

# Material characteristics of metalorganic chemical vapor deposition of Bi<sub>2</sub>Te<sub>3</sub> films on GaAs substrates

Yong-Chul Jung<sup>a</sup>, Jeong-Hun Kim<sup>a</sup>, Sang-Hee Suh<sup>b</sup>, Byeong-Kwon Ju<sup>c</sup>, Jin-Sang Kim<sup>a,\*</sup>

<sup>a</sup>Thin Film Materials Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, South Korea

<sup>b</sup>Center for Nanostructured Materials Technology, KIST, 39-1 Hawolgokdong, Seongbukgu, Seoul, South Korea

<sup>c</sup>Department of Electrical Engineering, Korea University, Seoul 136-791, South Korea

Received 13 September 2005; received in revised form 12 January 2006; accepted 13 January 2006

Available online 14 March 2006

Communicated by R. Fornari

## Abstract

Metal organic chemical vapor deposition has been investigated for growth of Bi<sub>2</sub>Te<sub>3</sub> films on (001) GaAs substrates using trimethylbismuth and diisopropyltelluride as metal organic sources. The results of surface morphology, electrical and thermoelectric properties as a function of growth parameters are given. The surface morphologies of Bi<sub>2</sub>Te<sub>3</sub> films were strongly dependent on the deposition temperatures. Surface morphologies varied from step-flow growth mode to island coalescence structures depending on deposition temperature. In-plane carrier concentration and electrical Hall mobility were highly dependent on precursor's ratio of VI/V and deposition temperature. By optimizing growth parameters, we could clearly observe an electrically intrinsic region of the carrier concentration at the temperature higher than 240 K. The high Seebeck coefficient (of  $-160 \mu\text{VK}^{-1}$ ) and good surface morphology of this material is promising for Bi<sub>2</sub>Te<sub>3</sub>-based thermoelectric thin film and two-dimensional superlattice device applications.

© 2006 Elsevier B.V. All rights reserved.

PACS: 72.20.Pa; 72.15.Jf; 85.80.Fi; 81.15.Gh; 68.55.Jk

Keywords: A3. Metalorganic chemical vapor deposition; B1. Bismuth compounds; B2. Thermoelectric materials

## 1. Introduction

The Bi<sub>2</sub>Te<sub>3</sub>, Sb<sub>2</sub>Te<sub>3</sub> and their alloys are generally used in thermoelectric devices due to their superior thermoelectric performance at room temperature [1]. The performance of thermoelectric materials at a temperature  $T$  is essentially related to a figure of merit  $ZT$ , which can be expressed as  $S^2\sigma T/\kappa$ , where  $S$  is the Seebeck coefficient,  $\sigma$  the electrical conductivity,  $T$  the temperature, and  $\kappa$  the thermal conductivity [2]. After Hicks and Dresselhaus [3] have introduced quantum-well concept to improve the  $ZT$ , research into the fabrication of low-dimensional structures with conventional thermoelectric materials has received much attention due to the possibility of enhancing the  $ZT$  [4]. Using low-dimensional structures for thermal conduc-

tivity reduction, Venkatasubramanian et al. [5] have experimentally shown the enhancement of the  $ZT$  by fabricating two-dimensional Bi<sub>2</sub>Te<sub>3</sub>/Sb<sub>2</sub>Te<sub>3</sub> superlattice structures. Thus, planar growth techniques to obtain high quality of Bi<sub>2</sub>Te<sub>3</sub>, Sb<sub>2</sub>Te<sub>3</sub> films are necessary to comply with the needs of two-dimensional thermoelectric devices. Several deposition processes such as thermal evaporation [6,7], sputtering [8], metal organic chemical vapor deposition (MOCVD) [9] and electrochemical deposition have been reported for deposition of Bi–Sb–Te thin films. Of these processes, MOCVD is a major technique to meet the requirements of artificially structured thermoelectric devices. In early study, Giani et al. [10] demonstrated MOCVD growth of Bi<sub>2</sub>Te<sub>3</sub> films on pyrex and silicon substrates. However, it is thought their samples are not suitable for the artificial superlattice structures due to polycrystalline features and rough surface morphologies. Venkatasubramanian et al. [9], successfully demonstrated

\*Corresponding author. Tel.: +822 958 5693; fax: +822 958 6720.

E-mail address: [jskim@kist.re.kr](mailto:jskim@kist.re.kr) (J.-S. Kim).

MOCVD growth of a few nanometer periods of  $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$  superlattice on GaAs substrates and confirmed their structures by XRD and TEM analysis.

However, no works have been reported on a systematic investigation of electrical and structural properties of  $\text{Bi}_2\text{Te}_3/\text{GaAs}$  thin films prepared by MOCVD process with details concerning the effects on the deposition parameters. Thus, in this paper, the influences on thermoelectric properties and electrical characteristics of thin  $\text{Bi}_2\text{Te}_3/\text{GaAs}$  films according to the deposition variables in MOCVD was explored and discussed. In parallel, the effects of growth parameters on structural properties and surface morphologies of  $\text{Bi}_2\text{Te}_3$  films were also investigated.

## 2. Experimental procedure

Epitaxial films of  $\text{Bi}_2\text{Te}_3$  were grown by MOCVD on GaAs substrates. The precursors for Te and Bi were diisopropyltelluride (DiPTe) and trimethylbismuth (TmBi) respectively. (001) GaAs wafer tilted  $4^\circ$  toward nearest [110] was used as substrate. Just before growth, GaAs substrates were etched in  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}:\text{H}_2\text{O}_2 = 5:1:1$  solution for 1 min, rinsed with deionized water, and then dried in pure dry nitrogen gas. MOCVD growth of  $\text{Bi}_2\text{Te}_3$  epitaxial layers was carried out at atmospheric pressure in two zone horizontal reactor [11] so designed as to minimize pre-reaction of Bi with Te precursor. Hydrogen is used as carrier gas. The schematic of the reactor is shown in Fig. 1. In the figure, temperature of susceptor at zone 1 was kept at  $380^\circ\text{C}$  for the complete cracking of DiPTe and TmBi. Growth of  $\text{Bi}_2\text{Te}_3$  films were taken place on graphite susceptor at zone 2, where the temperature could be controlled independently by inserting quartz spacer between two susceptors. The poor thermal conductivity of quartz spacer and its limited contact area with heated susceptors made it possible to control the temperature of susceptor at zone 2 lower than  $250^\circ\text{C}$ . The  $\text{Bi}_2\text{Te}_3$  films were grown at different substrate temperatures ranging from  $380$  to  $250^\circ\text{C}$ .

The surface morphology of  $\text{Bi}_2\text{Te}_3$  wafers was observed using a Nomarsky optical microscope and atomic force microscope. The structural properties of the films were estimated by X-ray diffraction with Cu  $\text{K}\alpha$  radiation

(Philips, X-PERT PRO-NMR). The electrical resistivity and Hall effect measurement were performed by the conventional van der Pauw method. The Seebeck coefficient was measured by connecting one side of the film to a metal block at constant temperature and the other side to a heat sink at room temperature.

## 3. Results and discussion

The surface morphology of the  $\text{Bi}_2\text{Te}_3$  was strongly influenced by the growth temperature. Fig. 2 shows micrographs of the surfaces of  $\sim 0.5\mu\text{m}$ -thick layers of  $\text{Bi}_2\text{Te}_3$  on GaAs with various growth temperatures ranging from  $380\sim 290^\circ\text{C}$ . For the sample grown at  $380^\circ\text{C}$ , the surface structure consists of somewhat regular array of surface terrace with preferred crystallographic orientation. It is thought that this might be caused by small tilt of substrate orientation with vicinal direction. This surface morphology suggests that the step-flow growth on a vicinal surface is attained at the substrate temperature of  $380^\circ\text{C}$ . The portion of step-flow growth mode has diminished gradually with decrease in substrate temperature below  $380^\circ\text{C}$ . At the lower growth temperature, island coalescence has been dominated because the diffusion length of adatoms on terrace is expected to be too small to migrate to a vicinal step front. These experimental results are well explained by a generalized Burton–Cabrera–Frank model of step-flow growth on a vicinal surface [12]. It should be noted that the values of the root mean square (RMS) roughness became smaller with decrease in substrate temperature and exhibited from 10 to 5 nm with changing the substrate temperature from  $380$  to  $290^\circ\text{C}$ . Here, all the  $\text{Bi}_2\text{Te}_3$  films showed only the (000 $l$ ) reflections in X-ray diffraction, indicating crystallographic  $c$ -axis growth of the films.

The precursor's ratio of DiPTe to TmBi ( $R_{\text{VI/V}}$ ) in MOCVD is one of the most important parameters. The electrical carrier concentration and conduction type can be controlled by the ratio of the partial pressure of the elements. In Fig. 3, we compare the in plane carrier concentration and mobility as a function of  $R_{\text{VI/V}}$  at two different growth temperatures. At the growth temperature of  $380^\circ\text{C}$ , two samples  $R_{\text{VI/V}}$  lower than 6 showed p-type conduction. On the other hand, all films had an n-type conduction at growth temperature of  $290^\circ\text{C}$ . Excess Bi (Te) generates p-type (n-type) carriers, which Harman et al. [13] attribute to the presence of antisite defects. It is reported that the excess tellurium present in the vapor phase compensates for the loss of Te in material during the growth and gives the n-type conduction to the layer [14]. The loss of Te would be higher at the high growth temperature due to high equilibrium Te vapor pressure of the film. Thus, p-type conduction could be qualitatively explained on the basis of above explanation. At the growth temperature of  $290^\circ\text{C}$ , however, n-type carrier concentration of the films was increased even decreasing  $R_{\text{VI/V}}$  lower than 6. Also we can see the mobility decreases to  $-10\text{cm}^2/\text{Vs}$

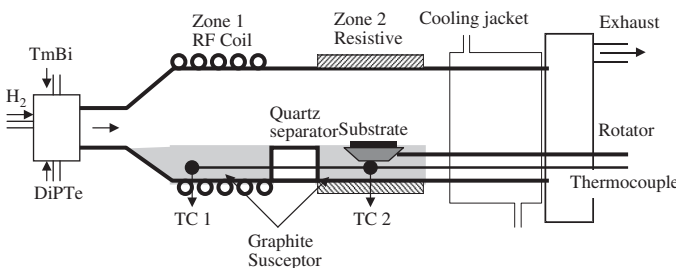


Fig. 1. Schematic of two-zone reactor which employs two graphite susceptors and quartz separator.

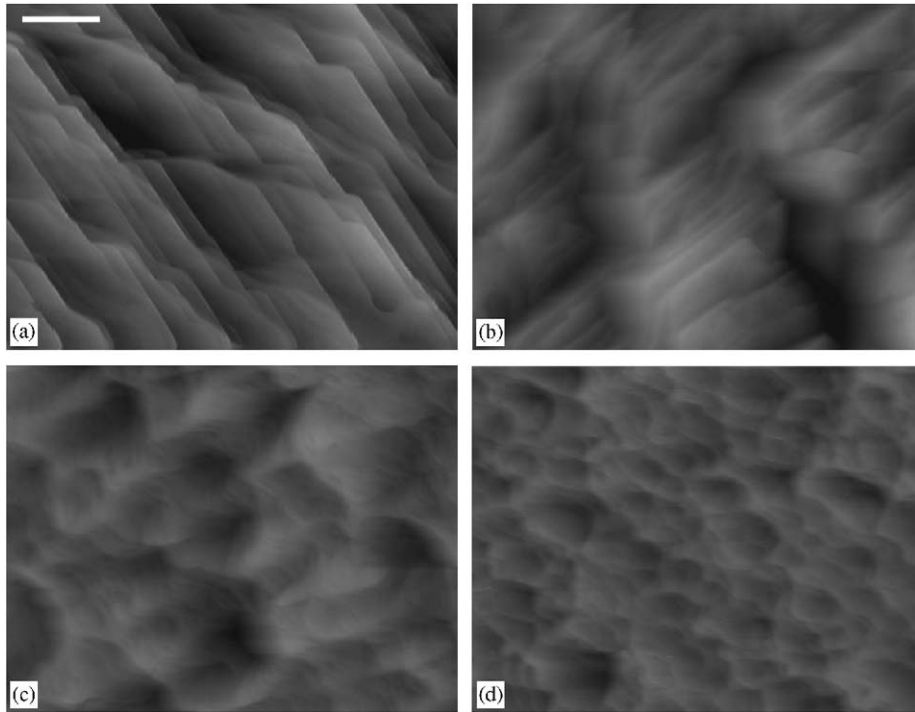


Fig. 2. Surface morphologies of Bi<sub>2</sub>Te<sub>3</sub> layers on (001) GaAs substrates grown at (a) 380 °C, (b) 350 °C, (c) 320 °C, and (d) 290 °C. Marker indicates 1 μm.

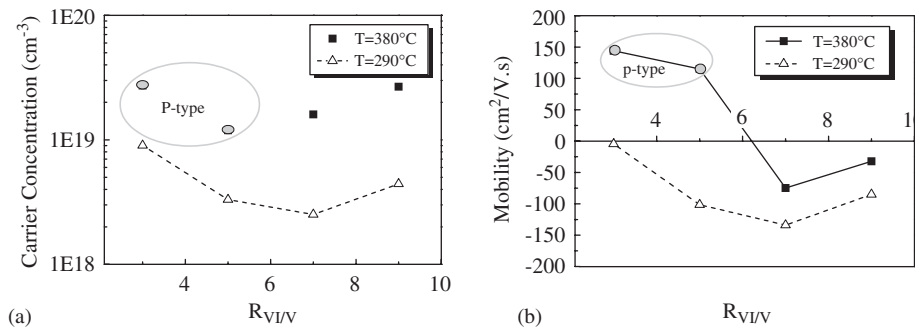


Fig. 3. In- plane carrier concentrations (a) and mobilities (b) of Bi<sub>2</sub>Te<sub>3</sub> layers as a function of  $R_{VI/V}$  at two different growth temperatures. Measurements were carried out at 300 K.

$V_s$  as the  $R_{VI/V}$  decreases to 3 at 290 °C. In this region, p-type carriers might be increased and compete with n-type carriers. One of the possible explanations for this disparity in results between  $R_{VI/V}$  and n-type carriers is thought to be caused by mixed conduction of p and n carriers in the films. Standard measurements of the resistivity and Hall coefficient provide only averaged values of both the carrier concentration and mobility, which may not represent any of the actual individual species. Hall measurements with changing the magnitude of magnetic field are needed to verify this.

Many workers have reported the electrical properties of Bi<sub>2</sub>Te<sub>3</sub> films. However, those films are often polycrystalline or nonstoichiometric composition resulting in high carrier concentrations ranging from  $10^{19}$  to  $10^{20}/\text{cm}^3$  at room temperature. Thus, the carriers are degenerate even at room temperature. Fig. 4 shows the temperature depen-

dence of carrier concentration and mobility of Bi<sub>2</sub>Te<sub>3</sub> thin film which was grown at 290 °C with precursor ratio of  $R_{VI/V} = 7$ . As shown in the figure, 0.5 μm- thick Bi<sub>2</sub>Te<sub>3</sub> layers are measured to be n- type with carrier concentration of  $\sim 3 \times 10^{18} \text{ cm}^{-3}$  in extrinsic region and the carrier concentration increases monotonically with increasing temperature beyond 240 K, indicating intrinsic region. It should be noted that our film is found to be in the intrinsic region at room temperature. This indicates that our Bi<sub>2</sub>Te<sub>3</sub> film has stoichiometric composition and high structural quality as long as nonstoichiometry and structural defect contribute doping level. From a plot of  $\text{Log} n_i$  vs.  $1000/T$ , we can estimate the energy gap  $E_g$  to be about 110 meV, which is somewhat lower than the value of 180 meV reported by Cho et al. [15]. The Hall mobility is gradually increased as the measuring temperature decreased. The Hall mobility versus temperature shows different slop with different

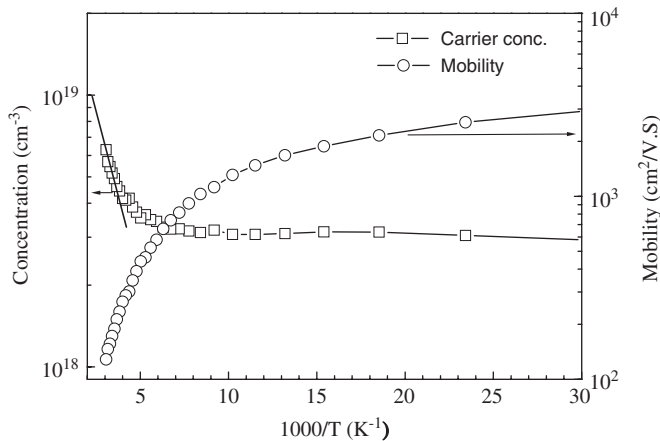


Fig. 4. Temperature dependence of carrier concentration and mobility of thin  $\text{Bi}_2\text{Te}_3$  films.

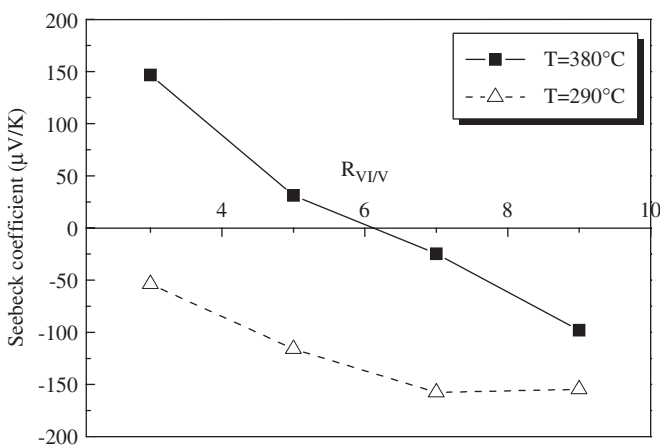


Fig. 5. In-plane Seebeck coefficient of  $\text{Bi}_2\text{Te}_3$  layers as a function of  $R_{\text{VI/V}}$  at two different growth temperatures. Measurements were carried out at 300 K.

temperature region. The appearance of these slopes can be explained by the dominance of different scattering mechanisms in different temperature region. The higher slope at higher temperatures indicates that polar optical phonon scattering is dominant in the region. The Hall mobility shows the value of  $1300 \text{ cm}^2/\text{V s}$  at temperature 100 K. Such a high value was observed for the first time in the thin  $\text{Bi}_2\text{Te}_3$  films of this work.

In plane Seebeck coefficient at room temperature for the samples in Fig. 3 is plotted in Fig. 5. For the samples grown at  $380^\circ\text{C}$ , the Seebeck coefficient was positive value of  $150 \mu\text{V K}^{-1}$  at  $R_{\text{VI/V}} = 3$  and gradually decreased with increasing  $R_{\text{VI/V}}$  to the value of  $-100 \mu\text{V K}^{-1}$  at  $R_{\text{VI/V}} = 9$ . At  $R_{\text{VI/V}} = 3, 5$ , the deficiency of Te in vapor phase might result in deficiency of Te in the solid phase and responsible for the positive Seebeck coefficient. On the other hand, for the samples grown at  $290^\circ\text{C}$ , found values were negative and absolute values were higher than those obtained for the growth temperature of  $380^\circ\text{C}$  in all precursor ratio of  $R_{\text{VI/V}}$  used in this experiment. These results are easily expected

from electrical properties of the films as shown in Fig. 3. The best value of the Seebeck coefficient was found to be equal to  $160 \mu\text{V K}^{-1}$ , which is somewhat lower compared to the bulk value. In  $\text{Bi}_2\text{Te}_3$ -related compounds, it is reported that the factors of the anisotropy of electro- and thermal conductivities are about 2–4, and of the Seebeck coefficient is 0.8–0.9 in the directions parallel and perpendicular to the crystallographic  $c$ -axis [5,16]. Thus, when we take into account that our Seebeck coefficient was measured in parallel to basal plane, this value would increase to 10 or 20% if measuring was made in crystallographic  $c$ -direction.

#### 4. Summary

We have grown  $\text{Bi}_2\text{Te}_3$  films on GaAs substrates using MOCVD system which employs a two-zone horizontal reactor.  $\text{Bi}_2\text{Te}_3$  films are grown along the preferred crystallographic orientation of the  $c$ -axis. The surface morphology was found to vary strongly with the deposition temperature. Distinct terracing was seen at high growth temperature of  $380^\circ\text{C}$ , and island coalescence has been dominated with decrease in temperature. The electrical and thermoelectrical characteristics of the film were shown to be dependent on VI/V precursor's ratio and growth temperature. For our MOCVD growth of  $\text{Bi}_2\text{Te}_3$  films, the best results were obtained for VI/V precursor's ratio of 7 and growth temperature of  $290^\circ\text{C}$ . The temperature dependence of carrier concentration and Hall mobility were measured for the film and clearly showed an electrically intrinsic region of the carrier concentration at the temperature higher than 240 K. Our results suggest that  $\text{Bi}_2\text{Te}_3$  film with good surface morphology and good electrical properties can be grown by MOCVD.

#### Acknowledgment

This research was supported by a grant(code #: 05K1501-02010) from Center for Nanostructured Materials Technology under 21st Century Frontier R&D Programs of the Ministry of Science and Technology, Korea.

#### References

- [1] G.E. Smith, R. Wolfe, J. Appl. Phys. 33 (1962) 841.
- [2] D.R. Lovett, Semi-Metals and Narrow-Band Gap Semiconductors, Pion, London, 1977, p. 181.
- [3] L.D. Hicks, M.S. Dresselhaus, Phys. Rev. B 47 (1993) 631.
- [4] M.S. Sander, R. Gronsky, T. Snads, A.M. Stacy, Chem. Mater. 15 (2003) 335.
- [5] R. Venkatasubramanian, E. Siivola, T. Colpitts, B. O' Quinn, Nature 413 (2001) 597.
- [6] H. Zou, D.M. Powe, G. Min, J. Vac. Sci. Technol. A 19 (2001) 899.
- [7] H. Zou, D.M. Powe, G. Min, J. Crystal Growth 222 (2001) 82.
- [8] C. Shafai, M.J. Brett, J. Vac. Sci. Technol. A 15 (2001) 2798.
- [9] R. Venkatasubramanian, T. Colpitts, E. Watko, M. Lamvik, N. El-Masry, J. Crystal Growth 170 (1997) 817.
- [10] A. Giani, A. Boulouz, F. Pascal-Delannoy, A. Fousaram, A. Boyer, Thin Solid Films 315 (1998) 99.

- [11] R. Venkatasubramanian, T. Colpitts, B. O'Quinn, S. Liu, N. El-Masry, M. Lamvik, *Appl. Phys. Lett.* 75 (1999) 1104.
- [12] C. Ratsch, M.D. Nelson, A. Zangwill, *Phys. Rev. B* 50 (1994) 14489.
- [13] T.C. Harman, S.E. Miller, H.L. Goeing, *Bull. Am. Phys. Soc.* 30 (1955) 35.
- [14] E. Charles, E. Groubert, A. Boyer, *J. Mater. Sci. Lett.* 7 (1988) 575.
- [15] S. Cho, Y. Kim, A. DiVenere, G.K. Wong, J.B. Ketterson, *Appl. Phys. Lett.* 75 (1999) 1402.
- [16] L. D. Ivanova, Y. V. Granatkina, Y. A. Sidorov, *Proceedings of the 16th International Conference on Thermoelectrics, 1997*, p. 111.