



## Nanowire Growth of Bi-Te Alloy by Electrodeposition<sup>†</sup>

J.H. PARK, B.S. AN and T.Y. LEE\*

Department of Advanced Materials Engineering, Hanbat National University, Daejeon 305-719, Republic of Korea

\*Corresponding author: E-mail: [tylee@hanbat.ac.kr](mailto:tylee@hanbat.ac.kr)

AJC-13299

Nanowires of Bi-Te alloy were grown in the porous anodic aluminum oxide template by electrodeposition. The compositions could be obtained from about 3 to about 40 at % Bi with varying the applied voltage and the concentration of electrolytes and confirmed by energy dispersive spectroscopy. As increasing Bi<sup>3+</sup> ion concentrations, the content of Bi in Bi-Te alloys increases. Mixture of Bi<sub>2</sub>Te<sub>3</sub> and Te phases were confirmed by X-ray diffraction.

**Key Words:** Nanowire, Bi<sub>2</sub>Te<sub>3</sub>, Bi-Te alloy, Electrodeposition.

### INTRODUCTION

Among promising clean and renewable energy sources, thermoelectric devices has been paid a lot of attention because the thermoelectric devices can directly convert waste thermal energy into electricity<sup>1,2</sup>. In addition, the devices has been already implemented in the microelectronic devices. In spite of its potential applicability, the efficiency has been low not enough for the expansion of applications. To improve the efficiency, many research and work has been done recently<sup>3-9</sup>. Nanowire structure of alternating phase is one of promising candidates<sup>10</sup>. Bi<sub>2</sub>Te<sub>3</sub> by electrodeposition has been considered as one of the promising thermoelectronic materials. In this research, nanowires of Bi-Te alloys were systematically studied in terms of electrodeposition, composition and phase identifications.

### EXPERIMENTAL

Bi-Te nanowires were electrodeposited in acidic nitric electrolytes with anodic aluminum oxide template of Whatman Inc. (Anodisc 13). The electrolytes were prepared by dissolving tellurium oxide (TeO<sub>2</sub>) and bismuth nitrate pentahydrate [Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O] in concentrated nitric acid. For the final concentration, deionized water was added. The concentrations of bismuth ions in electrolytes were from 0.5 to 20 mM Bi<sup>3+</sup> ion, respectively. The concentration of tellurium ions were fixed at 10 mM and the nitric acid at 1 M. Nominal pore size of anodic aluminum oxide is about 200 nm. As a seed layer for electrodeposition, gold film was sputtered on the back side of anodic aluminum oxide. Aluminum plate was used as a electrical path to supply electricity to sputtered Au film. Ag adhesive were

used to improve electrical contact between Au film and Al plate. Linear sweep voltammetry were performed to determine the applied potential by a potentiostat of Princeton applied research 273 A with a scan rate of 10 mV/s. Platinum (Pt) coated titanium (Ti) plate was used as conter electrode and Ag/AgCl (sat. KCl) of Fisher Scientific Inc. as reference electrode. Nanowire was grown with fixed applied potentials.

Phases were identified with X-ray diffraction and morphologies were observed with scanning electron microscopy and compositions were measured with energy dispersive X-ray spectroscopy.

### RESULTS AND DISCUSSION

Fig. 1(a) shows the linear sweep voltamograms (LSVs) of electrolytes of various Bi ions concentration with fixed Te ion concentration of 10 mM. The substrate for deposition is Au thin film on Si with Cr adhesion layer. As increasing the ion concentrations, the limit current of electrodeposition increases. The reduction peaks are shown about 0.0 V vs. Ag/AgCl (sat. KCl). The peak can result from the Bi-Te reduction reaction.



As increasing the Bi<sup>3+</sup> content in electrolyte, the peaks were shifted slightly positive because the reduction potential of Bi<sub>2</sub>Te<sub>3</sub> become more positive than those of Bi and Te.<sup>11,12</sup>

Fig. 1(b) shows the current density of Bi-Te alloy nanowire deposition in anodic aluminum oxide template. The sharp increase of current density results from the overgrown layer of Bi-Te alloys.

<sup>†</sup>Presented to the 6th China-Korea International Conference on Multi-functional Materials and Application, 22-24 November 2012, Daejeon, Korea

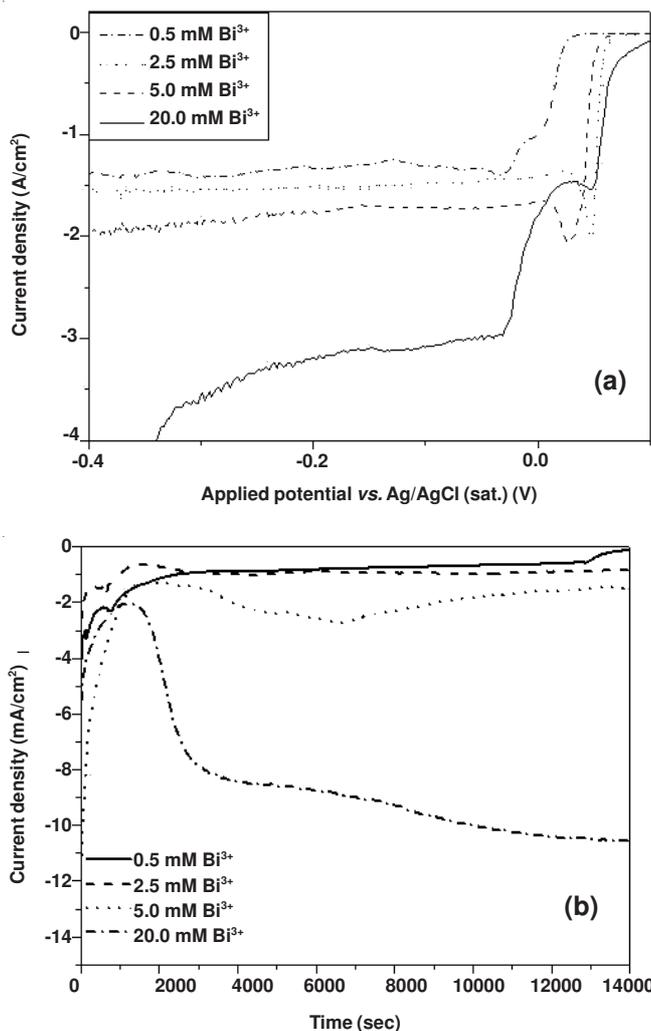


Fig. 1. Current density measurement of (a) linear sweep voltammetry and (b) Chronoamperograms

Fig. 2 shows SEM micrographs of nanowire deposited in electrolytes with 20 mM Bi<sup>3+</sup> and 10 mM HTeO<sub>2</sub><sup>+</sup>. From Fig. 2(a) the length of nanowires is about from 30 to 50 μm. In the higher magnification, the diameter of nanowire is about 300 nm.

Fig. 3 shows the concentration variation of Bi contents in nanowire. As increasing Bi<sup>3+</sup> in electrolytes from 10 mM to 20 mM, the content of Bi increases. And also, the decrease of applied potential increases the content of Bi in nanowire because the reduction potential of Bi<sup>3+</sup> is lower than that of Bi<sub>2</sub>Te<sub>3</sub>.

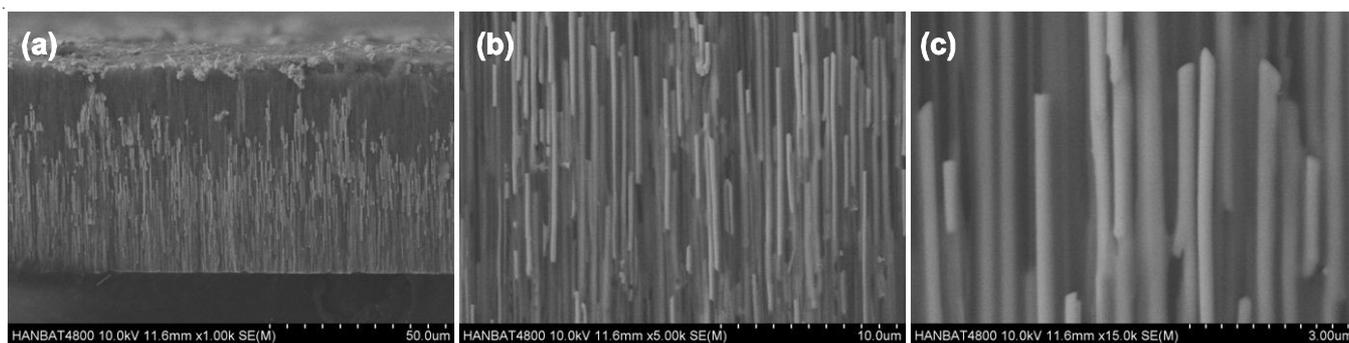


Fig. 2. SEM micrographs of nanowire deposited with 20 mM Bi<sup>3+</sup> ions and 10 mM HTeO<sub>2</sub><sup>+</sup> ions in an anodic aluminum oxide template (a) nanowire and overgrown Bi-Te alloys (b) low magnification of nanowire (c) high magnification

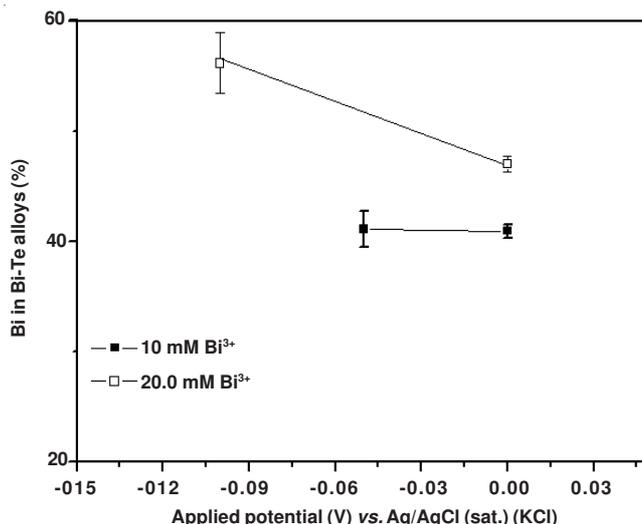


Fig. 3. Composition of Bi in Bi-Te nanowire with various applied potential and electrolyte concentration

Fig. 4 shows the X-ray diffraction patterns of nanowire with various content of Bi<sup>3+</sup> in electrolyte with applied potential of 0.05 V. From Fig. 3 and the phase diagram of Bi-Te alloy, if the Bi<sup>3+</sup> content of electrolyte is lower than 10 mM, only Bi<sub>2</sub>Te<sub>3</sub> and Te should be shown in XRD patterns. For 20 mM Bi<sup>3+</sup>, the phases must be identified further, even though the mixture of BiTe and Bi<sub>4</sub>Te<sub>3</sub> might be most possible.

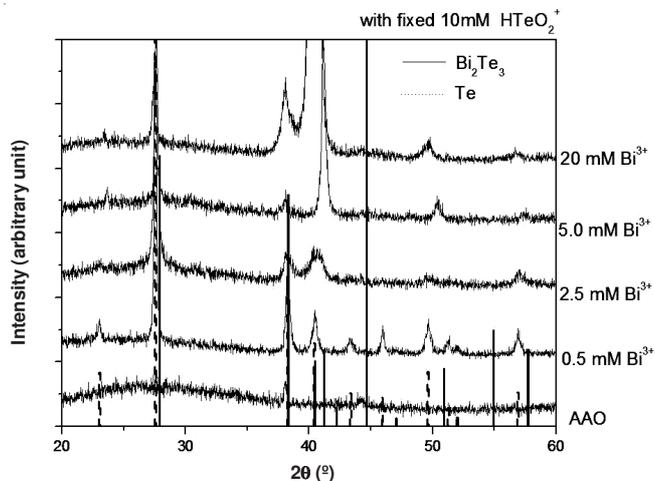


Fig. 4. XRD patterns of nanowire of various Bi<sup>3+</sup> ions in electrolytes

**Summary:** The Bi-Te nanowire with various composition were successfully fabricated by electrodeposition. The length and radius of nanowires are about 40  $\mu\text{m}$  and 300 nm, respectively. The composition varies from about 40 to about 60 at. % of Bi in nanowire. And the lower contents of Bi could be fabricated with lower content of  $\text{Bi}^{3+}$  ions in electrolytes. From XRD patterns, the phases of Te and  $\text{Bi}_2\text{Te}_3$  were identified.

#### ACKNOWLEDGEMENTS

The authors are grateful for the financial support from Leading Industry Office and Hanbat National University.

#### REFERENCES

1. L.E. Bell, *Science*, **321**, 1457 (2008).
2. A.I. Hochbaum, R. Chen, R.D. Delgado, W. Liang, E.C. Garnett, M. Najarian, A. Majumdar and P. Yang, *Nature*, **451**, 163 (2008).
3. T.C. Harman, P.J. Taylor, M.P. Walsh and B.E. LaForge, *Science*, **297**, 2229 (2002).
4. W. Wang, J. Goebel, L. He, S. Aloni, Y. Hu, L. Zhen and Y. Yin, *J. Am. Chem. Soc.*, **132**, 17316 (2010).
5. L.D. Hicks, T.C. Harman, X. Sun and M.S. Dresselhaus, *Phys. Rev. B*, **53**, R10493 (1996).
6. J.P. Heremans, C.M. Thrush and D.T. Morelli, *Phys. Rev. B*, **70**, 115334 (2004).
7. K.F. Hsu, S. Loo, F. Guo, W. Chen, J.S. Dyck, C. Uher, T. Hogan, E.K. Polychroniadis and M.G. Kanatzidis, *Science*, **303**, 818 (2004).
8. Y. Zhang, H. Wang, S. Kraemer, Y. Shi, F. Zhang, M. Snedaker, K. Ding, M. Moskovits, G.J. Snyder, and G.D. Stucky, *ACS Nano*, **5**, 3158 (2011).
9. Y.M. Lin, X. Sun and M.S. Dresselhaus, *Phys. Rev. B*, **62**, 4610 (2000).
10. G.Q. Zhang, Q.X. Yu, W. Wang and X.G. Li, *Adv. Mater.*, **22**, 1959 (2010).
11. B.Y. Yoo, C.-K. Huang, J.R. Lim, J. Herman, M.A. Ryan, J.-P. Fleurial and N.V. Myung, *Electrochim. Acta*, **50**, 4371 (2005).
12. M.S. Martín-González, A. Prieto, R. Gronsky, T. Sands and A. Stacy, *J. Electrochem. Soc.*, **149**, C546 (2002).