OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

CONTRACT: N00014-94-C-0088

PR Number 97-3134003ess-01

Bi_2Te_3/Sb_2Te_3 Superlattice Structures for High-ZT Thermoelectric Cooling Devices

Principal Investigator: Dr. Rama Venkatasubramanian

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Date Submitted: July 7, 1997

OFFICE OF NAVAL RESEARCH

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

PR Number: 97-3134003ess-01
Contract Number: N00014-94-C-0088
Contract Title: Bi_2Te_3/Sb_2Te_3 Superlattice Structures for High-ZT Thermoelectric Cooling Devices
Principal Investigator: Dr. Rama Venkatasubramanian
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a. Number of papers submitted to refereed journals, but not published: _1__

b. + Number of papers published in refereed journals: _2_

c. + Number of books or chapters submitted, but not yet published: ____

d. + Number of books or chapters published: ____

e. + Number of printed technical reports/non-refereed papers: ____

f. + Number of patents filed: _2*___

g. + Number of patents granted: ____

h. + Number of invited presentations: __2__

i. + Number of submitted presentations: _1___

j. + Promotions: __1__

k. Total number of Full-time equivalent Graduate Students and
Post-Doctoral associates supported during this period, under this R&T Project
Graduate Students: ____
Post-Doctoral Associates: ____
the number of
Minority* Graduate Students: ____
Minority* Post-Doctoral Associates: ____
and, the number of
Asian Graduate Students: ____
Asian Post-Doctoral Associates: ____

l. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant): ____

* One patent filed and one more to be filed

a. Papers Submitted to Refereed Journals/Proceedings, not published

1) R. Venkatasubramanian and T.S. Colpitts "Enhancement in Figure-of-Merit with Superlattice Structures for Thin-Film Thermoelectric Devices", Proc. of the Materials Research Society Symposium on Thermoelectric Materials - New Directions and Approaches, To be Published in 1997.

b. Papers Published in Refereed Journals

1) R. Venkatasubramanian, T. Colpitts, E. Watko, M. Lamvik, and N. El-Masry, "MOCVD of Bi_2Te_3, Sb_2Te_3 and their superlattice structures for thin-film thermoelectric applications", J. Crystal Growth, Vol 170, (1997) pp. 817-821.

2) R. Venkatasubramanian, "Thin-Film Superlattice and Quantum-Well Structures-A New Approach to High-Performance Thermoelectric Materials" Naval Research Reviews, Four/1996, Vol XLVIII, pp. 31-41.

f. Patents Filed

1) *Low-Temperature Chemical Vapor Deposition and Etching Apparatus and Method (Final Patent Filed Based on a temporary filing of USSSN/60/016,701)*

An apparatus and method for the growth and etching of materials where a substrate on which a film is being deposited or which is being etched is maintained at a lower temperature than a precursor cracking temperature. This invention is critical to the growth of single-crystalline Bi_2Te_3 and Sb_2Te_3 materials and high-quality superlattice structures in these materials. Also, the apparatus embodied in this invention is of generic relevance to the deposition and etching of a variety of electronic and other materials.

2) *Ultra- low resistivity contacts to Bi_2Te_3-related thermoelectric materials for high-performance thermoelectric devices (Invention Disclosure and Patent to be filed)*

This invention describes a method-using a combination of a special surface termination to a p-type Bi_2Te_3/Sb_2Te_3 superlattice or similar materials and a specific metallization scheme-to achieve extremely low contact resistivities (in the range of 2E-8 Ohm-cm^2). This would be critical to the successful application of thin-film Bi_2Te_3/Sb_2Te_3 superlattice structures in practical thermoelectric devices.

h. Invited Presentations

1) R. Venkatasubramanian, "Enhancement in Figure-of-Merit with Superlattice Structures for Thin-Film Thermoelectric Devices", 1997 Spring Meeting of Materials Research Society Symposium on Thermoelectric Materials - New Directions and Approaches, San Francisco, April 1997.

2) R. Venkatasubramanian, T.S. Colpitts, M. Lamvik, and N. El-Masry, "Growth and Characterization of Bi_2Te_3, Sb_2Te_3 and their Superlattice Structures", 1997 Meeting of American Association of Crystal Growth (West), Stanford Sierra Campus, June 1997.

i. Submitted Presentations

1) R. Venkatasubramanian, E. Siivola, T. Colpitts, T. Volckmann and H.B. Lyon, "Comparative Properties of Bi_2Te_3/Sb_2Te_3 Superlattice Structures and $Bi_{2-x}Sb_xTe_3$ Alloys", Presented at the American Physical Society Symposium on Novel Thermoelectric Materials I, Session F-27, Kansas City, March 1997.

j. Promotions

1) R. Venkatasubramanian, Promoted to Senior Research Engineer II and Leader for the Thermoelectrics Group, Center for Semiconductor Research, Research Triangle Institute.

a) Principal Investigator: Dr. Rama Venkatasubramanian

b) Current Telephone Number: (919)-541-6889

c) Cognizant ONR Scientific Officer : Dr. John Pazik

d) Description of Project: The goal of this project is to demonstrate factorial improvement in the thermoelectric figure-of-merit (ZT) with thin-film Bi_2Te_3/Sb_2Te_3 superlattice (SL) structures compared to state-of-the-art bulk $Bi_{2-x}Sb_xTe_3$ alloys for high-performance thermoelectric devices. The motivation for the use of SL structures has been the hypothesis that the atomic size and mass differences at the SL interfaces as well as the periodic SL structure result in enhanced phonon scattering leading to a reduction in lattice thermal conductivity. The SL structures, consisting of pure Bi_2Te_3 and Sb_2Te_3 materials, are also expected to offer higher electrical conductivities compared to alloyed materials through reduced alloy-scattering of carriers and therefore larger carrier mobilities. With a successful demonstration of the enhancement in the thermoelectric properties of the Bi_2Te_3/Sb_2Te_3 SL structures, another objective would be to address specific issues related to the development of a viable thin-film thermoelectric device technology.

e) Significant results during last year: Metallorganic chemical vapor deposition (MOCVD) has been shown to enable the growth of high-quality, thin-film, Bi_2Te_3, Sb_2Te_3 and their SL structures. The 3-ω method for the measurement of thermal conductivity of the thin-film SL structures and the $Bi_{2-x}Sb_xTe_3$ alloy films were established the previous year. ***Our initial data on the thermal conductivity of short-period Bi_2Te_3/Sb_2Te_3 SL structures, perpendicular to the SL interfaces, represented a first reported observation of a significant reduction (by a factor of five or more) in the thermal conductivity compared to those of solid-solution alloys [1].*** During last year, we have observed thermal conductivity values as low as 1.3 to 1.4 mW/cm-K in a 30Å/30Å Bi_2Te_3/Sb_2Te_3 SL; this is almost a factor of seven smaller than those of comparable $BiSbTe_3$ alloy thin-film. Similar low thermal conductivities have been observed in other optimized short-period SL structures. Measurement of the thermal conductivity values in a variety of Bi_2Te_3/Sb_2Te_3 SL structures suggest that a distinction can be made where certain types of periodic structures may correspond to an ordered alloy rather than an SL, and therefore, do not offer a significant reduction in thermal conductivity. *Our study also indicates that Bi_2Te_3/Sb_2Te_3 SL structures, with little or weak quantum-confinement, offer an improvement in the thermoelectric power factor over conventional alloys due to reduced alloy scattering in SL structures.* The power factor and the electrical transport data in the plane of the SL interfaces have been used to provide preliminary support for this argument. The higher mobility at 300K and the temperature dependence of the mobility in SL structures between 300K and 77K are consistent with the experimental observation that the Bi_2Te_3/Sb_2Te_3 SL structures offer higher Seebeck coefficients and thermoelectric power factor compared to typical commercial bulk alloys at cryogenic temperatures. These results offer evidence that the short-period SL structures potentially offer factorial improvements in the three-dimensional figure-of-merit (ZT_{3D}) compared to current state-of-the-art bulk alloys. During last year, we also developed low-resistivity contact metallization to p-type Bi_2Te_3/Sb_2Te_3 SL structures to enable the direct measurement of electrical resistivities perpendicular to the SL interfaces. Using a specially-terminated surface to the p-type Bi_2Te_3/Sb_2Te_3 SL and an optimized metallization scheme, we were able to obtain contact resistivities as low as 2.2E-8 Ohm-cm^2 in transmission line model measurements. We believe, such low-contact resistivities would be invaluable for a thin-film proto-type device development.

f) Summary of Plans for Next Years' work: We plan to grow micron-thick p-type Bi_2Te_3/Sb_2Te_3 SL structures and process them into small-area thermoelements to enable the measurement of the electrical resistivity and the Seebeck coefficient for the determination of the power factor perpendicular to the SL interfaces. This vertical power factor determination, in conjunction with the measurement of thermal conductivity perpendicular to the SL interfaces by the 3-ω technique, can provide the figure-of-merit (ZT) directly.

g) Graduate Students and Post-Doctoral Associates working on the project: None

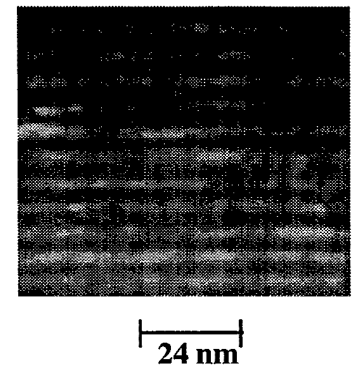
[1] R. Venkatasubramanian, T. Colpitts, E. Watko, and J. Hutchby, Proc. of 15th Inter. Conf. on Thermoelectrics (IEEE, Piscataway, NJ, 1996), Catalog No. 96TH8169, pp. 454-458

Bi_2Te_3/Sb_2Te_3 SUPERLATTICE STRUCTURES FOR HIGH-ZT THERMOELECTRIC COOLING DEVICES

R. Venkatasubramanian, Research Triangle Institute

OBJECTIVES:

- Demonstrate factorial improvement in figure-of-merit (ZT) with thin-film superlattice (SL) structures over state-of-the-art bulk materials
- Demonstrate thermal conductivity reduction in SL structures compared to bulk alloys due to additional phonon scattering mechanisms
- Demonstrate improved carrier mobility leading to higher electrical conductivity (σ) in SL structures, over bulk alloys, due to reduced alloy scattering of carriers
- Address critical issues in the development of thin-film thermoelectric cooling devices



TEM view of Bi_2Te_3/Sb_2Te_3 SL

APPROACH:

- MOCVD Growth of Bi_2Te_3, Sb_2Te_3 and their SL structures
- Characterize thermoelectric properties including thermal conductivity by 3-ω method
- Address key issues in developing practical thin-film devices like low-resistivity Ohmic contacts to Bi_2Te_3-related materials

ACCOMPLISHMENTS:

- Demonstrated good quality Bi_2Te_3/Sb_2Te_3 SL structures based on TEM data (shown above) and X-ray diffraction
- Experimental evidence for significant thermal conductivity reduction in Bi_2Te_3/Sb_2Te_3 SL structures
- Experimental evidence for higher Seebeck coefficient leading to improved power factor at 300K and cryogenic temperatures
- Potential for ZT improvement by a factor of 3 compared to state-of-the-art bulk alloys
- Demonstrated ultra-low resistivity contacts to Bi_2Te_3-related materials by *surface engineering* of the Bi_2Te_3/Sb_2Te_3 SL

TRANSITIONS & IMPACT:

- Teaming with Marlow Industries on experimental evidence for advantages of Bi_2Te_3/Sb_2Te_3 SL films for cryogenic cooling
- Potential ZT enhancement offered by SL thin films can have a major impact on cooling of ship-board and other electronics; cooling for superconducting and IR-devices operating near 77K

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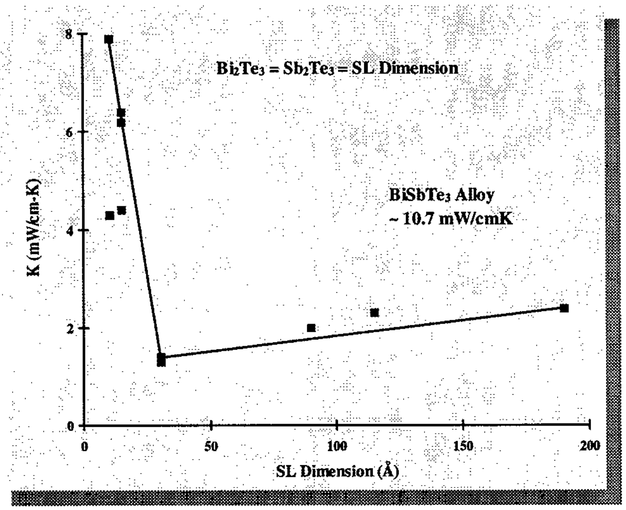
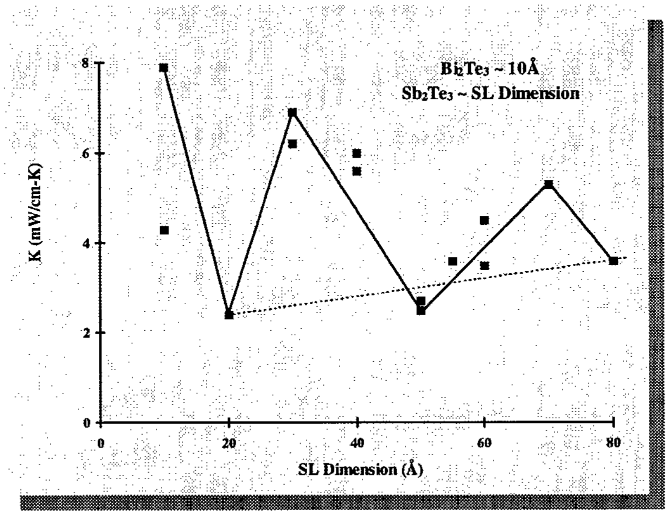
THERMAL CONDUCTIVITY REDUCTION IN SYMMETRICAL AND NON-SYMMETRICAL Bi_2Te_3/Sb_2Te_3 SL

Symmetrical SL



- Observed thermal conductivity of 1.3 to 1.4 mW/cm-K for 30Å/30Å SL

Non-Symmetrical SL



- Apparent minima in K when thickness of Bi_2Te_3 plus Sb_2Te_3 layers are multiples of unit cell size ~30 Å, ~60 Å, ~90 Å

- Factor of 7 reduction in thermal conductivity compared to $BiSbTe_3$ and $Bi_{0.5}Sb_{1.5}Te_3$ alloys at 300K
- Would directly translate into enhanced ZT if power factor *perpendicular to SL interfaces* are comparable to bulk alloys

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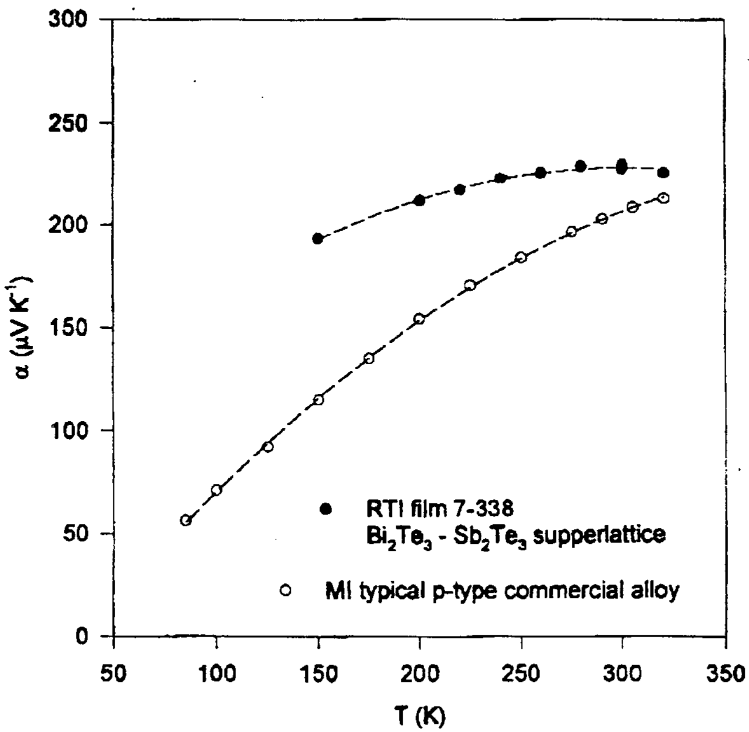
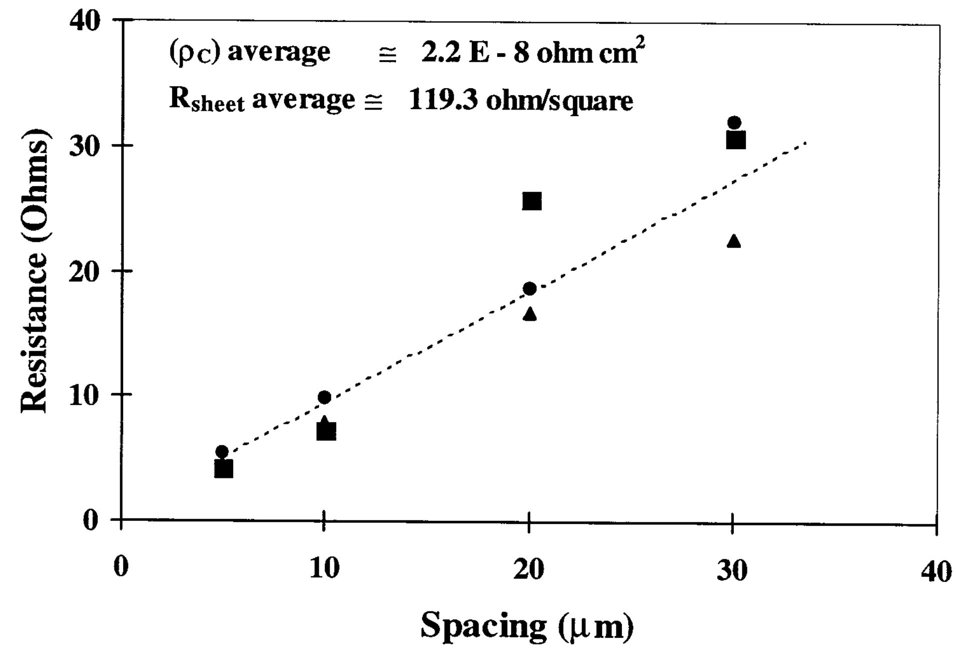
OTHER KEY RESULTS WITH Bi_2Te_3/Sb_2Te_3 SL STRUCTURES





- Bi_2Te_3/Sb_2Te_3 p-type SL structures offer higher Seebeck coefficients and power factor compared to typical commercial bulk alloys at 300K and cryogenic temperatures
- Bi_2Te_3/Sb_2Te_3 SL structures, with little or weak quantum-confinement, offer an improvement in the thermoelectric power factor over conventional alloys due to reduced alloy scattering
- Transmission line model (TLM) measurement to obtain contact resistivity
- A specially terminated surface to the p-type Bi_2Te_3/Sb_2Te_3 SL-*surface engineering*- and an optimized metallization scheme to achieve contact resistivities ~2.2 E-8 ohm-cm^2
- Significant for a prototype thin-film device development with SL structures

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