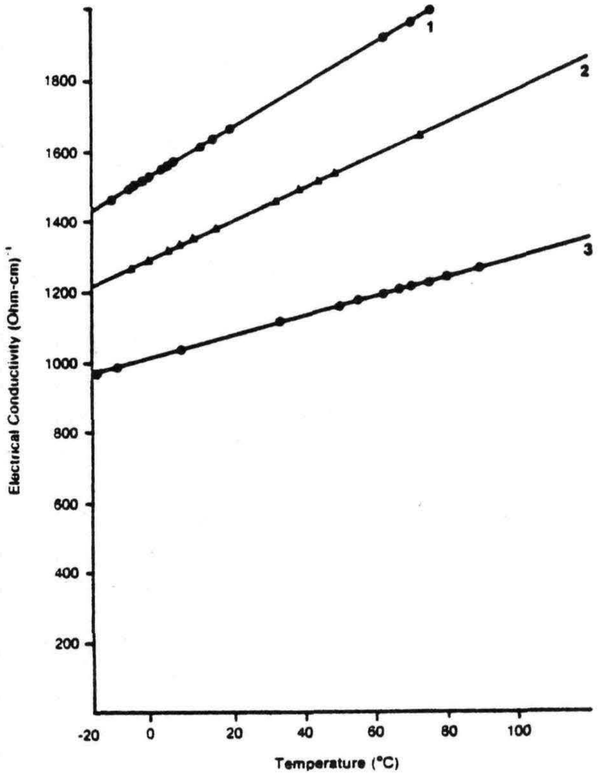

**Figure 2.** **Plot of Electrical Conductivity versus Temperature in Bismuth-Antimony Thin Films. (Antimony Concentration Increases from 1 to 3.)**

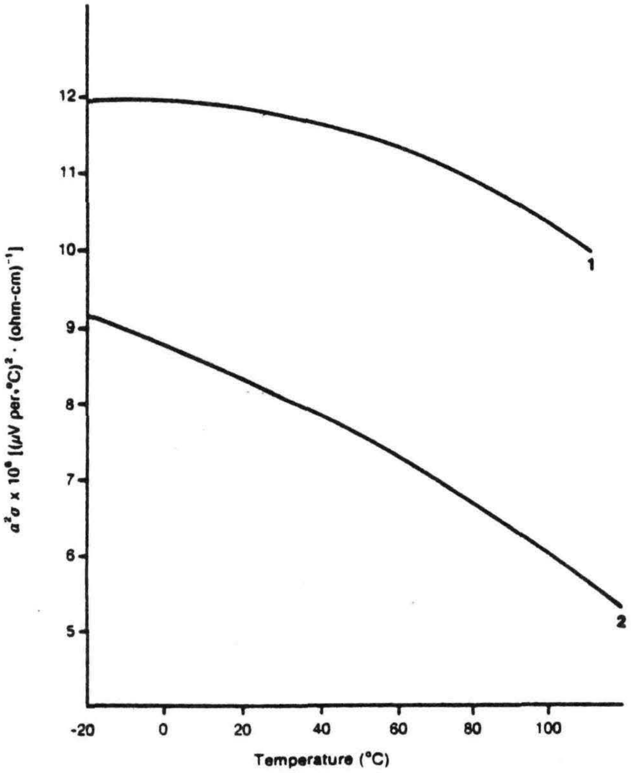

**Figure 3.** **Plot of $\alpha^2\sigma$ Factor versus Temperature in Bismuth-Antimony Thin Films. (Antimony Concentration Increases from 1 to 2.)**

## References

1. Jayadev, T. S. and Benson, D. K. "Thermoelectric Energy Conversion--Economic Electric Power from Low-Grade Heat." Proceedings of 3rd International Conference on Thermoelectric Energy Conversion. Arlington, TX; March 14, 1980.

2. Horst, R. B. and Williams, L. R. "Potential Figure of Merit of the Bi-Sb Alloys." Proceedings of 3rd International Conference on Thermoelectric Energy Conversion. Arlington, TX; March 14, 1980.

3. Harpster, J. "Vacuum Deposited TED's for Electric Device Chip Cooling." Proceedings of 2nd International Conference on Thermoelectric Energy Conversion. Arlington, TX; March 22, 1978.