# Metal organic vapor phase epitaxy of $BiSbTe_3$ films on (001) GaAs vicinal substrates

Jeong-Hun Kim, Dae-Yong Jeong, and Jin-Sang Kim[a)]
*Thin Film Materials Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, South Korea*

Byeong-Kwon Ju
*Department of Electrical Engineering, Korea University, Seoul 136-791, Korea*

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We have investigated the growth of $BiSbTe_3$ films by metal organic vapor phase epitaxy on (001) GaAs vicinal substrates. A detailed experimental study of the surface morphologies of $BiSbTe_3$ films grown on GaAs (001) vicinal surfaces was carried out and is discussed in this paper with a view to understanding the step-step interaction kinetics that result in step bunching. $BiSbTe_3$ layers grown on nominal (001) GaAs substrates exhibit triangular facet structures consisting of atomically flat plateau areas separated by steps. In contrast, the growth of films on vicinal substrates was found to result in regular arrays of terrace step structures. The formation of step bunches and rectangular terraces on such film surface is attributed to the preferential incorporation of adatoms at step or kink sites and lateral growth rate anisotropy. © *2006 American Institute of Physics*.
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## I. INTRODUCTON

$Bi_2Te_3$ and related compounds are often used in thermoelectric devices and several methods of fabricating such materials have been extensively studied.[1–3] After Hicks and Dresselhaus[4] introduced an alternative approach to improving the thermoelectric figure of merit of these materials, the fabrication of low dimensional structures with conventional thermoelectric materials has become the subject of significant research attention. Among the various ideas for low dimensional structures that have been presented, Venkatasubramanian *et al.*[5] have experimentally demonstrated the enhancement of the thermoelectric figure of merit through the fabrication of two dimensional $Bi_2Te_3/Sb_2Te_3$ superlattice structures. The planar growth process, metal organic vapor phase epitaxy (MOVPE) is an important technique for meeting the requirements of artificially structured thermoelectric devices. Venkatasubramanian *et al.*[6] have demonstrated the MOVPE growth of few nanometer thick periodic superlattices of $Bi_2Te_3/Sb_2Te_3$ on GaAs substrates, and confirmed the fabrication of these structures by using x-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses. Up to now, no detailed experimental study of the dependence of the thermoelectrical properties on surface morphologies of MOVPE $BiSbTe_3$ films on GaAs (001) vicinal surfaces has ever been carried out.

This paper presents the results of our experimental study of $BiSbTe_3$ thin films grown by MOVPE on GaAs (001) vicinal substrates. The surface morphologies and structural properties of these films on (001) GaAs vicinal substrates were investigated with a view to understanding the step-step interaction kinetics that lead to step bunching.

[a)]FAX: +822-958-6720; electronic mail: jskim@kist.re.kr

## II. EXPERIMENTAL PROCEDURE

The precursors we used for Te, Bi, and Sb were diisopropyltelluride (DiPTe), trimethylbismuth (TMBi), and triethylantimony (TESb), respectively. Epitaxial films of $BiSbTe_3$ were grown in a horizontal MOVPE reactor at atmospheric pressure under conditions that minimize the prereactions of Bi and Sb with the Te precursor. Hydrogen was used as the carrier gas. The total gas flow rate through the reactor was 4000 SCCM (SCCM denotes cubic centimeter per minute at STP). The precursor ratio $R_{Bi/Sb}$ ($R_{Bi/Sb}$ =TMBi partial pressure/TESb partial pressure) was maintained at 0.3 to produce $BiSbTe_3$. The Te:(Bi+Sb) ratio was fixed at 3 in order to compensate for possible Te losses due to reevaporation of Te during growth.

(001) GaAs surfaces tilted towards the [010] direction by 0°, 2°, 4°, and 10° were used as substrates. Just before growth, the GaAs substrates were etched in $H_2SO_4:H_2O:H_2O_2=5:1:1$ solution for 1 min, rinsed with de-ionized water, and then dried in pure dry nitrogen gas. To avoid uncertainties caused by the fluctuation of growth parameters in separate growth runs, the (001) GaAs substrates with various tilt angles were mounted close to each other on the same graphite susceptor.

The surface morphologies of the $BiSbTe_3$ wafers were examined using a Nomarsky optical microscope. The structural properties of the films were investigated with x-ray diffraction using Cu $K\alpha$ radiation (Philips, X'Pert Pro-NMR).

## III. RESULTS AND DISCUSSSION

The effects of growth temperature on the surface morphologies of the $BiSbTe_3$ films were investigated with the Nomarsky optical microscope. The surface morphologies of the films grown at various growth temperatures ranging from 300–450 °C on (001) GaAs substrates with 4° tilt are shown

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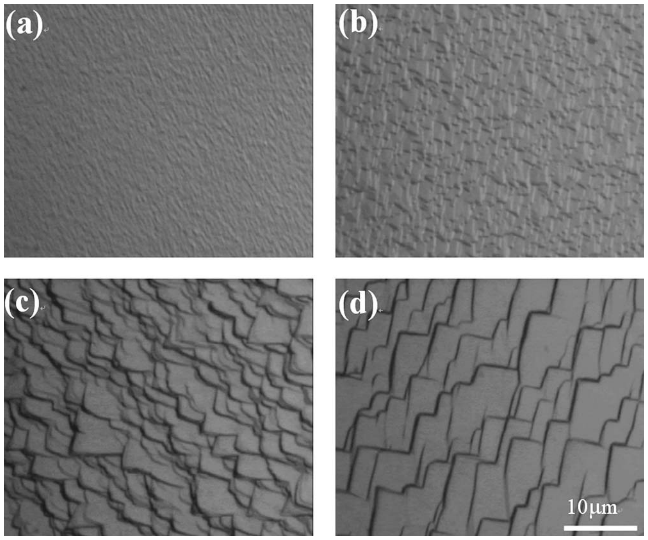


FIG. 1. Surface morphologies of $BiSbTe_3$ layers on (001) GaAs substrates tilted 4° toward [010] grown at (a) 300 °C, (b) 380 °C, (c) 400 °C, and (d) 450 °C.

in Fig. 1. The films grown above 380 °C were found to exhibit a regular array of terrace-step structures with a preferred crystallographic orientation, as shown in Figs. 1(b)–1(d). The step edges have a zigzag shape due to the misorientation of the substrates toward the [010] direction. This means that step-flow growth on the vicinal surfaces is attained at substrate temperatures above 380 °C. With an increase in the growth temperature, the terraces grow wider, as shown in Figs. 1(b)–1(d).

The step-flow growth mode is diminished with a decrease in the growth temperature below 380 °C. At low growth temperatures, it is thought that the diffusion length of adatoms on the substrate surfaces is too small for migration into the vicinal step front to occur, which results in three dimensional island nucleation and coalescence growth instead of step bunching. It should be noted that the lowest value of the root mean square (rms) roughness was 5 nm at a growth temperature of 300 °C. These results can be explained with a generalized Burton-Cabrera-Frank model of step-flow growth on vicinal surfaces.[7]

The surface morphologies of 1 $\mu$m thick $BiSbTe_3$ films grown on (001) GaAs substrates with 0°, 2°, 4°, and 10° tilt toward [010] are shown in Fig. 2. The $BiSbTe_3$ layer grown on the nominal (001) GaAs substrate has triangular facet structures of atomically flat plateau areas separated by steps. The orientations and sizes of the facet structures are inhomogeneous. In contrast, for the layers grown on substrates tilted 2°, 4°, and 10°, no triangular facet structure was observed. For the layers grown on the (001) GaAs vicinal substrates, step bunching arose because the terrace width is larger than that calculated from the substrate misorientation angle. The surface structure consists of a regular array of surface terrace-step structures.

As the surface is tilted from the exact (001) orientation, an array of atomic steps is formed on the surface. For GaAs with a zinc blende crystal structure, step edges are likely to be formed along the ⟨110⟩ directions with (111)*A* or (111)*B* planes.[8] A schematic diagram of a [001] view of a low index

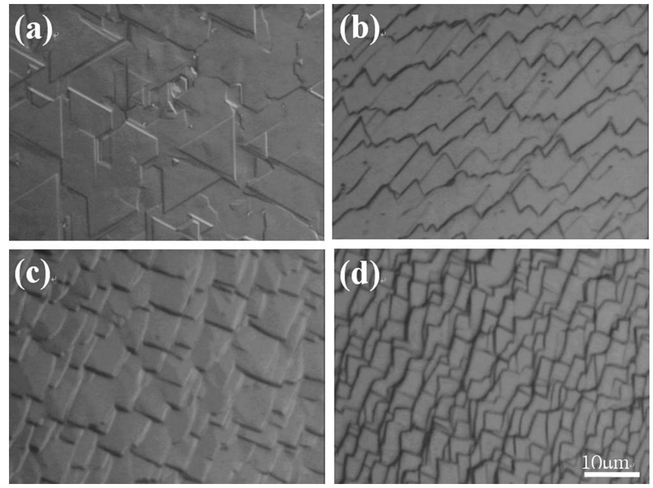


FIG. 2. Surface morphologies of $BiSbTe_3$ layers on (a) nominal (001) GaAs and substrates tilted (b) 2°, (c) 4°, and (d) 10° toward [010]. All samples were grown at 450 °C.

cubic crystal plane is shown in Fig. 3(a). For a (001) GaAs substrate tilted toward [010], the surface structure consists of (001) terraces; one side has a (111)*A* step edge and the other side has a ($\bar{1}$11)*B* step edge, as shown in Fig. 3(b). Thus, an increased number of atomic kink sites is expected to form as the tilt angle increases. According to the classical growth model, the probability of the incorporation of adatoms into the kink sites is higher than that on the flat terrace surfaces. This effect would enhance the initial two dimensional step flow growth. Thus, the use of a substrate tilted appropriately

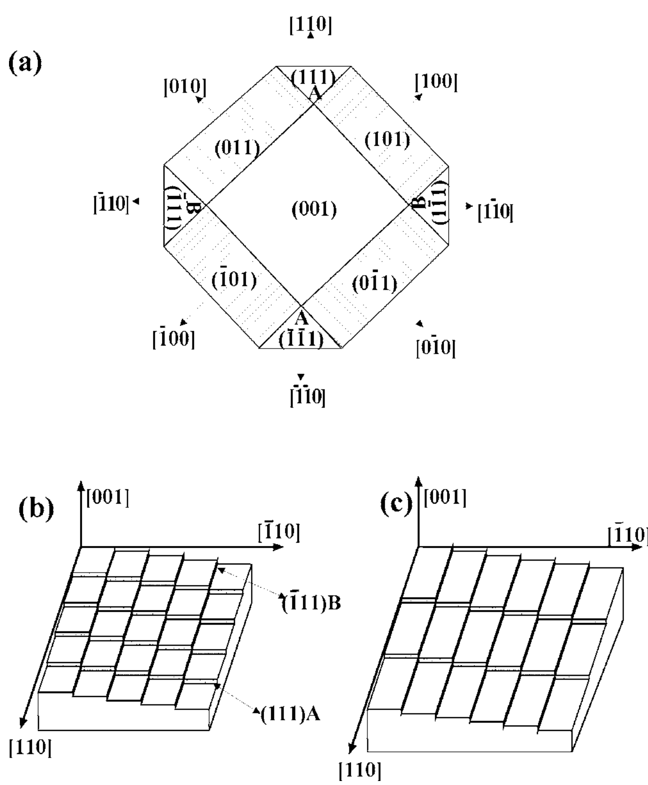


FIG. 3. (a) Schematic diagram of the [001] view of low index cubic crystal planes. (b) Microstructure of a (001) GaAs surface tilted toward [010], and (c) a bunched step surface structure due to the lateral growth rate anisotropy between the (111)*A* and (111)*B* steps.

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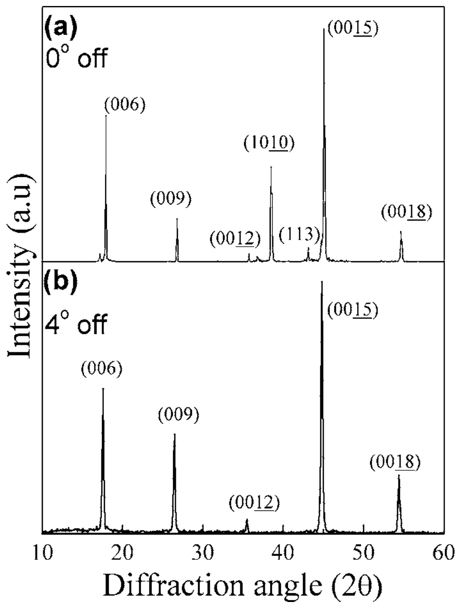


FIG. 4. XRD patterns of $BiSbTe_3$ layers on (a) a nominal (001) GaAs substrate and (b) a substrate tilted 4°.

in a certain direction is one of the ways to promote layer-by-layer growth over three-dimensional island growth. The high density of steps induced by a large miscut angle may result in smaller terrace areas, as for the film on a substrate tilted 10° [Fig. 2(d)].

On the (001) vicinal surface, the lateral growth rates of [110] and [$\bar{1}$10] would be different because of the anisotropic nature of the (111)*A* and ($\bar{1}$11)*B* step edges. If the lateral growth rate for the [110] direction is much faster than that for the [$\bar{1}$10] direction, step bunching is expected to occur more readily along [110] than along [$\bar{1}$10]. As a consequence, the initially square flat terraces [Fig. 3(b)] expand anisotropically to become rectangular with their large axis in the [110] direction as shown in Fig. 3(c). In the $BiSbTe_3$ films on (001) GaAs vicinal GaAs substrates, rectangular terraces in which one side of the step edge is larger than the other are also observed [Figs. 2(b)–2(d). This means that lateral growth rate anisotropy is also present in MOVPE of $BiSbTe_3$ on (001) GaAs vicinal substrates.

The crystal structures of the films grown on vicinal (001) GaAs surfaces were studied using XRD. To obtain diffraction patterns for the films grown on vicinal substrates, specimens were rotated to the same amount of miscut angles for the parallel alignment of x-ray beam with crystallographic (001) GaAs surface. Figure 4 shows the x-ray diffraction patterns of $BiSbTe_3$ films on a nominal (001) substrate and a GaAs substrate tilted 4°. All the peaks in the diffractogram were indexed as due to the rhombohedral crystal structure of $BiSbTe_3$. Table I gives the standard values of the x-ray powder data given by Ref. 9 along with the data obtained in the present work. The peak positions are fairly well matched with the standard values within the error range. From this table, it is clear that the present film have a strong (001) preferred orientation. The (00*l*) reflections, $l=6$, 9, 12, 15, and 18, are only observed in the film with a substrate tilted by 4°, which indicates that the film is single crystalline with a preferential growth direction along the *c* axis. However, the $BiSbTe_3$ layer on the nominal (001) GaAs substrate exhibits additional peaks [Fig. 4(a)]. The additional peaks indicate that the film contains crystallites with orientations other than along the *c* axis perpendicular to the substrate plane. This result might be the outcome of three-dimensional island growth in the initial growth stages. In the MOVPE growth of $BiSbTe_3$ on GaAs, it might be very difficult to obtain two-dimensional layered structures because of the large in-plane lattice mismatch between GaAs and $BiSbTe_3$ (22%). The use of vicinal (001) GaAs substrates is one of the ways to promote layer-by-layer growth over three-dimensional island growth. It is thought that the initial nucleation of $BiSbTe_3$ crystallites preferentially occurs at kink or step sites with a crystallographic *c* orientation. Thus it is possible to maintain a single crystal structure as growth proceeds. On the other hand, on nominal (001) GaAs substrates, it might be possible that the initial crystallites have random orientations and so result in different crystallographic crystallites as growth proceeds.

## IV. CONCLUSION

Epitaxial growth mechanisms are strongly dependent on surface structure and growth conditions. In this study, the MOVPE growth of $BiSbTe_3$ was performed on nominal (001) and vicinal GaAs substrates. The formation of step bunches on the film surface is attributed to the preferential incorporation of adatoms at step or kink sites. Further, the

TABLE I. X-ray diffraction data for $BiSbTe_3$ thin films grown by MOVPE and standard pattern.

| | Standard pattern[a] | | $BiSbTe_3$ on (001) GaAs | | $BiSbTe_3$ on (001) GaAs tilted 4° | |
|---|---|---|---|---|---|---|
| *h k l* | $2\theta$ | Intensity (%) | $2\theta$ | Intensity (%) | $2\theta$ | Intensity (%) |
| 0 0 6 | 17.490 | 5.4 | 17.90 | 65 | 17.60 | 60 |
| 0 0 9 | 26.365 | 0.3 | 26.75 | 18 | 26.5 | 39 |
| 0 1 5 | 27.932 | 100.0 | ⋯ | ⋯ | ⋯ | ⋯ |
| 0 0 12 | 35.404 | 0.1 | 35.70 | 3 | 35.5 | 5 |
| 1 0 10 | 38.076 | 35.1 | 38.45 | 40 | ⋯ | ⋯ |
| 1 1 3 | 42.671 | 0.5 | 43.05 | 5 | ⋯ | ⋯ |
| 0 0 15 | 44.667 | 5.7 | 45.05 | 100 | 44.8 | 100 |
| 0 0 18 | 54.271 | 1.4 | 54.60 | 13 | 54.4 | 23 |

[a]Reference 9.

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rectangular shape of the terraces on the film has been explained in terms of lateral growth rate anisotropy. We found that good crystal quality can be achieved by using vicinal (001) GaAs substrates: these substrates provide layer-by-layer growth rather than three-dimensional island growth.

## ACKNOWLEDGMENT

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[1] H. Zou, D. M. Powe, and G. Min, J. Cryst. Growth **222**, 82 (2001).
[2] C. Shafai and M. J. Brett, J. Vac. Sci. Technol. A **15**, 2798 (2001).
[3] Y.-C. Jung, J.-H. Kim, S.-H. Suh, B.-K. Ju, and J.-S. Kim, J. Cryst. Growth **290**, 441 (2006).
[4] L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B **47**, 16631 (1993).
[5] R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'Quinn, Nature (London) **413**, 597 (2001).
[6] R. Venkatasubramanian, T. Colpitts, E. Watko, M. Lamvik, and N. El-Masry, J. Cryst. Growth **170**, 817 (1997).
[7] C. Ratsch, M. D. Nelson, and A. Zangwill, Phys. Rev. B **50**, 14489 (1994).
[8] T. Sukui and H. Saito, J. Vac. Sci. Technol. B **6**, 1373 (1988).
[9] PDF No. 721835, PCPDFWIN Version 2.1, JCPDS-ICDD, 2000.

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