ELECTRONIC FILE AVAILABLE

UCRL-JC-123753
PREPRINT

CONF-960334-4

**Synthesis and Evaluation of
Thermoelectric Multilayer Films**

A. V. Wagner, R. J. Foreman, L. J. Summers,
T. W. Barbee Jr., and J. C. Farmer

RECEIVED
JUL 01 1996
OSTI

This paper was prepared for submittal to the
ICT96 XV International Conference on Thermoelectrics
Pasadena, California
March 25, 1996

March 21, 1996

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

HH
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

SYNTHESIS AND EVALUATION OF THERMOELECTRIC MULTILAYER FILMS

Andrew V. Wagner, Ronald J. Foreman, Leslie J. Summers,
Troy W. Barbee Jr., and Joseph C. Farmer

*Chemistry and Materials Science Department
Lawrence Livermore National Laboratory
7000 East Avenue Livermore, CA 94550 USA*

Abstract

The deposition of compositionally-modulated $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ thermoelectric multilayer films by magnetron sputtering has been demonstrated. Structures with a period of $140\text{\AA}$ are shown to be stable to interdiffusion at the high deposition temperatures necessary for growth of single-layer crystalline films with $ZT > 0.5$. These multilayers are of the correct dimension to exhibit the electronic properties of quantum well structures. Furthermore it is shown that the Seebeck coefficient of the films is not degraded by the presence of this multilayer structure. It may be possible to synthesize a multilayer thermoelectric material with enhanced ZT by maximizing the barrier height through optimization of the composition of the barrier.

Introduction

While thermoelectrics are used in countless temperature sensing applications, their use for electrical power generation or cooling is limited by their relatively low efficiency compared to mechanical heat engines and CFC/HCFC based refrigeration cycles. Theoretical predictions by Hicks and Dresselhaus suggest that using 2D quantum confinement of the charge carriers in multilayer thermoelectric materials may lead to a substantial increase in the figure of merit (Z).^[1-2] Enhanced thermoelectric properties in quantum well (QW) layers have been recently demonstrated with samples synthesized with MBE.^[3] However, to make thermoelectric multilayer materials commercially viable, it is essential to extend the MBE work and grow QW materials with a high Z by an established high deposition rate technique like sputtering.^[4,5] Expertise in the field of multilayer deposition by sputtering has been developed at Lawrence Livermore National Laboratory through extensive work on multilayer x-ray optics and other materials^[6-8].

In this work we demonstrate the effectiveness of magnetron sputtering to synthesize thermoelectric multilayer materials with potential for 2D QW behavior. Compositionally-modulated $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ multilayer films have been chosen for this investigation for several reasons. First, these materials have the best thermoelectric properties at room temperature. Thus, any increase in performance which can be achieved will produce a superior technological material. Second, the bandgap can be varied by changes in the Bi:Sb and Te:Se ratios without

introducing any other elements. We show that the inevitable interdiffusion between layers does not degrade the Seebeck coefficient by excessive doping of the QW material.

Experimental procedures

Deposition by magnetron sputtering:

Three characteristics of the sputtering process have enabled the deposition of multilayer thermoelectric films with abrupt interfaces. First, sputtering gives steady deposition rates which allow synthesis of multilayer samples with individual layers of uniform thickness. Second, it allows multicomponent materials to be deposited from a single source without many of the compositional shifts associated with thermal evaporation techniques. Third, the argon ions from the sputtering gas can be used to bombard the growing film at low energies by biasing the substrates. This ion bombardment can be used to change the growth morphology by imparting extra energy to the growth surface. Unlike increases in temperature, which also increase surface mobility, low energy ion bombardment does not cause interdiffusion of the layers which have already been deposited.

The films discussed here were all synthesized in a system originally designed to fabricate multilayer X-ray optics. The system is cryogenically pumped and usually achieves base pressures of approximately 1×10^{-7} torr prior to sputtering. Substrates are mounted on an electrically-isolated heated stage which rotates below two magnetron sputtering guns. The sputter sources are usually operated at an argon pressure around 0.016 torr and a power of 10 watts to give deposition rates of about $5 \text{ \AA/s}$ directly under the gun. Multilayer samples are synthesized by alternately sweeping the substrates under the magnetron sputter sources, one depositing a conduction layer and the other depositing a barrier layer. Single-layer films are made by using a single source and either sweeping under the source or positioning the substrate directly below the source. A computer controls the position and slew rate of the stage, as well as the sources allowing automated deposition. Temperature, gas pressure, and gun parameters are logged by the computer as a function of time.

Film property measurement:

When measuring the thermoelectric properties of thin films, it is very important to make sure that substrate interference is eliminated. For this reason we have chosen to

Figure 1. Effect of deposition conditions on film growth. SEM micrographs of a series of films deposited on mica substrates: a) Rough growth morphology of a film deposited at 300°C; b) film grown at 400°C. c) an isolated crystallite in an otherwise highly textured film. Deposition started at 340°C to reduce nucleation of non-textured grains while a 380°C growth temperature leads to the best thermoelectric properties.

deposit all of our films on insulating substrates so that there are no possible contributions to the measured electrical properties from the substrate. The Seebeck coefficient is measured by bridging the sample between two stages which are independently temperature controlled from the boiling point of liquid nitrogen 77 K to about 700 K. K-type thermocouples are attached to both ends of the sample with electrically-conductive silver paint. The thermocouple leads are used to measure the temperature of each end of the film as well as measure the potential generated between the ends of the film by the temperature gradient. The Seebeck coefficient of the thermocouple wires, which is well known can then be used to compute the absolute Seebeck coefficient of the film. Typically a temperature gradient of $\sim 15^\circ\text{C}$ is maintained by the data logging and control computer as the samples are heated through the desired temperature range. Details of this technique are described in earlier publications^[9,10].

Resistivity was measured at room temperature with a digital ohm meter. These measurements were confirmed by using an AC version of the van der Pauw technique. A two probe technique was used to measure resistivity as a function of temperature from 77°K to about 700°K. A square bipolar current pulse was passed through the sample, and a lock-in amplifier was used to measure the voltage drop between two independent probes.^[9,10]

Single-crystal mica substrates were chosen for these experiments. Although mica has the hexagonal in-plane symmetry of the films, they are not lattice matched. Mica is a particularly useful substrate since it can be acquired as large areas which are atomically smooth. The ability to work with large area films deposited on mica increases the reliability of our measurements. The characteristics of thin mica sheets which are strong, flexible and electrically insulating make it an ideal material for thin-film device applications.

The thin mica substrates do not make good thermal contact with the stage making them difficult to heat. This problem has

been overcome by the use of a "hot walled" environment developed to maintain the stoichiometry of the film. Without heating the shields around the sample, the temperature of the substrates would be in radiative equilibrium at a temperature between the temperatures of the stage and chamber. Finally, the mica substrates can withstand the temperatures required for growth of high-quality films.

Results

Single layer films:

The first step in the development of multilayer films is to deposit flat high electrical quality, single-layer films of the component materials. $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ was used for the QW. This material was chosen so that a small amount of interdiffusion from the barrier material $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2(\text{Te}_{0.5}\text{Se}_{0.5})_3$ the optimum p-type bulk material will be achieved in the QW. The primary issue arising in the deposition of the $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ system is maintaining the ratio of $(\text{Bi}+\text{Sb}):(\text{Te}+\text{Se})$. Slight shifts in composition change the doping and thus affect the electronic properties. In vapor deposition this is compounded by the different vapor pressures of the elements. Since Te has the highest vapor pressure, it is re-evaporated from the growing film when depositing on a hot substrate^[11]. By increasing the Te concentration in the QW sputtering target to a composition of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_4$, an overpressure of Te can be achieved. This Te overpressure is found to increase the ZT achievable in the quantum well material by allowing higher temperature deposition. An excess Te barrier target has not yet been tried. To further enhance this overpressure a "hot wall" technique has been developed. The sputtering gun and the heated substrate table are surrounded by a heated shield. The best results have been achieved when the shield temperature is from 30 to 60°C above that of the substrates.

An extensive series of samples were synthesized in order to optimize sputtering conditions both in terms of morphology and

Figure 2. X-ray θ - 2θ diffraction scan of the single layer film shown in figure 1c illustrating the (003) family of peaks from the $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ film. All the other peaks are mica substrate peaks showing that the film is extremely well textured.

Figure 3 X-ray rocking curve taken by scanning θ with the detector set at the 2θ condition for the (0,0,15) peak. FWHM 0.15° .

electronic properties. The effect of temperature and deposition parameters on film morphology can be seen in figure 1. The SEM micrograph shown in figure 1a illustrates one of our first films deposited at a stage temperature of 300°C and substrate bias of -25 V . This deposition was without an excess Te target or the "hot walled" environment. The resulting rough morphology is not suitable for multilayer growth. The micrograph shown in figure 1b clearly demonstrates the improvement caused by increased deposition temperature and the "hot walled" environment. This sample was deposited at approximately 400°C in the hot walled environment with an excess Te target. The bias was lowered to -15 V and only used for the first 30 seconds of deposition. Figure 1c illustrates improved film morphology achieved by beginning the deposition at a reduced temperature. This film was deposited under the same conditions as the film shown in 1b except the deposition was started at 350°C and raised to 380°C during deposition. The sputter deposition rate was also reduced by a factor of four.

Figure 4. X-ray diffraction scan of a multilayer film. The peak at 45° is the (0,0,15) peak from the film. The mica substrate peak goes off scale to the right. The other peaks are the multilayer satellite peaks showing that the film is compositionally modulated with a period of $140\text{\AA}$. The dotted line is to aid the eye showing the mica substrate reflections for Cu K_β , $K_{\alpha 1}$ and $K_{\alpha 2}$ from left to right.

Crystal perfection was investigated using x-ray diffraction. The films are typically highly textured with the c axis along the growth direction. In a typical x-ray diffraction scan only the (003) family of peaks can be seen along with the mica substrate peaks (figure 2). X-ray rocking curves confirm that deviations of the c axis from the growth direction are small (figure 3).

Despite the large variation in the individual electronic properties caused by variation in doping, the overall performance of the films measured by ZT (assuming a thermal conductivity of bulk material of the same resistivity $0.014\text{ W/cm}^2\text{K}$) was not nearly as variable. Increasing the deposition temperature up to about 380°C was found to improve the ZT of the films. It was not possible to control Te losses and morphology sufficiently above this temperature. Films with $\text{ZT} > 0.5$ at room temperature can consistently be grown, with values for the best films as high as 0.6. Although these values are below the value of $\text{ZT} \sim 1$ for optimized bulk material this may be partly a result of the assumed thermal conductivity. Phonon scattering at the grain boundaries in the films may reduce the thermal conductivity below that of bulk material, thus helping enhance ZT.

Figure 5. Bright field TEM micrograph of the $140\text{\AA}$ period multilayer film. Diffraction contrast with a Fresnel defocus condition clearly shows the layering.

		Seebeck resistivity ZT		
		$\mu\text{V/K}$	$10^{-3}\Omega\text{cm}$	
Well	$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$	118	0.53	0.56
Barrier	$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_{1.5}\text{Se}_{0.5}$	210	5.30	0.18
Multilayer		140	1.40	0.30

Table 1 Measured electrical properties of single-layer and multilayer films at room temperature. The dimensionless figure of merit was calculated assuming a thermal conductivity of $0.014 \text{ W/cm}^2\text{K}$.

Multilayer experiments:

Compositionally modulated $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ structures have been deposited. Their structure was investigated both by x-ray diffraction and TEM. The x-ray diffraction scan of a $140\text{\AA}$ film is shown in figure 4. The intense satellite peaks on either side of the (0,0,15) peak verify the sample is a multilayer, and allows the accurate determination of the bilayer repeat length from the satellite peak separation. These satellite peaks and the main peak width prove that the layers grew epitaxially on each other. Films with bilayer repeat length as little as $50\text{\AA}$ have been deposited and show high-angle x-ray diffraction satellite peaks.

TEM allows the layered structure to be visualized, and verifies that the barrier and well are approximately of equal thickness (figure 5). Although grain boundaries can be seen, selected area diffraction suggests that most of the crystallites have about the same orientation in plane as well as the extremely strong out of plane orientation also observed by x-ray diffraction. This in-plane orientation suggests that during the nucleation phase of film growth there was an epitaxial relation with the mica substrate. The epitaxial relation between the layers is evident both at the resolution shown here and in high resolution TEM images where the lattice planes can be traced across the interface.

Single-layer QW and barrier films were deposited and characterized for comparison with multilayer results. Figure 6 shows the Seebeck coefficient for these films as a function of

Figure 6. Absolute Seebeck coefficient as a function of temperature. (o) Single layer film of material used as the quantum well; (+) Single layer film of the barrier material; (x) with a period of $140\text{\AA}$.

temperature. The barrier material was found to have a relatively high Seebeck coefficient. Although the barrier material has a lower ZT than the well material, it will also make a positive contribution to the ZT of the multilayer. The Seebeck coefficient of the multilayer is also shown and lies between that of the QW and barrier materials.

The resistance and dimensions were measured for these three samples. The value of the resistivity was calculated and is given in table 1. The temperature dependence of the resistivity is shown in figure 7. The resistivity of the multilayer was found to be slightly less than half that of the QW material. Making a direct comparison here is difficult since the different materials could have had different doping levels. A more informative comparison is that of ZT for each of the films. ZT for the multilayer is found to be approximately the average of the ZT of the two component layers. No evidence of an increase in ZT has been found for this combination of QW and barrier if one assumes that the thermal conductivity of the multilayer is the same as that of the components.

Discussion

Interdiffusion of the layers of multilayer samples has been found to be an important experimental problem in many of the proposed thermoelectric multilayer systems. We have explored $\text{Bi}_{0.9}\text{Sb}_{0.1}/\text{PbTe}_{0.8}\text{Se}_{0.2}$ and $\text{Bi}_{0.9}\text{Sb}_{0.1}/\text{Bi}_2\text{Te}_3$ films.^[9] In both cases it was found that small amounts of interdiffusion of electrically active species can drastically change dopant concentration and adversely affect thermoelectric properties such as the Seebeck coefficient. Here we have demonstrated that in the compositionally-modulated $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ system interdiffusion does not degrade the Seebeck coefficient of the films. With the experimental demonstration that thermoelectric properties of material can be enhanced by quantum confinement,^[3] the next step is showing an enhancement of performance in a system where the degradation caused by the barrier material does not outweigh the benefits achieved by quantum confinement of the charge carriers. The $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ system shows great promise as such a

Figure 7. Resistivity as a function of temperature. (o) Single layer film of material used as the quantum well; (+) Single layer film of the barrier material; (x) Multilayer with a period of $140\text{\AA}$.

system.

The thermal conductivity in the barrier layer dictates that the barrier width must be kept as thin as possible so that losses in the barrier layer do not exceed gains made by quantum confinement. To achieve confinement with the thinnest possible barrier layer, a composition must be selected with the greatest possible barrier height. The failure to achieve enhanced thermoelectric properties in the measured film is probably due to insufficient barrier height. Similar observations were made during our investigation on the $\text{Bi}/\text{Bi}_{0.86}\text{Sb}_{0.14}$ multilayer system.^[10] Although high-quality layered structures were produced, the small bandgap of the $\text{Bi}_{0.86}\text{Sb}_{0.14}$ was not sufficient to confine the charge carriers in the Bi layer and no improvement in the thermoelectric properties was observed. Dopant and impurity states in the bandgap of the barrier material may also be degrading the structure. Efforts to optimize the barrier material, both by changing composition and by reducing states in the bandgap are continuing. Confinement with a small barrier height could also be achieved by making wider barrier layers. Characterizing the mobility of the charge carriers as a function of barrier width should help us explore these questions.

The bandgap of these materials must be studied as a function of composition over the entire phase field in order for the optimal barrier material to be determined. Sputter deposition combined with IR spectroscopy will be a powerful technique for exploring the effect of stoichiometry on the bandgap.

Along with the potential of using the multilayer structure to alter the electronic properties of the film, layering may also effect the thermal conductivity of the films. In this work we have assumed the thermal conductivity of the films to be that of bulk $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2(\text{Te}_{0.95}\text{Se}_{0.05})_3$ with the same resistivity. It is quite possible that the multilayer structure will decrease the thermal conductivity of the films by scattering phonons. This effect would increase the ZT of the thermoelectric films. If this effect is large, it is possible that multilayer films are already superior to bulk thermoelectric materials. Techniques for accurately measuring the in-plane thermal conductivity of these thin films are currently being explored.

Conclusions

We have shown that sputtering can be used to deposit high quality $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ material. We have found that the hot walled environment and excess Te target material both are important for the synthesis of high quality films. The deposition temperature was critical. Deposition must start at a relatively low temperature to achieve wetting of the mica substrate, and then increase to provide the highest quality film growth.

We have shown that $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ multilayers are stable enough that deposition temperatures of 380°C can be used so that high quality material can be deposited. ZT of the multilayer structure shown here with a period of 140Å and approximately equal layer thickness is found to be an average of the value for the component materials.

Sputtering has been shown to be a powerful technique for depositing thermoelectric materials. Not only have we shown it to be a valuable laboratory research tool, but the ability to scale the process up for production makes it particularly attractive.

Large-area, high-rate sputter deposition already plays an important role in industry. Once it has been demonstrated that attractive thermoelectric materials can be produced by sputtering in the laboratory, the technology, equipment and trained manpower already exist to make the transition to industry.

Acknowledgments

Funding for this project was provided by the United States Department of Energy, Office of Basic Energy Sciences (OBES), W. Polansky, program manager. We gratefully acknowledge D. Makowiecki for use of the sputtering chamber. This work was done under the auspices of the U.S. DOE by Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

References

- [1] L.D. Hicks, M.S. Dresselhaus, "Effect of Quantum-Well Structures on the Thermoelectric Figure of Merit," *Phys. Rev. B*, **47**, 12727-12731, 1993.
- [2] L.D. Hicks, M.S. Dresselhaus, "Use of Quantum-Well Superlattices to Obtain a High Figure of Merit from Nonconventional Thermoelectric Materials," *Appl. Phys. Lett.* **63**, 3230-3232, 1993.
- [3] L.D. Hicks, T.C. Harman, X. Sun, and M.S. Dresselhaus, "Experimental Study of the Effect of Quantum-Well Structures on the Thermoelectric Figure of Merit," *Phys. Rev. B Rapid* **53**, 1996 (in press).
- [4] J.C. Farmer, T.W. Barbee Jr., G.C. Chapline Jr., R.J. Foreman, L.J. Summers, M.S. Dresselhaus, and L.D. Hicks, "Sputter Deposition of Multilayer Thermoelectric Films: An Approach to the Fabrication of Two-Dimensional Quantum Wells," *Proc. of the XIII International Conference on Thermoelectrics*, Kansas City, Missouri 217-225, 1994.
- [5] J.C. Farmer, T.W. Barbee Jr., R.J. Foreman, L.J. Summers, "Deposition and Evaluation of Multilayer Thermoelectric Films," *Proc. Symp. on Microstructures and Microfabricated Systems, 185th Electrochem. Soc. Meeting*, San Francisco, CA. **94-14**, 231-242, 1994.
- [6] T.W. Barbee, Jr., "Multilayer Synthesis by Physical Vapor Deposition," in *Synthetic Modulated Structures*, ed. L. Chang and B.C. Giessen, Academic Press, New York, 313-337, 1985.
- [7] T.W. Barbee, Jr. and D.L. Keith, "Synthesis of Metastable Materials by Sputter Deposition Techniques," *Proc. of the Fall Meeting of the Metallurgical Society of AIME*, Pittsburgh, PA, October 5-9, 1980.
- [8] T.W. Barbee, Jr., "Multilayer Optics for the Soft X-ray and Extreme Ultra-Violet," *Physica Scripta*, **T31**, 147-53, 1990.
- [9] A.V. Wagner, R.J. Foreman, L.J. Summers, T.W. Barbee, Jr., J.C. Farmer, "Multilayer Thermoelectric Films: A Strategy for the Enhancement of ZT," *Proc. 30th Intersociety Energy Conversion Engineering Conference*, Orlando, Florida, **3**, 87-92, 1995.
- [10] A.V. Wagner, R.J. Foreman, L.J. Summers, T.W. Barbee, Jr., J.C. Farmer, "Multilayer Thin Film Thermoelectrics Produced by Sputtering," *Proc. of the XIV International Conference on Thermoelectrics*, St. Petersburg, Russia, 283-287 1995.
- [11] H. Noro, K. Sato, H. Kagechika, "The Thermoelectric Properties and Crystallography of Bi-Sb-Te-Se Thin Films Grown by Ion Beam Sputtering," *Journal of Applied Physics*, **73**, 1252-1260 1993.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.