

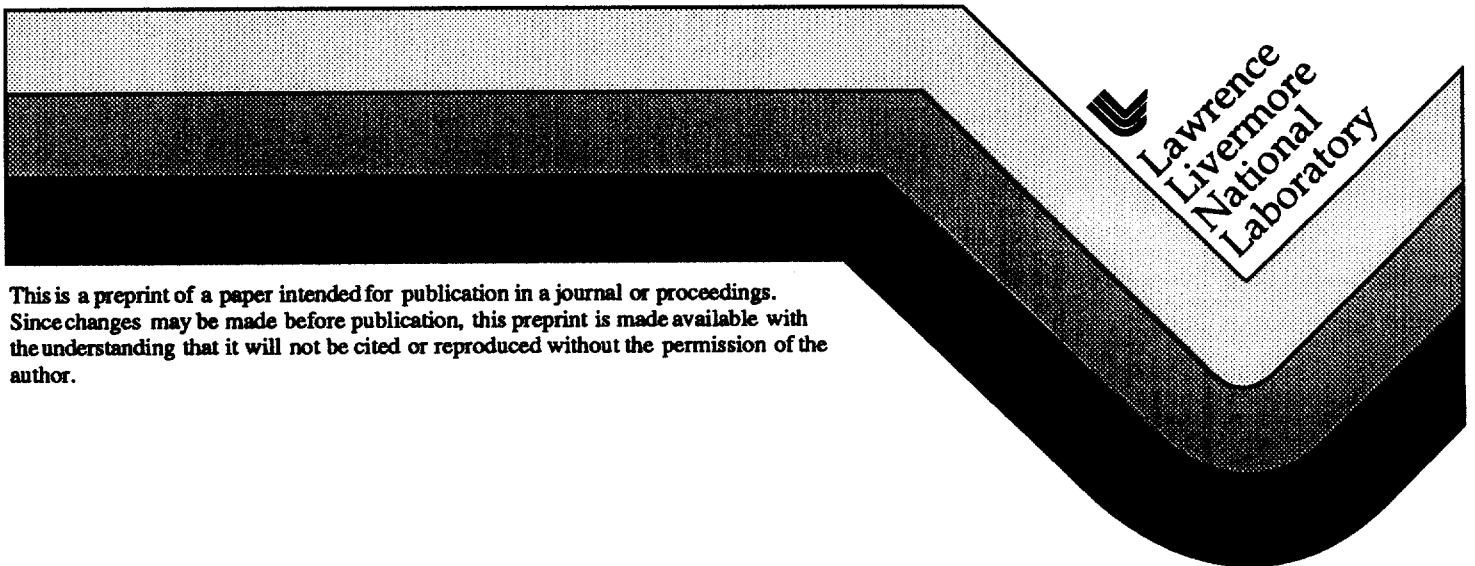
UCRL-JC-123993
PREPRINT

Sputter Deposition of Semiconductor Superlattices for Thermoelectric Applications

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

This paper was prepared for submittal to
Materials Research Society 1996 Fall Meeting
Boston, MA
December 2-6, 1996

November 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.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California 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 the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

SPUTTER DEPOSITION OF SEMICONDUCTOR SUPERLATTICES FOR THERMOELECTRIC APPLICATIONS

ANDREW V. WAGNER, RONALD J. FOREMAN, JOSEPH C. FARMER,
TROY W. BARBEE JR.

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

ABSTRACT

Theoretical dramatic improvement of the thermoelectric properties of materials by using quantum confinement in novel semiconductor nanostructures has lead to considerable interest in the thermoelectric community. Therefore, we are exploring the critical materials issues for fabrication of quantum confined structures by magnetron sputtering in the lead telluride and bismuth telluride families of materials. We have synthesized modulated structures from thermoelectric materials with bilayer periods of as little as 3.2 nm and shown that they are stable at deposition temperatures high enough to grow quality films. Issues critical to high quality film growth have been investigated such as nucleation and growth conditions and their effect on crystal orientation and growth morphology. These investigations show that nucleating the film at a temperature below the growth temperature of optimum electronic properties produces high quality films. Our work with sputter deposition, which is inherently a high rate deposition process, builds the technological base necessary to develop economical production of these advanced materials. High deposition rate is critical since, even if efficiencies comparable with CFC based refrigeration systems can be achieved, large quantities of quantum confined materials will be necessary for cost-competitive uses.

INTRODUCTION

The thermoelectric effect uses the thermal energy transported by charge carriers to produce solid-state cooling with electrical current flow or, conversely, to take advantage of thermal diffusion of charge carriers in a thermal gradient to produce a current. The use of thermoelectric materials to generate current has a wide range of applications, ranging from temperature sensing "thermocouples" to electrical power generators for interplanetary spacecraft. The application of thermoelectrics for cooling or heating is primarily limited by its efficiency which is lower than that of conventional gas cycle refrigeration. However, since thermoelectric devices have no moving parts, they can easily be made very small and relatively inexpensively. They also produce no vibrations, making them ideal for coupling with optical or infrared sensors. Although they have not replaced CFC and related refrigeration systems for large-scale cooling of food or buildings where efficiency is very important, thermoelectric coolers are being mass produced for portable food coolers where their small size and light weight are important.

Recently developed semiconductor technology and theory may provide a route to engineering higher efficiency materials, which could greatly expand the use of thermoelectric materials bringing the advantage of solid-state coolers to a substantially broader range of applications. 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 thermoelectric figure of merit, Z .^{1,2} The figure of merit is defined as:

$$Z = \frac{S^2}{\Lambda\rho} \quad (1)$$

where ρ , S , and Λ are the electrical resistivity, Seebeck coefficient, and the thermal conductivity, respectively. Multiplying by temperature, T , gives the dimensionless figure of merit, ZT : the materials parameter which characterizes the optimal performance of the material in a device, both in terms of efficiency as well as maximum achievable cooling. High Z material could enable the use

of thermoelectric cooling for important applications which are currently beyond the accessible temperature range for thermoelectric materials such as high temperature superconductor devices. The increase in efficiency would also be of great benefit to cooling infrared detector and night vision equipment which are battery powered.

Enhanced thermoelectric properties have been recently reported in the quantum well layers of PbTe/Pb_{1-x}Eu_xTe multilayer samples synthesized by molecular beam epitaxy.^{3,4} However, to make thermoelectric multilayer materials commercially viable, it is essential to extend the MBE work and grow structures with a high *Z* by established high deposition rate techniques. The expertise necessary to grow such materials by sputter deposition has been developed at Lawrence Livermore National Laboratory through extensive work on multilayer x-ray optics and other novel multilayer materials.^{5,6} At LLNL, we apply this multilayer sputter deposition technology to demonstrate the effectiveness of magnetron sputtering to synthesize thermoelectric multilayer materials with potential for 2D quantum well behavior. The ability to synthesize state-of-the-art thermoelectric materials in thin film form is essential to using thin film technology to engineer the properties of these materials. We thus begin our work by focusing on the understanding and control of the composition and structure of thin films of the individual materials needed for the well and barrier in the multilayer sample. We present parallel work on two families of semiconductor materials which are good candidates for achieving improved ZT through quantum confinement in multilayer films. One system is based on the good thermoelectric material lead telluride, PbTe, where a compatible barrier material, necessary for making quantum well structures, can be made by the partial substitution of Eu for Pb which widens the bandgap. The other system considered here is the bismuth telluride solid solution with antimony and selenium, (Bi_{1-x}Sb_x)₂(Te_{1-y}Se_y)₃, which is presently the best room temperature thermoelectric material. In this system the bandgap can be widened to form barrier material for quantum well structures by changing the ratios of the constituent materials.

EXPERIMENTAL PROCEDURE

We synthesized all the films for these experiments using magnetron sputtering. The sputter system is cryogenically pumped and 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 or more magnetron sputtering guns. The sputter sources are usually operated at an Ar pressure around 16 millitorr at a power of 10 W giving deposition rates of about 5 Å/s directly under the gun. Multilayer samples are synthesized by alternately positioning the substrates under the two magnetron sputter sources. Single-layer films are made by positioning the substrate directly below a single source. Sample doping is achieved by periodically passing a growing film under a second magnetron source sputtering dopant material at a low rate. A computer controls the position and slew rate of the stage, as well as the power to the sputter sources, allowing automated deposition of complex layered structures. Temperature, gas pressure, and gun parameters are logged by the computer during the deposition.

Shields are mounted around the guns to reduce cross contamination between the sputter sources. These shields are heated to form a hot walled environment around the deposition area which serves two purposes. First, it helps maintain the substrate temperature at the deposition temperature, which is important for thin mica or kapton substrates which are in radiative equilibrium with their surroundings. Second, re-evaporation of Te from these hot surfaces maintains an overpressure of this high vapor pressure element above the substrate. The combination of the hot wall technique and excess Te incorporated in the target is required for the growth of stoichiometric films.

RESULTS

This section presents the results from investigation of the single-layer and multilayer films of two families of thermoelectric materials. High quality single-layer films must be synthesized and understood in order to effectively fabricate multilayer films. Therefore, we first present work on

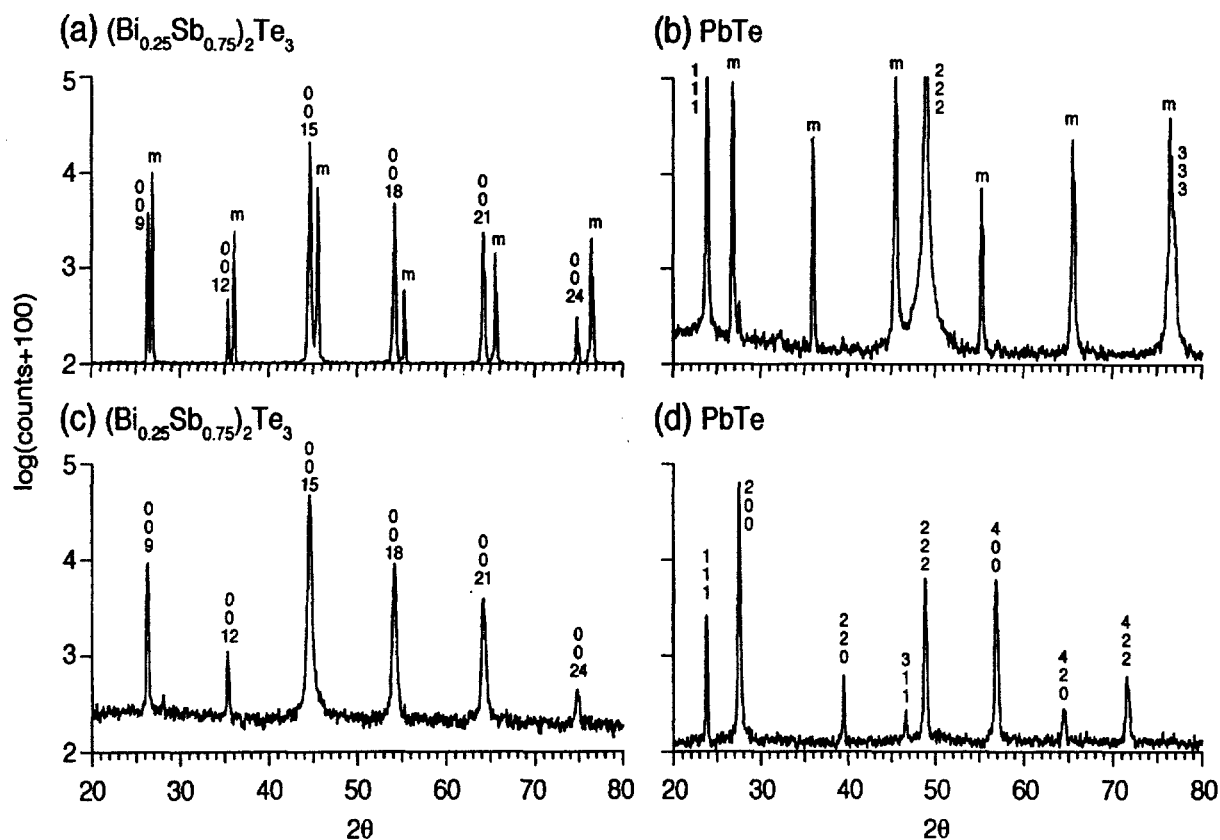


Figure 1: X-ray diffraction scans. a) $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ film on mica showing strong c axis orientation. b) PbTe film on mica showing a well textured (111) film. c) $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ film on glass showing strong c axis orientation. d) PbTe film on glass showing random texture. Mica substrate reflections are labeled m.

control of growth morphology and electrical quality of PbTe and $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ single-layer films. Then, preliminary results are presented for the PbTe/ $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ multilayer system, and our success with the synthesis of compositionally modulated $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ multilayers.

Control of growth morphology for single-layer films

Single-layer film growth morphology is critical to the subsequent growth of two component multilayer films. It is important that growth be controlled in such a way as to maintain a planar growth surface since growth topography dictates both interfacial and quantum well layer quality in multilayer films. Increasing growth temperature was found to improve electrical properties in both systems considered here as long as stoichiometry was maintained. Above an optimal temperature, however, surface morphology was observed to degrade. Increased surface mobility at high temperatures leads to faceting of individual grains. This was found to be a limiting problem in the $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ system where occasional misoriented grains quickly grew into large platelets at high temperatures.⁷ Surface grooving along grain boundaries is also observed in films grown at high temperatures. Not only does the temperature affect crystal growth, it also has a strong effect on nucleation of the films. At low deposition temperatures, a large number of small grains nucleate and films are observed to grow with a fine-grained columnar crystal structure. Films grown at higher temperatures have higher atomic surface mobility and are observed to have a larger grain size. Increasing the temperature even more led to degradation of the crystallographic texture.

In both material systems, it was found that the optimal growth sequence was to nucleate the films at a temperature below that used for growth. For PbTe, smooth well oriented films were nucleated at a temperature of 250°C and then the temperature was raised to 315°C during growth. Higher temperatures were found to work best for $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ with nucleation at 350°C and growth at 380°C.

| use | material | thickness | Seeb. | resistivity | thermal conductivity | ZT | Hall mobility |
|------------|--|-----------|-----------------|--------------------------|-------------------------|------|----------------------------|
| | | μ | $\mu\text{V/K}$ | $10^{-3}\Omega\text{cm}$ | $\text{W/cm}^2\text{K}$ | | $\text{cm}^2/\text{V sec}$ |
| reference | PbTe | bulk | -200 | 1.5 | 0.02 | 0.4 | 1600 |
| well | PbTe | 1 | -125 | 1.25 | 1 | 0.19 | 320 |
| reference | $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_{2.9}\text{Se}_{0.1}$ | bulk | 220 | 1.0 | 0.014 | 1.0 | 300 |
| well | $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ | 0.88 | 118 | 0.53 | 1 | 0.56 | 130 |
| barrier | $\text{Bi}_{0.5}\text{Sb}_{0.5}\text{Te}_{1.5}\text{Se}_{1.5}$ | 0.56 | 210 | 5.3 | 1 | 0.18 | 37 |
| multilayer | $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ | 0.7 | 140 | 1.4 | 1 | 0.30 | 50 |

Table 1: Measured electrical properties of single layer and multilayer films. State of the art bulk values are also listed as a reference for comparison with measured values of the films. The thermal conductivity used for calculation of ZT was that of the bulk. This is only a rough guide in the $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ system since the thermal conductivity will depend on the composition as well as doping levels.

Films were grown on BaF_2 , Mica, glass, silicon nitride and kapton substrates. Those deposited on freshly cleaved (111) BaF_2 and Mica under these conditions have a mirror like surface. SEM investigation at 30,000X showed a flat featureless surface on these specular films only occasionally interrupted by a misaligned grain. X-ray diffraction on the specular films shows they are well oriented. Bi_2Te_3 has a rhombohedral structure related to that of Bi, and is composed of planes of Bi and Te atoms.⁸ As shown in Figure 1a, films are found to grow along the c direction (with respect to the hexagonal representation of the structure). The inplane crystal structure of films grown on mica was found by plan view TEM electron diffraction to be a mosaic single crystal. Conversely, Figure 1b shows PbTe which has the NaCl structure grows with a strong (111) texture. While BaF_2 is a good choice for a substrate being nearly lattice matched with both films, we show here that excellent growth morphology can also be achieved on mica. Mica is a good substrate for our thermoelectric investigations since it cleaves into large atomically smooth surfaces with hexagonal symmetry and is much easier to work with than BaF_2 . It also makes a good substrate for device work since it can be cleaved into very thin sheets. This is important for thin film devices since thermal conduction in the substrate degrades device performance.⁹

Growth of oriented films on the amorphous substrates was more difficult. As shown in Figure 1c, oriented growth has been achieved in the $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ system. However for PbTe films grown on amorphous substrates, the x-ray diffraction shows a nearly random orientation of the film (Figure 1d). The differing growth rates of the different crystalline orientations then cause the surface to become faceted and rough at deposition temperatures required to achieve the best thermoelectric performance.

Electrical properties

Doping is a critical issue for electrical performance in semiconductor thermoelectric materials. For both of these materials Te tends to re-evaporate from the surface during growth so maintaining an excess supply of Te to the growth surface is critical in achieving stoichiometry. The measured Seebeck coefficient and resistivity of otherwise undoped films is a powerful method for monitoring the stoichiometry since excess of either component in compound semiconductors will act as a dopant. $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ films were found to be p-type showing that they were always slightly Te deficient despite the excess Te. Changing the Te overpressure by changing the temperature of the shields around the guns, however, was used as a means of controlling the doping level.

Undoped PbTe films were of very high resistivity and either n or p-type depending on exact growth conditions, demonstrating good stoichiometry. To optimize the thermoelectric properties of PbTe, a small amount of Bi was added to the film during deposition by occasionally sweeping the growing film under a second sputtering gun which was depositing Bi at a low rate. With Bi

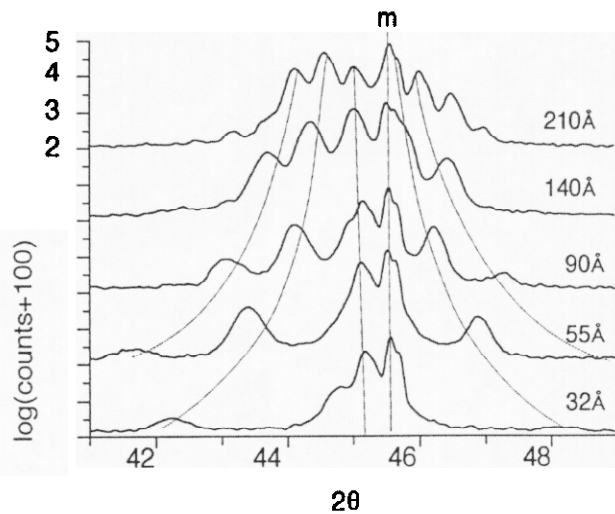


Figure 2: X-ray diffraction of a series of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3/\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_{1.5}\text{Se}_{1.5}$ multilayer films of varying thickness. The mica substrate peak is labeled m. The central peak is the films (0,0,15) peak with multilayer satellite peaks on either side.

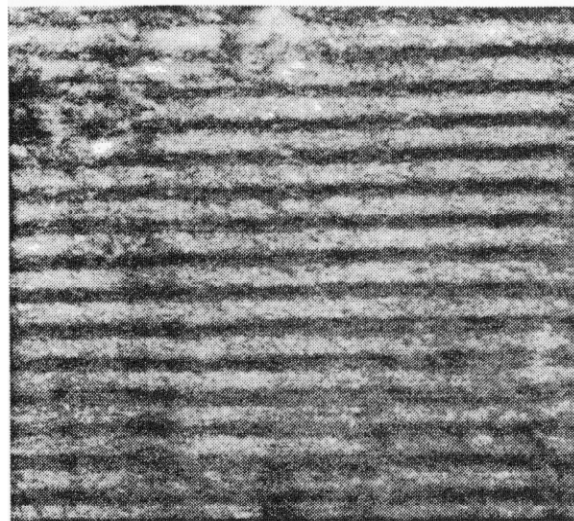


Figure 3: Bright field TEM micrograph of the 140 Å period $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3/\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_{1.5}\text{Se}_{1.5}$ multilayer film. Diffraction contrast with a Fresnel defocus condition clearly shows the layering.

doping, the film resistivity dropped by about three orders of magnitude and showed consistent n type conductivity. Although the doping was introduced in a periodic very thin layer, there is no evidence it did not diffuse uniformly into the film either by segregation at the growth surface or by bulk diffusion.

Table 1 lists values for the electrical properties of single layer films measured at room temperature. Care was taken to use insulating substrates and AC measurement techniques while making these measurements as previously reported¹⁰. Preliminary results from in-plane thermal conductivity measurements of these thin films indicate that for PbTe films the thermal conductivity is very close to that of the bulk. For $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$, however, the thermal conductivity in the thin film samples measured was higher than reported for optimized bulk material, presumably as a result of the very high doping level in the particular samples investigated. For this reason, bulk values of the thermal conductivity will be assumed in calculating the dimensionless figure of merit in Table 1 until these results can be confirmed.

Multilayer systems

Having achieved the desired growth surface in single layer PbTe films, an effort was made to grow $\text{PbTe}/\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ multilayer films. Unfortunately, only weak evidence for multilayer structure was found by x-ray diffraction in these films. This has been attributed to oxidation of the Eu which is thought to have occurred during preparation of the sputter target by powder processing.

In the $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ system, we have achieved considerable success in growing multilayer structures by varying the Te:Se ratio between layers. It was thought that by exchanging Se for Te in this solid solution the bandgap could be widened to form a barrier material for a thermoelectric quantum well structure. Multilayer structures have been grown using the optimum deposition parameters determined from the single-layer experiments discussed earlier. Satellite peaks in the high angle x-ray diffraction patterns (Figure 2) show that multilayer materials have been grown with evidence of periodicity in structures with bilayer repeat lengths as small as 32 Å. In Figure 3, TEM of a 140 Å bilayer repeat length film shows clear layering with approximately equal layer thickness. These results show that it is possible to grow multilayer structures in the $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ system by magnetron sputtering and that they are stable at the temperatures which have been determined necessary to grow optimal electrical quality films.

DISCUSSION

For single layer films, the dimensionless figure of merit of sputter deposited films is below that of optimum bulk material. This difference is a result of additional charge carrier scattering in these thin films as can be seen from Hall mobility measurements shown in Table 1. Charge carrier scattering either from impurities or from matrix or dopant atoms on the wrong site are thought to be the cause of the reduced mobility. Considerable improvement in the figure of merit is expected by the reduction in chamber background pressure during deposition, which is caused by outgasing from the heated shield assemblies.

In Table 1 the electrical properties of the $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ multilayer films are listed besides those of the single layer films. The failure to achieve enhancement in the dimensionless figure of merit in these films can be attributed to insufficient barrier height of the barrier material. Infrared spectroscopy has been used to examine barrier height in these materials and little difference between proposed barrier and well materials is observed. Results of our IR investigation are difficult to interpret, however, because of high doping levels combined with interference fringes in these thin films.

Although the barrier composition chosen in the work to date is not adequate to produce quantum confinement it is possible that by changing the composition a wider bandgap material can be found. Several other elements also form limited solid solutions with this system and are potential candidates as barrier materials.

CONCLUSIONS

The conditions for the growth of PbTe and $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ thermoelectric thin films by magnetron sputtering have been optimized. By nucleating the film at a temperature below the growth temperature, smooth well oriented films have been grown on both BaF_2 and mica. Structures with the appropriate dimensions for quantum confinement have been fabricated from thermoelectric materials using sputtering. These structures have been shown to be stable at deposition temperatures necessary to grow high quality materials. In order to achieve quantum confinement in the $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ system, higher bandgap barrier materials are needed which are compatible with the growth of quality thin film thermoelectric materials developed here.

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 and Mark Wall for TEM analysis. This work was done under the auspices of the U.S. DOE by Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. UCRL-JC-123993

REFERENCES

1. L.D. Hicks, M.S. Dresselhaus, *Phys. Rev. B* **47**, 12727 (1993).
2. L.D. Hicks, M.S. Dresselhaus, *Appl. Phys. Lett.* **63**, 3230 (1993).
3. L.D. Hicks, T.C. Harman, X. Sun, and M.S. Dresselhaus, *Phys. Rev. B Rapid* **53**, 10493 (1996).
4. T.C. Harman, D.L. Spears and M.J. Manfra, *Journal of Electronic Materials* **25**, 1121 (1996).
5. T.W. Barbee, Jr., in *Synthetic Modulated Structures*, ed. L. Chang and B.C. Giessen, (Academic Press, New York, 1985) pp. 313-337.
6. T.W. Barbee, Jr., *Physica Scripta*, **T31**, 147 (1990).
7. A.V. Wagner, R.J. Foreman, L.J. Summers, T.W. Barbee, J.C. Farmer, in *Proc. of the XV International Conference on Thermoelectrics*, Pasadena, CA 1996 (IEEE, Piscataway, NJ) pp. 459-463.
8. A. Krost, P. Grosse, in *Physics of Narrow Gap Semiconductors*, edited by E. Gornik, H. Heinrich, L. Palmethofer (Lecture Notes in Physics, **152**, NY : Springer, 1982) pp 49-53.
9. A.V. Wagner, R.J. Foreman, L.J. Summers, T.W. Barbee, J.C. Farmer, in *Proc. of the XV International Conference on Thermoelectrics*, Pasadena, CA 1996 (IEEE, Piscataway, NJ) pp. 269-273.
10. A.V. Wagner, R.J. Foreman, L.J. Summers, T.W. Barbee, J.C. Farmer, in *Proc. 30th Intersociety Energy Conversion Engineering Conference* **3**, Orlando, FL (ASME, NY, 1995) pp. 87-92.

Technical Information Department • Lawrence Livermore National Laboratory
University of California • Livermore, California 94551

