



## FABRICATION AND CHARACTERIZATION OF A BISMUTH TELLURIDE BASED NANOSTRUCTURED MACROSCOPIC THERMOELECTRIC DEVICE

Dinesh Pinisetty  
Ph.D. Candidate

Faculty Advisor: Dr. Ram V. Devireddy

### ABSTRACT

Driven by the interweaving curiosity of improving the thermoelectric figure of merit and recent predictions<sup>1,2</sup>, investigation of low dimensional nanostructured materials had been the focus of intensive research during the last few decades. The suitability of the thermoelectric materials for thermoelectric cooling applications is estimated based on the dimensionless thermoelectric figure of merit:  $ZT = S^2\sigma T/\kappa$ , where  $T$ ,  $S$ ,  $\sigma$ ,  $\kappa$  are absolute temperature, Seebeck coefficient, electrical conductivity and thermal conductivity, respectively<sup>3</sup>. For near room temperature applications, bismuth-telluride ( $\text{Bi}_2\text{Te}_3$ ) based bulk materials have been proved to possess the greatest thermoelectric figure of merit<sup>4</sup>. Good target materials for the fabrication of low dimensional nanostructured materials for thermoelectric applications are  $\text{Bi}_2\text{Te}_3$  based materials.  $\text{Bi}_2\text{Te}_3$  films<sup>5,6</sup>,  $\text{Bi}_2\text{Te}_3$  nanowires<sup>7,8</sup> and  $\text{Bi}_2\text{Te}_3$  nanotubes<sup>9</sup> had been fabricated by variety of methods. These classical processes, however, often resulted in disassociation of the  $\text{Bi}_2\text{Te}_3$  and a consequential lack of stoichiometry; and also, are not suitable for depositing in holes or onto irregularly shaped substrates. Such problems can be alleviated by using electrodeposition. Electrodeposition, offers the advantages of low synthesis temperature, low cost, and large area deposition with high growth rates. Electrodeposition had been successfully applied earlier to the production of  $\text{Bi}_2\text{Te}_3$  low dimensional materials<sup>10,11</sup>.

A working thermoelectric device consists of n-type and p-type leg elements assembled thermally in parallel and electrically in series. Electrodeposition makes the introduction of doping agents unnecessary by allowing  $\text{Bi}_2\text{Te}_3$  to be doped into n-type or p-type semiconductors by simply increasing or decreasing, the deposition potential. When the deposit is tellurium rich the alloy behaves as an n-type semiconductor, and when the deposit is bismuth rich the alloy shows a p-type semiconductor behavior. Arrays of n-type and p-type  $\text{Bi}_2\text{Te}_3$  nanowires and nanotubes, were fabricated on a gold coated polycarbonate membrane using electrodeposition. A macroscopic device comprised of the nanostructures is being designed to act as a thermoelectric cooler (TEC) for use with biological systems<sup>12</sup>.

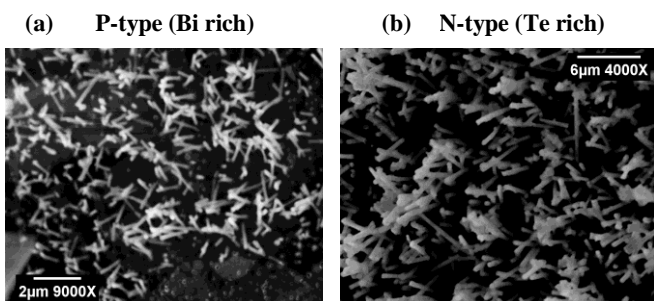
### EXPERIMENTAL

Electrodeposition of bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) was carried out in a typical three electrode setup. Track etched polycarbonate (PC) (Poretics PCTE, GE Osmonics, Minnetonka, MN) porous membranes sputtered with gold on one side were used as working electrodes. The manufacturer specified pore diameters ranged from 20 nm to 2 micrometers, while the membrane thickness was 8 microns in the PC. Pore diameters of 400nm and 100nm were used for the fabrication of nanotubes and nanowires, respectively. The gold surface was kept in contact with a copper plate held inside a polyetheretherketone (PEEK) stationary holder and a circular area of 2.25 cm<sup>2</sup> was exposed to the electrolyte for electrodeposition. A square platinum mesh counter electrode was placed above the working electrode. Both the counter electrode and working electrode were held horizontal in the electrolyte. A saturated calomel reference electrode (SCE) was used to control the potential at the working electrode. The electrolyte for nanostructures deposition had an initial concentration of 0.01 M bismuth oxide and 0.01 M tellurium oxide in 2 M  $\text{HNO}_3$  at a pH of 0.25. All experiments were carried out with a BAS-Zahner potentiostat/function generator. A p-type semiconductor was deposited at a DC potential of -400 mV vs SCE and an n-type semiconductor was deposited at -65mV vs SCE.

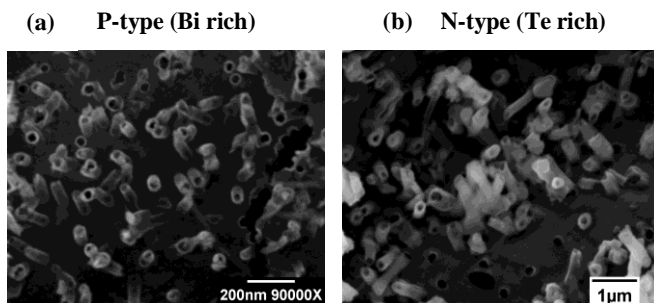
Scanning electron microscopy (JEOL 840A SEM operated at 20 kV) was utilized to observe the electrodeposited nanowires or nanotubes. In order to view the nanostructures using the SEM, the PC membrane was dissolved in  $\text{CH}_2\text{Cl}_2$  and the dried sample was mounted on a double-sided copper tape. The composition analysis of the deposited BiTe samples was performed with Wavelength Dispersive Spectrometry (WDS), using a JEOL 733 superprobe operated at an accelerating voltage of 15 kV and a probe current of 10  $\mu\text{A}$ . The Seebeck coefficient measurements were taken in the Dept. of Physics, LSU using a custom built device<sup>13</sup> and the electrical resistance measurements were taken using a four point probe method on a physical property measurement system (PPMS, Quantum Design, Inc.).

## RESULTS AND DISCUSSION

Arrays of bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) nanowires or nanotubes might be important from the standpoint of making novel macroscopic nanostructured peltier coolers with high cooling capacity. In Figure 1, an SEM image of  $\text{Bi}_2\text{Te}_3$  nanowires obtained by electrodeposition inside a PC membrane with 100nm diameter pores, is shown. Figure 1(A) shows an array of  $\text{Bi}_2\text{Te}_3$  nanowires deposited at a higher overpotential of  $-0.4$  V for 1 hr. The WDS composition analysis for this sample showed an average of 58% bismuth and 42% tellurium. Bismuth rich composition suggests that it is a p-type semiconductor. Figure 1(B) shows an array of bismuth-telluride nanowires deposited at a lower overpotential of  $-0.065$ V for 3 hr. The WDS composition analysis for this sample showed 38% bismuth and 62% tellurium. Tellurium rich composition suggests that it is an n-type semiconductor.



**Figure 1: SEM of electrodeposited bismuth-telluride nanowires, (a)  $-0.4$  V vs SCE (b)  $-0.065$  V vs SCE.**



**Figure 2: SEM of electrodeposited bismuth-telluride nanotubes, (a)  $-0.4$  V vs SCE (b)  $-0.065$  V vs SCE.**

Figure (2) depicts the SEM image of  $\text{Bi}_2\text{Te}_3$  nanotubes<sup>14</sup> obtained by electrodeposition using a PC membrane with 400nm diameter pores. Figure 2(A) shows an array of  $\text{Bi}_2\text{Te}_3$  nanotubes deposited at a higher overpotential of  $-0.4$  V for 1 hr. The WDS composition analysis for this sample showed 65% bismuth and 35% tellurium. Bismuth rich composition suggests that it is a p-type semiconductor. Figure 2(B) shows an array of bismuth-telluride nanotubes deposited at a lower overpotential of  $-0.065$ V for 5 hr. The WDS composition analysis for this sample showed an average of 36% bismuth and 64% tellurium. Tellurium rich composition suggests that it is an n-type semiconductor.

The Seebeck coefficient ( $S$ ) was measured by mounting the sample on a custom built device, such that it had good electrical contact between the heater and heat sink. One end of the device was a Constantan reference sample with a known Seebeck coefficient of  $S_R = 40$   $\mu\text{V}/\text{K}$ . Therefore the Seebeck coefficient of a sample was given by:  $S_S = (\Delta E_S/\Delta E_R) \cdot S_R$  where  $\Delta E_S$ ,  $\Delta E_R$  stand for the voltage drop across the sample and reference for a constant temperature drop ( $\Delta T$ ). The best n-type Seebeck coefficient obtained was  $-56$   $\mu\text{V}/\text{K}$ , at an over potential of  $-0.065$ V.

## CONCLUSIONS

In this study PC membranes with pore diameters of 100nm and 400nm were used as templates to fabricate  $\text{Bi}_2\text{Te}_3$  nanowires and nanotubes respectively. Electrodeposition conditions which yielded either p-type or n-type bismuth-telluride ( $\text{Bi}_2\text{Te}_3$ ) nanostructures, either nanotubes or nanowires were found and a bulk TEC device with a p-type and n-type bismuth-telluride ( $\text{Bi}_2\text{Te}_3$ ) nanostructures is fabricated. Further work will quantify the temperature drop across the nanostructures, thermal conductivity and estimate the thermoelectric figure of merit ( $ZT$ ).

## ACKNOWLEDGMENTS

Dinesh Pinisetty is supported by an Economic Development Assistantship (EDA) fellowship from the Louisiana State University.

## REFERENCES

1. Hicks, L. D., and Dresselhaus, M. S., Phys. Rev. B, 1993, **47**, pp. 12727-12731.
2. Hicks, L. D., and Dresselhaus, M. S., Phys. Rev. B, 1993, **47**, pp. 16631-16634.
3. Rowe, D., CRC Handbook on Thermoelectrics, CRC Press, London.
4. Wood, C., Rep. Prog. Phys., 1988, **51**, pp. 459-539.
5. Venkatasubramanian, R., et al., J. Cryst. Growth, 1997, **170**, pp. 817-821.
6. Boyer, A., and Cisse, E., Mat. Sci. Eng. B, 1992, **13**, pp. 103-111.
7. Zhang, Z., et al., Chem. Of Mater., 1999, **11**, pp. 1659-1665.
8. Sun, T., et al., Mat. Lett., 2006, **60**, pp. 2534-2537.
9. Zhao, X. B., et al., App. Phys. Lett., 2005, **86**, pp. 062111(1-3).
10. Sapp, S. A. et al., Adv. Mater., 1999, **11**, pp. 402-404.
11. Prieto, A. L., et al., J. Am. Chem. Soc., 2001, **123**, pp. 7160-7161.
12. Prabhakar, A., M.S. Thesis, 2006, LSU.
13. Balamurugan, S. et al., Phys. Rev. B, **74**, pp. 172406.
14. Davis, D. M. et al., ECS Transactions, **6**, pp. 253-260.