

STRUCTURAL PHASE TRANSITIONS AND OPTICAL CONTRAST IN AMORPHOUS Sb_2Se_3 : Sn FILMS

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This paper reports the phase transition and optical properties of the $(\text{Sb}_2\text{Se}_3)_{100-x}\text{Sn}_x$ ($x=0, 5$) films. The resistance-temperature measurements show an increase in the phase transformation temperature and no new phase has been crystallized with the addition of Sn in the parent alloy. The optical gap decreases while an increase in tailing parameter have been found with the addition of Sn. The crystallization of the films at the transformation temperature results in the decrease of the optical gap with anomalous change in the tailing parameter. A large change in the optical contrast with the maxima at the 430nm is important to tailor the new materials for the information storage applications.

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1. Introduction

Chalcogenide glasses and thin films have been studied in the last two decades because of their potential use in optoelectronic and technological applications such as photoresists, image storage, and memory switching etc. The current interest in the chalcogenide based systems is to study the characteristics of phase transformations such as the optical contrast, sheet resistance, role of impurity and optimization of device characteristics for the need of growing information storage devices [1, 2]. The GeSbTe system is one of the most commonly used chalcogenide-based phase change materials used in rewritable storage media, since its discovery by Ovshinsky in the 1960s [3]. The tie line compositions on GeTe and Sb_2Te_3 two binaries in the space diagram for this ternary diagram along with some binaries such as Sb_2Te (Se), Ge(Sn)Sb and InSb have been found to be promising materials for the next generation memories [4]. Impurity additive in the doped in the binary and ternary systems have also been studied in order to improve the material properties for the improved device performances along with to understand the basic physics behind the transformation process. The additives (Si, Sn, Pb etc.) in the GST improve much of the phase change characteristics and device performance as evidenced from the recent literature [5-8]. The inclusion of Sn containing layer offers a mean to tailor the phase transitions in the Ge-chalcogenide films in the GeTe/SnSe and $\text{Ge}_2\text{Se}_3/\text{SnTe}$ bilayer systems, results in incorporation of Sn in the active films as evidenced by the time resolved x-ray diffraction techniques [9]. However, the interest in investigating the different systems on the phase change characteristics and transformation process still found to be an important aspect to the development of new memory systems. Therefore, the present work describes the role of Sn additive on the structural phase transformations and the reflectivity contrast of the Sb_2Se_3 films for their probable application in this emerging technology.

2. Experimental details

Thin films of bulk $(\text{Sb}_2\text{Se}_3)_{100-x}\text{Sn}_x$ ($x=0, 5$) samples were deposited in a high vacuum ($\sim 10^{-5}$ torr) by using HINDHIVAC coating unit (Model no. 12A4D). Well-cleaned glass substrates

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placed at room temperature as substrates and the source material taken in molybdenum boats were used for the deposition [10]. The amorphous nature/crystalline phases have been studied using the PANalytical X'pertPRO system with Cu as the anode material, operated at 35mA and 40 kV. Post-deposited Al electrodes in coplanar geometry (length 10.0mm and gap spacing 3.0 mm) were used for resistivity measurements. The resistance-temperature measurements were carried out in the running vacuum using the two probe method. The annealing at the transformation temperature for different film samples have been performed using the substrate heater with temperature controller under the running vacuum conditions ($\sim 10^{-5}$ torr) for 1h. The transmittance with respect to the glass slide and specular reflectance measurements with respect to the highly reflecting aluminum mirrors have been taken using the UV-Vis spectrophotometer (lambda 35, Perkin Elmer, Japan) in the 220-1100nm spectral region.

3. Results and discussion

Fig. 1 shows the resistance versus temperature plot for the $\text{Sb}_2\text{Se}_3:\text{Sn}$ films. The value of the resistance decreases by two order of magnitude at the phase transformation temperature. It has been observed that the phase transition temperature increases from 180 °C for $x=0$ to 220 °C for the $x=5$ in the $(\text{Sb}_2\text{Se}_3)_{100-x}\text{Sn}_x$ thin films. The strong bond formation of Sn with the Se as compared to the Sb and associated change in the local structure of the parent system results in the increase in the transformation temperature. Similarly, an increase in the transformation temperature with the enhancement in the crystallization speed or decreases the operation time of the devices for the Sn additive in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ system has been reported [7, 8]. The comparison of the dc activation energy (temperature range; 140-180 °C) reveals an increase from 0.38 ± 0.02 eV (for $x=0$) to 0.69 ± 0.03 eV (for $x=5$). A decrease in the value of dc activation energy when measured in the lower temperature range has been reported previously [10] and attributed to the change in the density of defect states in the mobility gap of the material. These results can be attributed to the change in the dominant conduction process; the nature of those strongly depends on the temperature range of measurement in these amorphous systems [11].

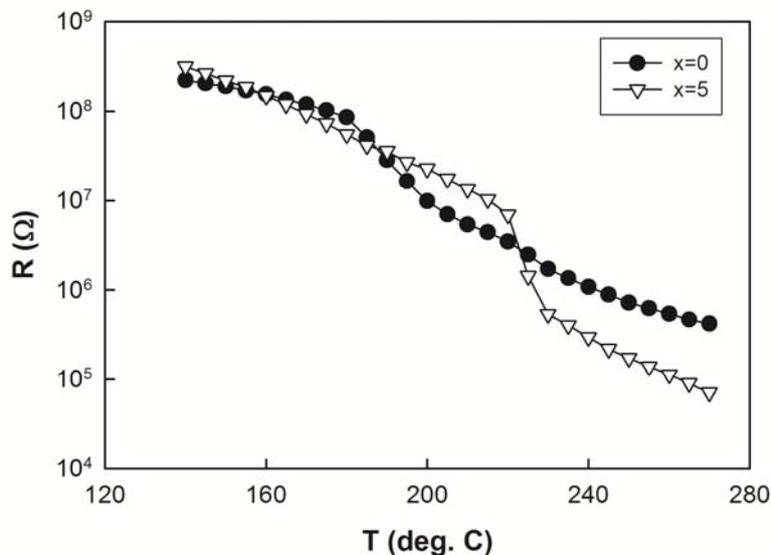


Fig. 1. The resistance-temperature curves for $(\text{Sb}_2\text{Se}_3)_{100-x}\text{Sn}_x$ films.

Fig. 2 shows the XRD diffractograms for the $(\text{Sb}_2\text{Se}_3)_{100-x}\text{Sn}_x$ thin films. The as-prepared and annealed (at 200°C for $x=5$) films do not show any crystallization while annealing above the transformation temperature results in the crystalline phases and have been compared using the JCPDS, 1997. The formation of crystalline Sb_2Se_3 phase in the parent alloy, with a decrease in the relative intensity or no additional peaks for the Sn-phase has been observed. This confirms that the

Sn additive only results in the structural modification or influences the crystalline phases in the parent alloy and results in a change in its electrical conduction process.

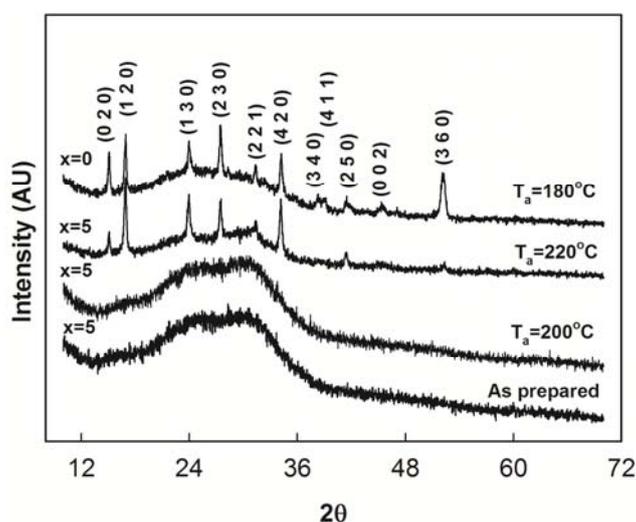


Fig. 2. XRD patterns for the as-prepared and devitrified $(\text{Sb}_2\text{Se}_3)_{100-x}\text{Sn}_x$ films. The crystalline peaks are indexed for the Sb_2Se_3 phase in the present case.

From the optical transmittance and the reflectance spectra of the films, the value of the absorption coefficient has been calculated using the relation: $\alpha = (1/d) \cdot \ln\{(1-R)/T\}$, where 'd' is the thickness of the film. The absorption coefficient so obtained has been found to lie between 10^4 to 10^5 cm^{-1} near the fundamental absorption region and the optical gap is calculated using the Tauc's relation: $\alpha h\nu = B(h\nu - E_0)^2$, where E_0 is the optical gap and B is a measure of the disorder in these amorphous systems. Fig. 3 shows the plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for the as prepared films. The value of optical gap (E_0) and tailing parameter (B^{-1}) is found to be 1.28eV, $0.37 \mu\text{eV}\cdot\text{cm}$ for $x=0$ and 1.23eV, $1.17 \mu\text{eV}\cdot\text{cm}$ for $x=5$ film samples. This shows that the decrease in the value of the optical gap accompanies with the increase in the tailing parameter showing the increase in the disorder in the material due to the development of partial ionic character of the Sn-Se bonds formed and/or the shifting of the lone pair electrons of the chalcogen atoms. The inset of figure 3 shows the reflectance with wavelength for the as-prepared films. The absence of long range order results in the broad spectral dependence in the interband region characteristics of the amorphous films while the increase in the reflectance with the Sn content can be regards as the increase in the metallic content.

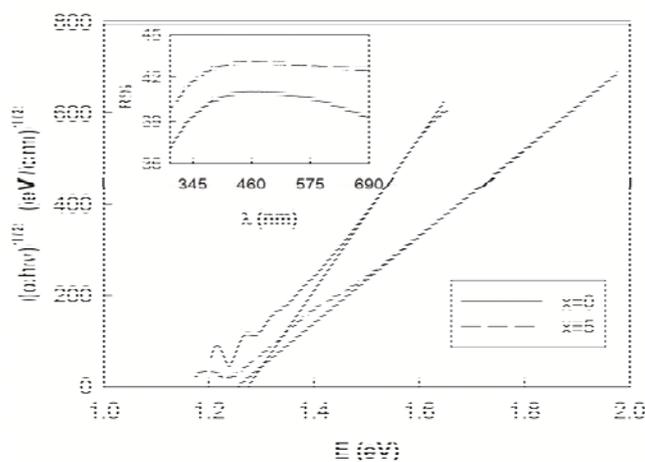


Fig. 3. Variation of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for the as prepared $(\text{Sb}_2\text{Se}_3)_{100-x}\text{Sn}_x$ films and the inset picture shows the reflectance versus wavelength for the same films.

The reflectivity contrast of a material is one of the most important optical parameters, the large value of which depicts a high signal to noise ratio for the rewriteable optical storage materials. The reflectivity contrast (C) is defined as [12], $C = \{(R_C - R_A)/R_C\} * 100$, where R_C and R_A are the reflectivities of the crystalline and amorphous states respectively. Fig. 4 shows the reflectivity contrast curves with wavelength for the $x=5$ film samples annealed at the transformation temperature for 1h. A large change in the reflectivity contrast has been observed with the Sn additive in this binary. In the parent alloy films the value of reflectivity contrast is less than 1% or a decrease in the reflectivity near the blue wavelength of the visible spectrum have been observed, while the Sn additive results in the large change in the contrast and found to observed a maxima at the 430nm or the wavelength of interest for the blue ray discs. This shows that the reflectivity contrast shows a maxima in its value i.e. it red/blue shifts with the Sn addition in the binary. The value of the optical gap and tailing parameter (E_o and B^{-1}) have also been calculated and found to be 1.01eV, 1.39 μ eVcm for $x=0$ and 1.12eV, 0.43 μ eVcm for $x=5$ film samples respectively. The value of the optical gap is found to decrease for the devitrified films. While the tailing parameter value follows an anomalous behavior, as its value is found to increase for the $x=0$ film and decreases for the $x=5$ film samples. It can be attributed to the layered structure of the parent binary alloy, and crystallization leads to the increased disorder in the film. The enhancement in interlayer connectivity or change in the network connectivity with Sn additive in this binary stiffens the network and/or increasing the order structure in the crystalline state. However, no new diffraction peaks observed in the figure 2 with Sn additive and increase in the transformation temperature, also supports the above result. These results suggests that the Sn additive results in the structural modification and/or the electronic structure of the material and tailoring the optical behavior in such a way that its importance for the development of the optical media for the emerging technology.

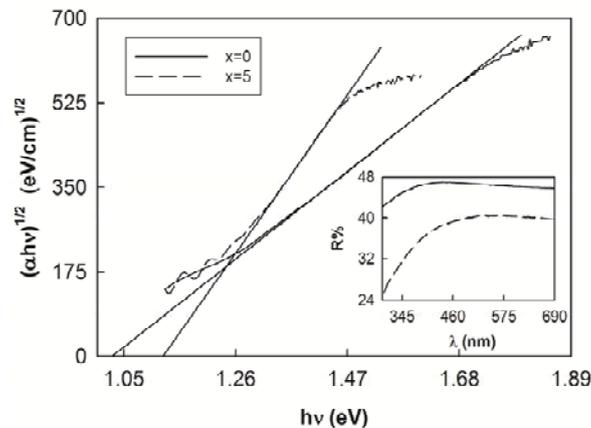


Fig. 4. Variation of $(\alpha hv)^{1/2}$ versus hv for the annealed $(Sb_2Se_3)_{100-x}Sn_x$ films and the inset picture shows the reflectance versus wavelength for the same films.



Fig. 5. Variation of the reflectivity contrast with wavelength for the $(Sb_2Se_3)_{95}Sn_5$ films.

4. Conclusions

The phase transformation characteristics such as transformation temperature, crystalline phases, optical contrast as well as the optical properties was reported for the $(\text{Sb}_2\text{Se}_3)_{100-x}\text{Sn}_x$ ($x=0, 5$) films. Phase transformation temperature increases while no new phases were observed with Sn addition. The value of the optical gap decreases with an increase in the tailing parameter, showing an increase in the disorder for the parent films. The annealing results in the decrease of the optical gap, but the value of optical contrast have been found to be enhanced to larger extent. These results suggest that the Sn addition results in the better optical contrast with an increase in the transformation temperature of the Sb_2Se_3 films and can be useful for the optimization of the parameters for the high density optical media storage applications.

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