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Crystallization kinetics in $(AgSbTe)_x(In_{1-y}Sb_y)_{1-x}$ films used in optical data storage

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In phase change recording, higher linear densities can be achieved with materials in which crystallization is dominated by growth. AgInSbTe alloy based thin films appear to be the latest promising materials for optical data storage that has drawn worldwide attention. In these films, marks can be written with sharper edges and lower jitter. Films of $(AgSbTe)_x$ $(In_{1-y}Sb_y)_{1-x}$ material with different compositions ($x = 0.2, 0.3, 0.4$ keeping $y = 0.7$) were deposited using thermal evaporation technique under a high vacuum of 10^{-6} torr. The results of Differential Scanning Calorimetry (DSC) under non-isothermal conditions with different heating rates (5, 10, 15, 20° K/min) are reported and discussed here. The glass transition temperature T_g and the onset crystallization temperature T_c were found to be dependent on the composition as well as on the heating rate. The activation energy for glass transition E_g and the activation energy for crystallization E_c are calculated using Kissinger's equation and their compositional dependence is discussed. The glass forming ability lies in the range 0.4–0.6.The present investigations indicate that the above-mentioned quaternary material with a typical composition ($x = 0.2$) is good for phase change optical memory. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

The rewritable phase-change optical disc combines the high reliability of long-term data storage with the high performance characteristics of single-beam direct overwrite [1].

In phase change discs, the crystallization speed of the recording material determines the erasing time. Therefore it is very important to know the crystallization mechanism of the phase change material [2]. Two active layer compositions are currently employed, although probably several others would be feasible. One is the four-component AgInSbTe (represented by AIST) and the other one is the three-component GeSbTe (represented by GST). They have different crystallization behaviors, which have consequences for the storage process. For good disc performance, the concern is with the uniformity of the layer thickness and the layer composition across the disc [3], besides other parameters. AIST based materials are most suitable for high data rate optical recording. AIST alloy has found application as the recording layer in compact disc (CD-RW), digital versatile disc–rewritable (DVD-RW) [4, 5] media, and other promising commercial phase change optical discs. Further this material is currently preferred for groove only phase change recording formats, because they allow higher linear densities and intrinsically low jitter. Lower jitter value is attributed to the mechanism by which amorphous marks are erased, i.e. via growth of the crystalline edge towards the mark center, resulting in the marks with well-defined edges [6]. The study of crystallization of a glass upon heating can be undertaken in several different ways. In calorimetric measurements two techniques are generally employed for the study of the crystallization behavior upon heating : Isothermal and non-isothermal crystallization analysis [7]. In the isothermal method the sample is brought quickly to a temperature above the glass transition temperature T_g and the heat evolved during crystallization process at a fixed temperature is recorded as a function of time. In the other method the sample is heated from the room temperature, generally at a fixed rate (β) and the heat evolved is recorded as a function of temperature.

In the present work we have concentrated on the thermal properties and studied the crystallization behavior.

The parameters of crystallization for $(AgSbTe)_x$ $(In_{1-y}Sb_y)_{1-x}$ ($x = 0.2, 0.3, 0.4$ and $y = 0.7$) films under non-isothermal conditions have been calculated. In order

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to optimize the material (for best performance), the effect of composition on the crystallization mechanism has been studied.

2. Experiment

2.1. Alloy preparation

Bulk alloys of different compositions were prepared by the melt quenching technique. The chemical formula $(AgSbTe)_x\ (In_{1-y}Sb_y)_{1-x}$ has been used, with $x < 0.5$ and $y = 0.7$, as suggested in the literature [4]. Appropriate amount of constituent elements of 5N purity were melted together in evacuated sealed quartz ampoules at a pressure of 10^{-6} torr. The ampoules were kept in a rocking furnace (at 1150°C for 30 h) to ensure the melt is homogenous. The samples were then quenched in liquid nitrogen to ensure the amorphization of the alloy. The quenched samples were removed from ampoules by keeping the ampoules in a mixture of HF for about 24 h. Quartz gets dissolved in HF and the samples thus obtained were of gray colour.

2.2. Film preparation

The films (∼100 nm thickness) for different compositions of the alloy were deposited under a high vacuum of $\sim 10^{-6}$ torr, using thermal evaporation technique. Before depositing the films, glass and quartz slides were adequately cleaned. The substrate is first cleaned in a dilute solution of detergent. To remove the detergent solution from the substrate, a hot water spray rinse followed by an overflow rinse is carried out. In the next step, a boiling solution of hydrogen peroxide (teepol) is used for conversion of organic materials to water soluble compounds. Finally to remove the peroxide film, the substrate is first dipped in hot distilled water and thereafter it is soaked for about 15 min in deionised water. The substrate are then dried and loaded into a vacuum system for depositing the film.

X-ray Diffraction analysis of the films for different composition was carried out and the as-deposited films were found amorphous in nature as reported earlier [8, 9]. The compositions of the as-deposited film were verified using ESCA-750 (Shimadzu Corporation, Japan). The variation in composition with respect to initial values of constituent elements was of the order of 2%. The films so obtained were then subjected to thermal analysis (DSC).

2.3. DSC analysis

Non-isothermal analysis of the films was done using RIGAKU DSC-150 calorimeter. The graphs for three different compositions (x = 0.2, 0.3, 0.4) at four different heating rates of 5, 10, 15 and 20° K/min in the temperature range 20–400°C. The thermograms have been shown in Figs 1 and 2 respectively.

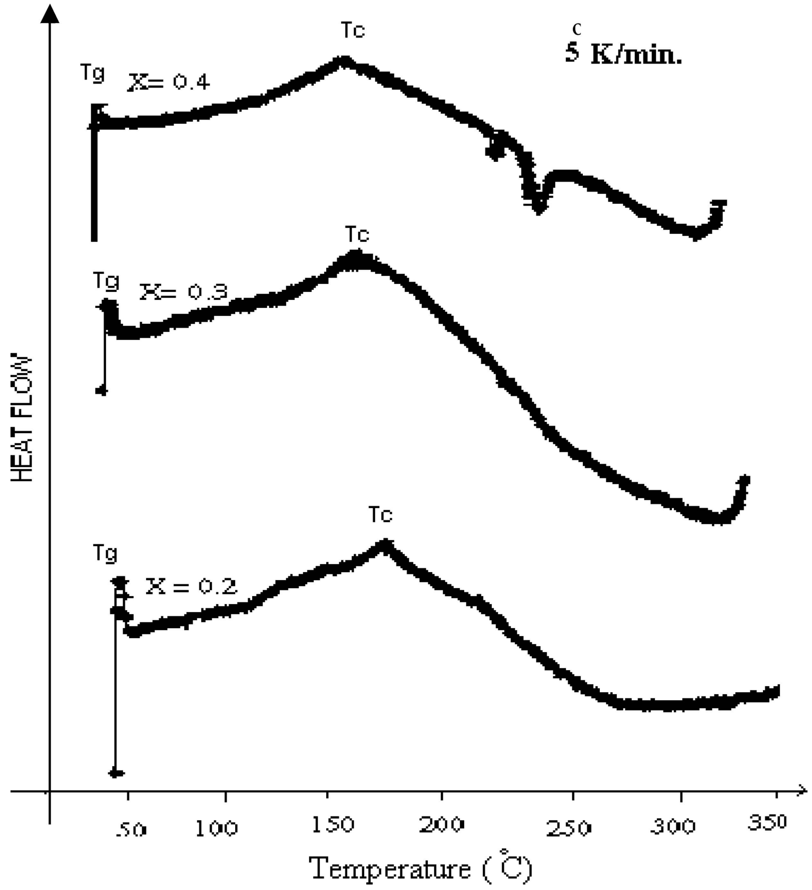

Figure 1 DSC Curves recorded for $x = 0.2, 0.3, 0.4$ (heating rate : 5° K/min).

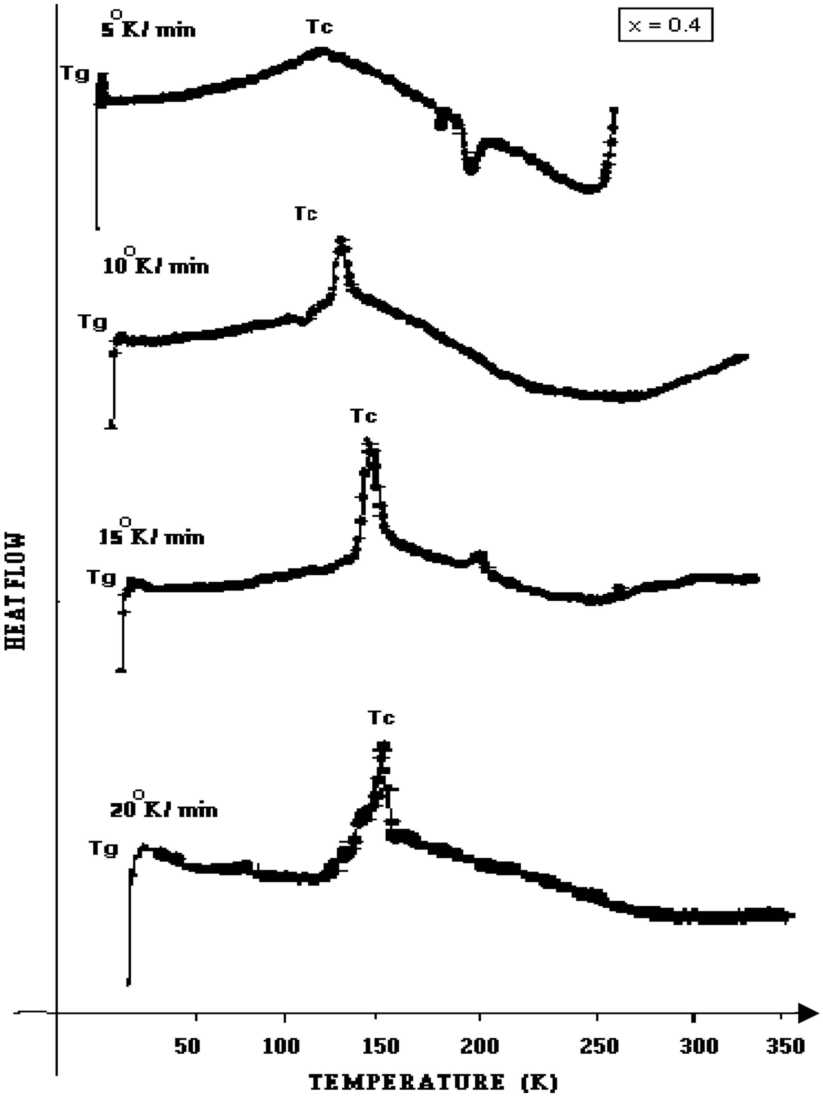

Figure 2 DSC Curves recorded for different heating rate of 5, 10, 15,20° K/min ($x = 0.4$).

3. Results

DSC thermograms for the compositions $(\mathrm{AgSbTe})_x(\mathrm{In}_{1-y}\mathrm{Sb}_y)_{1-x}$ with $x = 0.2$, 0.3 and 0.4 for a typical heating rate β of 5°C K/min are shown in Fig. 1. The pattern is found to be same for other heating rates also. Values of T_g and T_c are given in Table I respectively. The glass transition temperature T_g and the crystallization temperature T_c are marked in Fig. 1. It can be noted that all thermograms (for $x = 0.2$, 0.3, 0.4) show a single T_g, which shifts, towards higher temperature with the diminishing value of x ($x = 0.4$ to $x = 0.2$). This is also depicted in Table I. The first exothermic peak gives T_c, which also shows same behavior.

For a typical composition of $x = 0.4$ and $y = 0.7$, the heating rate dependence of T_g and T_c is shown in Fig. 2. It can be observed that, as the heating rate is increased T_g and T_c shifts towards the higher temperature. Also in some cases (at heating rate of 15°K/min) another very small exothermic peaks were observed, as shown. This may be attributed to the presence of some insignificantly low phases, which might have formed with increase in temperature, and there contribution will be neglected. Results have been summarized in Table I.

The value of T_m was measured separately and found to be (693.4°K) From the value of T_g, T_c and T_m glass forming ability k_g, and ratio of T_g/T_m of the film has been

TABLE I T_g and T_c of AgInSbTe films for different heating rates: 5, 10, 15, 20°K/min (for $x = 0.2$, 0.3, 0.4)

	Glass transition temperature (T_g) *K*				Crystallization temperature (T_c) *K*			
x	5 (K/min)	10 (K/min)	15 (K/min)	20 (K/min)	5 (K/min)	10 (K/min)	15 (K/min)	20 (K/min)
0.2	307.74	321.16	340.3	350.88	431.97	435.904	440.9	444.44
0.3	302.29	317.15	328	348.43	428.89	432.5	437.1	440.53
0.4	299.34	306.81	317.48	338.98	427.9	429.49	430.46	432.9

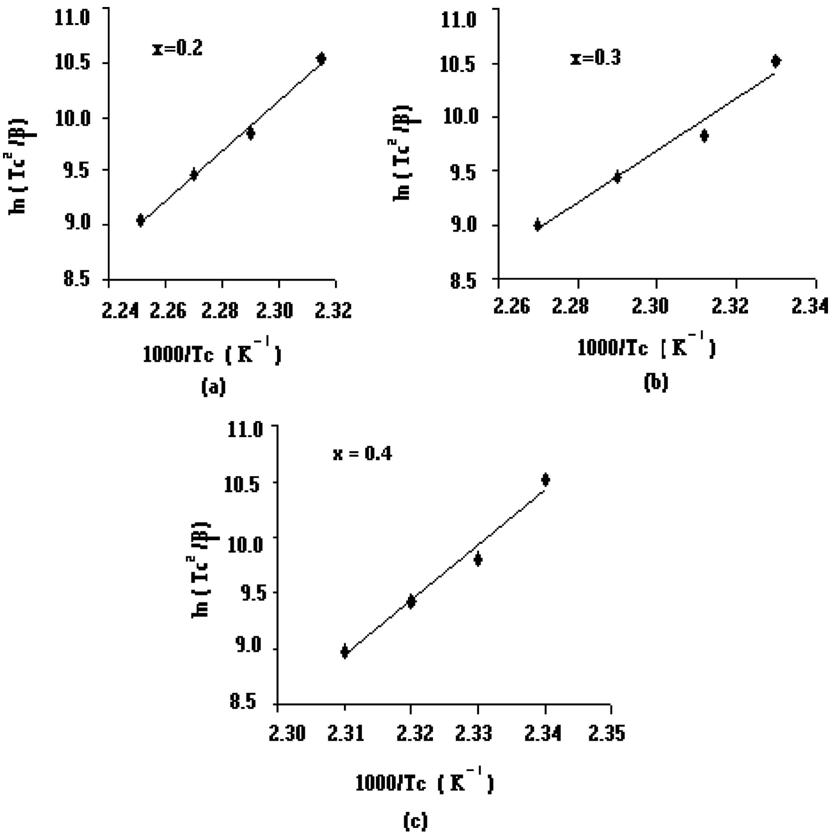

Figure 3 (a), (b) and (c): Kissinger's plots of ln $\left(\beta/T_c^2\right)$ versus $1/T_c$ for different compositions ($x = 0.2, 0.3, 0.4$) of AIST.

calculated and given in Table II. It can be noted that the value of T_g/T_m increases as the value of x decreases or in other words Ag concentration decreases. Further the value of k_g lies between 0.4–0.6, confirming that AIST material is a potential candidate for phase change optical memories.

The non-isothermal crystallization kinetics on these samples has also been studied using Kissinger's method [10], which predicts a shift in T_c towards higher temperature with an increase in heating rate, i.e.,

$$\ln\left(\beta/T_c^2\right) = (-E_c/K_B T_c) + \ln(K_B k/E_c) \qquad (1)$$

where E_c, K_B and k are the crystallization activation energy, Boltzmann constant, and frequency factor, respectively.

It is observed that the plot of ln $\left(\beta/T_c^2\right)$ versus $1/T_c$ for different compositions (for our experimental data) gives a linear dependence as shown in Figs. 3a–c. It follows Kissinger's equation (Equation 1) for T_c and E_c has been estimated from this equation.

Fig. 4 indicates the variation of E_c with respect to composition. To start with, activation energy rises slowly with increase in Ag content and then increases very sharply (after $x = 0.3$). It may be concluded that as the value of x increases more and more activation energy is required for crystallization which is not desirable. This implies that lesser is the doping of Ag (small x) content higher will be degree of crystallization. In the present case $x = 0.2$ should give the best results.

Similarly the dependence of T_g on composition for a given heating rate gives the value of activation energy E_g for glass transition. Replacing T_c by T_g and E_c by E_g in Kissinger's Equation 1, we find that E_g shows the same behavior as E_c and is minimum for $x = 0.2$. Therefore it may be concluded that AIST material for given composition with $x = 0.2$ will give best results.

TABLE II Glass forming ability (K_g) and T_g/T_m of AgInSbTe Films for different heating rates: 5, 10, 15, 20°K/min (for $x = 0.2, 0.3, 0.4$)

	Glass Forming Ability $K_g = (T_c - T_g)/(T_m - T_c)$				T_g/T_m			
x	5 (K/min)	10 (K/min)	15 (K/min)	20 (K/min)	5 (K/min)	10 (K/min)	15 (K/min)	20 (K/min)
0.2	0.4752	0.4456	0.398	0.375	0.44	0.463	0.491	0.506
0.3	0.4786	0.442	0.4257	0.364	0.436	0.457	0.473	0.502
0.4	0.48	0.4648	0.4297	0.360	0.4317	0.4425	0.458	0.486

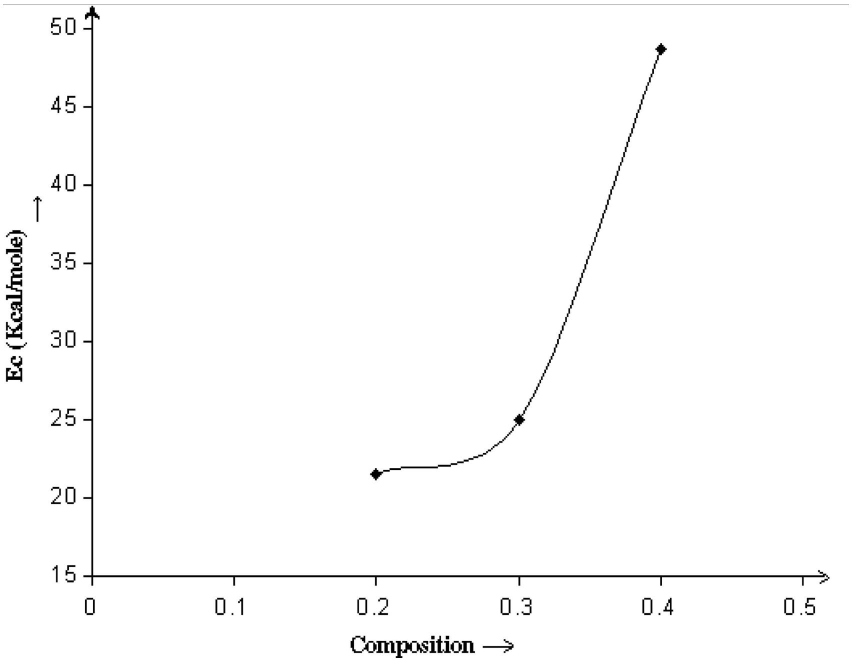

Figure 4 Activation energy for crystallization (E_c) as a function of composition ($x = 0.2$, 0.3 0.4).

4. Discussion

Our earlier work [8, 9] based on XRD analysis of different compositions annealed at different temperatures, reveal that single phase ($AgInTe_{2)}$ is prominent when the annealing is carried out at higher temperature (400°C). These study have shown that as the value of x is decreased and the annealing temperature is increased, the crystalline peak of $AgInTe_2$ gets sharper, indicating better crystallization and existence of single phase. To further confirm these results, thermal analysis of the films has been reported here. DSC results, Figs 1 and 2 show that the crystallization temperature (T_c) and glass transition temperature (T_g) depend on the heating rate as well as on composition variation. Further, these curves show single glass transition temperature T_g.

It can be further confirmed from Table I, that better glass forming ability (GFA) can be achieved with lower concentration of Ag ($x = 0.2$). As we know that doping of Ag leads to lower jitter value and higher linear densities [6], at the same time it will lead to an increase in both activation energy for crystallization and activation energy for glass transition (not desirable).

Microstructural changes (using SEM) reported elsewhere [11], indicate that there is a grater crystallization tendency in glasses containing lower concentration of Ag (lower value of x). XRD results [9], also indicate that there is better crystallization when Ag content is lower.

The present investigations (Thermal Analysis) also indicate that lower value of E_c and E_g are obtained as we move from higher to loer value of Ag content ($x = 0.4$ to $x = 0.2$). Therefore, one has to find a trade off between lower jitter values (higher linear density) and smaller activation energy (faster crystallization).

UV-VIS-NIR analysis of these films already done by us to ensure that AIST material is most suited for optical data storage in desired wavelength region [12].

Hence it can be concluded that AIST chalcogenide based glasses with typical composition for $x = 0.2$ and $y = 0.7$ is a better choice for phase change optical data storage erasable media.

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References

1. T. AKIYAMA, M. UNO, H. KITAURA, K. NARUMI, R. KOJIMA, K. NISHIUCHI and N. YAMADA, *Jpn. J. Appl. Phys.* **40** (2001) 1598.
2. J. PARK, M. R. KIM, W. S. CHOI, H. SEO and C. YEON, *ibid.* **38** (1999) 4775.
3. G. F. ZHOU and B. A. J. JACOBS, *ibid.* **38** (1999) 1625.
4. H. IWASAKI, M. HARIGAYA, O. NONOYAMA, Y. KAGEYAMA, M. TAKAHASHI, K. YAMADA, H. DEGUCHI and Y. IDE, *ibid.* **32** (1993) 5241.
5. E. MURAMATSU, A. YAMAGUCHI, K. HORIKAWA, M. KATO, S. TANIGUCHI, S. JINNO, M. YAMAGUCHI, H. KUDO and A. INOUE, *ibid.* **37** (1998) 2257.
6. H. J. BORG, P. W. M. BLOM, B. A. J. JACOB, B. TIEKE, A. E. WILSON, I. P. D. UBBENS and G. F. ZHOU, Philips Optical Disc Technology Centre, Glaslaan 1, 5616LD Eindhoven, The Netherlands.

Joint International Symposium on Optical Memory and Optical Data Storage July 1999. Koloa, Hawaii.

7. M. A. ABDEL-RAHIM, *J. Non-Cryst.Solids*. **24** (1998) 121.
8. G. MONGIA and P. K. BHATNAGAR, in Proceedings of Novel Optical System Design and Optimization, by The International Society of Optical Engineering (SPIE) **4768** (2002) 136.
9. GEETA MONGIA and P. K. BHATNAGAR, *J. Optical Engng*. **42,** (1) (2003) 148.
10. H. E. KISSINGER, *J. Res. Nat. Bur. Stand*. **57** (1956) 217.
11. G. MONGIA and P. K. BHATNAGAR, in Proceedings of 'PHOTONICS WEST', International conference on advance optical data storage, by SPIE, 4938 (2003) 77.
12. G. MONGIA and P. K. BHATNAGAR, *J. Opt. Engng*. Vol. **42**(11) (2003) 3274.

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