Effect of Bi substitution on phase transformation studies for $Ge_{22}Sb_{22}Te_{56}$ thin films

J. KUMAR*, R. THANGARAJ[a], T. STEPHEN SATHIARAJ[b]
Department of Physics, Arni University, Kangra, Himachal Pradesh, India
[a]*Department of Physics, Guru Nanak Dev Univeristy, Amritsar-143005, India*
[b]*Department of Physics, University of Botswana, Botswana*

The effect of Bi substitution on phase transformation in $Ge_{22}Sb_{22}Te_{56}$ (GST) chalcogenide system has been studied. Partial substitution of Bi upto 2 at% has been found to increase the phase transformation temperature of the GST. On further substitution of Bi (i.e. ~4 and 6 at %) the films were found to exhibit increased room temperature conductivity. Optical study shows the partial decrease in bandgap for $Ge_{22}Sb_{20}Bi_2Te_{56}$ composition in comparison to pure GST. XRD investigation of annealed samples reveals that Bi substitution retains NaCl type crystalline structure of GST.

(Received May 26, 2011; accepted September 15, 2011)

Keywords: Ge-Sb-Te, Thin film, Bi substitution

1. Introduction

Present day optical and electrical storage media owes its existence to the seminal work of Ovshinsky. The phenomenon of reversible switching in amorphous semiconductors discovered by him, laid the basis for storage media [1, 2]. The principle behind the phase change optical storage is based on a thermally induced reversible transformation between amorphous and crystalline phases of the film. Amorphous area embedded in crystalline surrounding act as a bit of information. Different materials can be melt-quenched to form an amorphous state but few of them exhibit high contrast in optical properties between the amorphous and crystalline state. Hence, few materials have the combination of unique properties that found in phase change materials and used for optical storage devices [3]. The large optical contrast indicates that the atomic arrangement differs considerably between the amorphous and crystalline states. On the other hand, the atomic rearrangement on re-crystallization proceeds very fast (on a timescale of ten to one hundred nanoseconds) [4, 5]. It is interesting to note that the required contrast in electrical conduction is much easier to meet, so there might be many more candidates for non-volatile memory than for rewriteable optical storage [3].

Doping is one of most effective methods to improve the phase transition (or transformation) properties of these materials. So, efforts have been made to dope a small amount of impurity elements such as Co, Ti, Ag, Cr, O_2, N_2, Sn, Bi and In into $Ge_2Sb_2Te_5$ films to improve optical recording performance [6-15]. $Ge_{22}Sb_{22}Te_{56}$ (GST) is most widely used as the active medium for phase change optical media viz. CD and DVD's. In this work, we choose Bi element doping into $Ge_{22}Sb_{22}Te_{56}$ to prepare Bi: GST films by thermal evaporation method. The transformation process of microstructure and optical properties of the Bi: GST films have been presented.

2. Experimental

Bulk $Bi_xGe_{22}Sb_{22-x}$ Te_{55} (x = 2, 4, 6) alloys were prepared by melt quenching technique. The constituent elements (99.999% purity) were weighed according to their atomic percentage and were sealed in a quartz ampoule (length ~10 cm, internal diameter ~6 mm), in a vacuum of ~10^{-5} mbar. The sealed ampoule was kept in a vertical furnace for 48 h and the temperature was raised to 1000 °C, at a rate of 4-5°C/min. The ampoule was rocked constantly to ensure homogeneous mixing of the melt. Ampoule was allowed to cool down at room temperature slowly. Ampoule was taken out of the furnace at room temperature and broken carefully to extract the sample [$Bi_xGe_{22}Sb_{22-x}$ Te_{55} (x = 2, 4, 6)].

Thin films of the above-mentioned compositions Bi:GeSbTe alloys were prepared by thermal evaporation method using Hind High Vacuum Coating Unit (Model No. 12A4D). Well cleaned glass slides were used as substrates. The substrates were maintained at room temperature during deposition and the pressure was below 10^{-5} mbar in the chamber during the deposition. The films were left inside the vacuum chamber after deposition for 24 h to attain metastable equilibrium as suggested by Abkowitz (1984) [16]. The chemical compositions were determined by using EDAX attached with Scanning Electron Microscope (Philips XL 30 ESEM system). The average composition of each thin film was obtained by measurement at three different regions of the film. The amorphous nature of the thin films was ascertained from the XRD spectra. The XRD spectra were obtained using Cu-K_α radiation from PW3710 mpd controlled XRD system with a PW1830 generator. Absence of the sharp peaks in the XRD diffractograms confirms the amorphous nature of the bulk as well as thin films. The XRD study has also been performed on the films annealed above phase transformation temperature to reveal the structure of these glassy materials. The transmittance (T) w.r.t. air and specular reflectance (R) of thin films were measured at room temperature using UV-VIS-NIR spectrophotometer (VARIAN Cary 500) in the 200-3000nm wavelength range.

4. Results and discussion

4.1 Sheet resistance measurements:

Fig. 1 shows the sheet resistance measurements of $Ge_{22}Sb_{22-x}Bi_xTe_{56}$ (x=0, 2, 4, 6) films at a heating rate of 2.5 °C/min from room temperature to 200°C under vacuum ~ 10^{-5} mbar. All these measurements were performed by recording the current values on regular temperature intervals. The resistance decreases continuously in the lower temperature range until an abrupt drop appears at the temperature of ~125 °C. The reduction in sheet resistance on the first transition is around three orders of magnitude. With further heating to 200 °C, the second drop is observed at a temperature of ~150 °C. The as-prepared films of Bi (x= 4 and 6) are crystalline since no sharp drop in sheet resistance was observed. The room temperature conductivity is also high for these compositions. The first and second phase transformation temperature for $Ge_{22}Sb_{20}Bi_2Te_{56}$ was 118 and 144°C respectively.

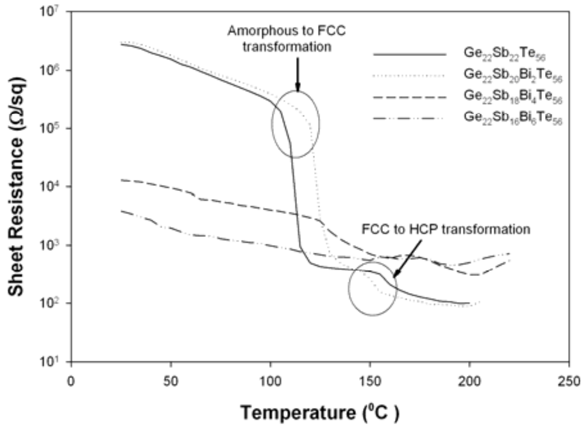

Fig. 1. Temperature dependent resistance measurements of $Ge_{22}Sb_{22-x}Bi_xTe_{56}$ (x= 0, 2, 4, 6) chalcogenide films.

4.2 Structural properties

Fig. 2 presents the XRD patterns of pristine $Ge_{22}Sb_{22-x}Bi_xTe_{56}$ (x = 2, 4, 6) films. The sharp peaks at (012) and (104) in case of as-deposited films with Bi concentration 4 and 6 at% were observed. The peaks were identified as that of BiSb phase using JCPDS file (1997). These results indicate that these films were crystalline in their pristine state. The pattern shows evidence for a peak at the position for the (012) in the $Ge_{22}Sb_{20}Bi_2Te_{56}$ scan at the bottom, it is very small but there is a rise in the background coinciding with the peaks in the other two patterns. Fig. 3 shows the XRD scans for $Ge_{22}Sb_{22}Te_{56}$ and $Ge_{22}Sb_{20}Bi_2Te_{56}$ films. Curve (i) in each block belongs to the X-ray scan of pristine samples. Absence of sharp peak shows that the pristine films are in the amorphous state. Curve (ii) and (iii) belongs to films annealed at 170 and 225°C for 10 minutes. The peak positions analysis reveals the metastable structure as a face-centered cubic (FCC), and the lattice constant *a* = 6.007±0.0012Å. The lattice constant value lies between 5.988±0.008Å and 6.027±0.005Å previously reported values for pure GST (Friedrich *et al* 2000) [17]. It confirms that the first abrupt drop close to 125 °C in the sheet resistance measurement correspond to the transition to a HCP-type structure. Thus, Bi doping also facilitates the structural transformation from FCC to HCP. Phase separation was not observed for lower concentrations of Bi. Therefore, doped Bi might randomly occupied the vacancy of $Ge_{22}Sb_{22}Te_{56}$ or be segregated at the grain boundaries.

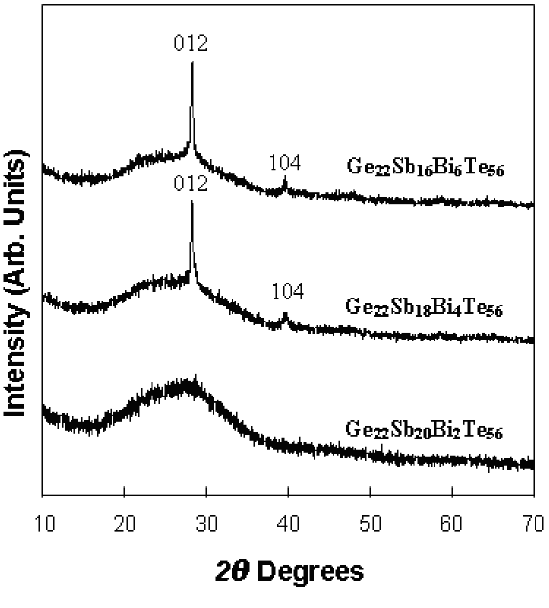

Fig. 2. XRD scans for as- prepared $Ge_{22}Sb_{22-x}Bi_xTe_{56}$ (x = 2, 4, 6) chalcogenide films.

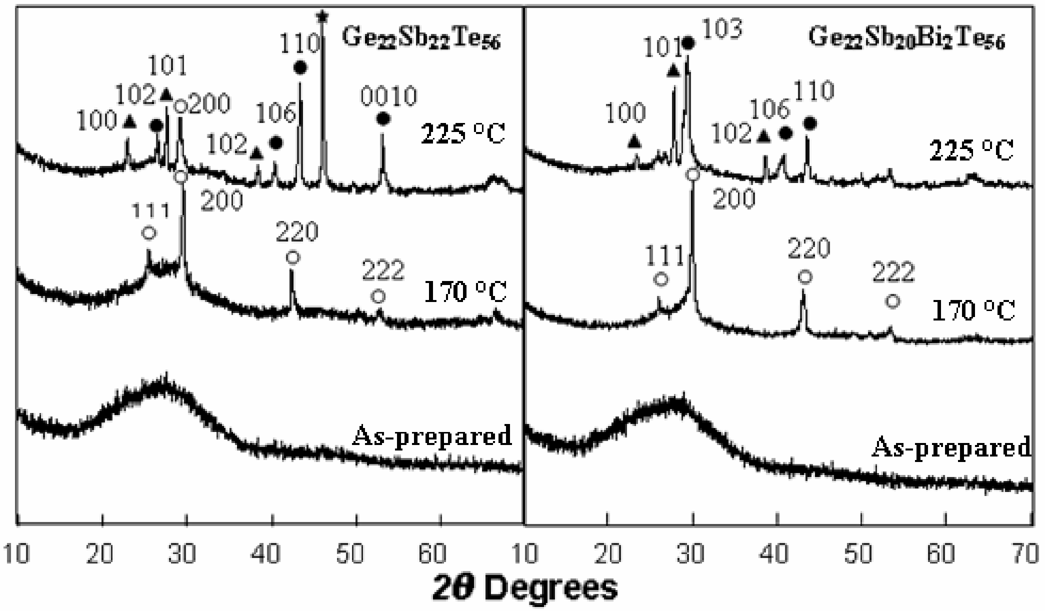

Fig. 3. X-ray diffraction scans of $Ge_{22}Sb_{22-x}Bi_xTe_{56}$(x = 0, 2) films annealed at different temperatures. (★) Unknown peak, (▲)Te Phase, (•)GST hcp lattice, (o) GST fcc Lattice.

4.3 Optical properties

In order to obtain the optical band gap E_g, the transmission and reflection spectra of the thin films of different compositions were analyzed. The optical bandgap can be calculated from the spectral dependence of the absorption coefficient, α [18]. The absorption coefficient (α) of the films has been calculated from the transmission and reflection data using the relation

$$\alpha = \left(\frac{1}{t}\right)\ln\left\{\frac{(1-R^2)}{(2T)} + \left\{\frac{(1-R)^2}{(2T)^2} + R^2\right\}^{1/2}\right\} \tag{1}$$

where R, T and t represents reflectance, transmittance and thickness of the thin film.

Fig. 4 represents plots of $(\alpha h\nu)^{1/2}$ vs $h\nu$ for films of $Ge_{22}Sb_{22}Te_{56}$ and $Bi_2Ge_{22}Sb_{20}Te_{56}$ obtained at room temperature. The value of E_g for films is determined by extrapolation of the linear part of $(\alpha h\nu)^{1/2}$ vs $h\nu$ plot to energy axis. The dependence of E_g, as a function of film composition, is shown in Fig. 4. Figure shows that there is a small decrease in the optical band gap from 0.59 to 0.53 *eV* as the content of Bi increases to 2 at%. The decrease in the band gap with increased Bi content occurs because the latter creates localized states in the band gap [19]. The observed decrease of E_g for Bi 2 at% can be explained by the increased tailing of the conduction band [19].

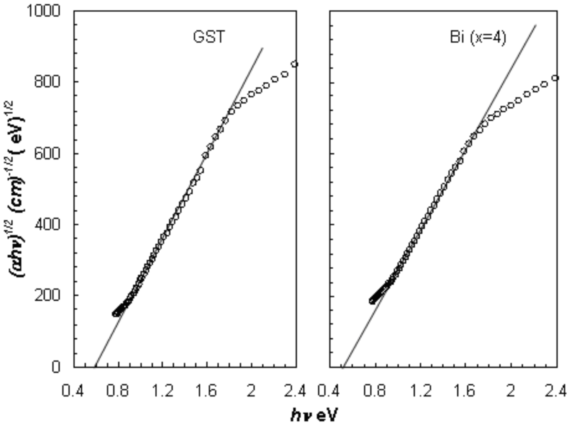

Fig. 4. Plots of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for $Ge_{22}Sb_{22}Te_{56}$ (GST) and $Ge_{22}Sb_{20}Bi_2Te_{56}$ films.

The stability of the amorphous marks (bits) at room temperature can be estimated by considering the phase transformation temperature. The increase in phase transformation temperature with Bi 2 at%, shows the room temperature stability over pure GST. Optical and structural properties do not show significant change with partial substitution of Bi, indicated by small decrease in the optical band gap from 0.59 to 0.53 eV as the content of Bi increases to 2 at%.

Since, no noticeable phase transformation was observed for higher concentrations of Bi (Fig. 1), the optical analysis is not presented here. The lattice constant is found to lie in the range of previously reported values for pure GST. These measurements indicate that Bi substitution preserves the NaCl type structure of GST.

5. Conclusion

The high contents of Bi for Sb are found to obstruct the amorphization of thin films deposited by thermal evaporation technique and thus increase in the room temperature conductivity of the material was observed. The FCC structure of the GST is found to remain preserved for small substitutions of Bi indicated by the unchanged values of lattice constant. Also, discs made using partially Bi substituted $Ge_{22}Sb_{22}Te_{56}$ chalcogenide material as the active layer would have a long archival life. This is due the relatively high phase transformation temperature.

References

[1] S. R. Ovshinsky, Phys. Rev. Lett. **21**, 1450 (1968).
[2] S. R. Ovshinsky, Proc. 9th Symp. on Phase Change Recording, PCOS 44 (1997).
[3] M. Wuttig, N. Yamada, Nature Materials **6**, 824 (2007).
[4] M. Chen, K. A. Rubin, R W. Barton, Appl. Phys. Lett. **49**, 502 **(**1986).
[5] N. Yamada, E. Ohno, N. Akahira, K. Nishiuchi, K. Nagata, M. Takao, Proc. of the Int. Symp. on Optical Memory **26**, 61 **(**1987).
[6] R. T. Young, D. Strand, J. G. Hernandez, S. R. Ovshinsky, J. Appl. Phys. **60**, 4319 (1986).
[7] A. Hirotsune, Y. Miyauchi, M. Terao, Appl. Phys. Lett. **66**, 2312 (1995).
[8] R. Kojima, S. Okabayashi, T. Kashihara, K. Horai, T. Matsunaga, E. Ohno, N. Yamada, T. Ohta, Jpn. J. Appl. Phys. Part 1, **37**, 2098 (1998).
[9] G. F. Zhou, B. A. J. Jacobs, Jpn. J. Appl. Phys. **38**, 1625 (1999).
[10] D. Z. Dimitrov, Y. Lu, M. Tseng, W. Hsu, H. Shieh, Jpn. J. Appl. Phys. **41**, 1656 (2002).
[11] S. Gu, L. Hou, Q. Zhao, R. Huang, Chin. Opt. Lett. **1**, 716 (2003).
[12] C. Lie, P. Kuo, W. Hsu, T. Wu, P. Chen, S. Chen, Jpn. J. Appl. Phys. **42**, 1026 (2003).
[13] E. Prokhorov, G. Trapaga, E. Morales-Sanchez, M. Hernandez-Landaverde, Y. Kovalenko, J. Gonzalez-Hernandez, J. Appl. Phys. **96**, 1040 (2004).
[14] X. Cheng, L. Bo, S. Z. Tang, F. S. Lin, C. Bomy, Chin. Phys. Lett. **22**, 2929 (2005).
[15] K. Wang, C. Steimer, D. Wamwangi, S. Ziegler, M. Wutting, Appl. Phys. A **80**, 1611 (2005).
[16] M. Abkowitz, Polym. Eng. Sci. **24**, 1149 (1984).
[17] I. Friedrich, V. Wedenhof, W. Njoroge, P. Franz, M. Wuttig, J. Appl. Phys. **87**, 4130 (2000).
[18] J. Tauc, Amorphous and Liquid Semiconductors. (London:Plenum Press) (1974).
[19] H. El-Zaheda, A. El-Korashy, Thin solid Films **376**, 236 (2000).

---

*Corresponding author: jitenderapd@gmail.com