

Kinetic Analysis of Crystallization Processes in In₆₀Se₄₀ Thin Films for Phase Change Memory (Pram) Applications

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Abstract: In the present work, a systematic investigation of crystallization kinetics of In₆₀Se₄₀ alloy has been made. Thin films of In₆₀Se₄₀ alloy were prepared by thermal evaporation using Edward Auto 306 evaporation system. Electrical measurements at room temperature and upon annealing at different heating rates were done by four point probe method using Keithley 2400 source meter interfaced with computer using Lab View software. The dependence of sheet resistance on temperature showed a sudden drop in resistance at a specific temperature corresponding to the transition temperature at which the alloy change from amorphous to crystalline. The transition temperature was also found to increase with the heating rates. From the heating rate dependence of peak crystallization temperature (T_p) the activation energy for crystallization was determined using the Kissinger analysis. The films were found to have an electrical contrast of about six orders of magnitude between the as-deposited and the annealed states, a good quality for PRAM applications. The activation energies were determined to be 0.354 ± 0.018 eV.

Keywords: Chalcogenide Materials, Phase Change Memory, Crystallization Temperature, Transition Temperature

1. Background

Chalcogenide glasses containing sulfur (s), selenium (se) or tellurium (Te) constitute a rich family of vitreous semiconductors. There has been intense research activity based on these glasses (Lathrop and Eckert 1989; Rao and Mohan 1980; Asokan *et al.*, 1889; Balasubramanian and Rao 1994; Kolobov *et al.*, 2005 and Kumar *et al.*, 2008) in the view of basic physics as well as device technology. The freedom allowed in the preparation of glasses in varied composition brings about changes in their short-range order and thus results in variation of their physical properties. It is therefore easy to tailor their various properties as desired for technological applications.

These materials have a wide range of applications such as making optical fibres, memory devices, reversible phase change optical recording (Suri *et al.*, 2006). Besides the wide commercial device applications like switching, memory and xerography etc of Se, it also exhibits a unique property of reversible transformation (Aggarwal and Sanghera, 2002;

Tanaka, 1989) a property that makes it very useful in memory devices. Se based glasses can be heated above glass transition temperature and then quenched to amorphous or cooled slowly to crystalline with each of these two reversible states having distinct optical and electrical properties which is the basis for a digital phase change memory device. It is known that addition of a metal [indium (In), bismuth (Bi), antimony (Sb), silver (Ag), tin (Sn), arsenic (As), lead (Pb), zinc (Zn)] or chalcogen (S, Te) to Se can bring remarkable alterations in properties and reduce ageing. The effects of impurities on the electronic properties of amorphous chalcogenide glasses have been the subjects of serious debate ever since their discovery.

2. Materials and Methods

2.1. Thin Film Deposition

Indium and Selenium were prepared by Thermal evaporation technique. Microscope slides having dimensions 2.54cm x 7.62cm were used as substrates. The substrates

were thoroughly cleaned before placing them on substrate holder directly above the evaporation boat. About 0.1g of the fine powder of a mixture of Indium and Selenium was placed on the molybdenum boat and the material heated. The vapour deposited on the substrates forming thin films of $\text{In}_{60}\text{Se}_{40}$.

2.2. Sheet Resistance Measurement

Electrical resistivity measurements of thin films were done using the four point probe arrangement adopting the van der Pauw method. With a symmetrical square geometry adopted, the probe leads were connected to the Keithly Source Meter for voltage and current measurements. Figure 1 shows a schematic diagram of four-point probe resistivity measurement. Current of 1.0×10^{-10} A was applied through the contacts A and B and potential drop across D and C measured as shown in figure 1 (a). The switching of the probe tips on the sample was done and the same amount of current applied through the contacts A and D. Potential drop was again measured across the contacts B and C as illustrated in figure 1 (b). The measured values of current, voltage drops and film thickness were used to compute sheet resistivity. The sheet resistance was also measured upon annealing. Thermal annealing was done by placing $\text{In}_{60}\text{Se}_{40}$ thin films in a quartz tube of the electric furnace where argon was ambient. The furnace was programmed to heat the sample at a particular heating rate. The heating rates ranged from 25°C to 250°C.

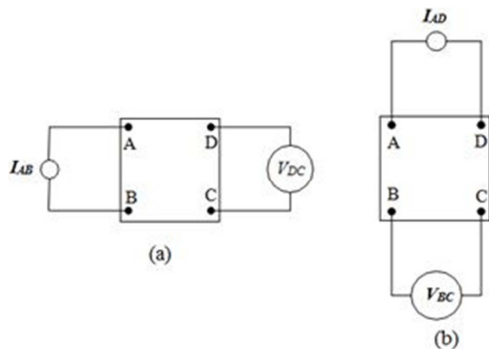


Fig. 1. A schematic diagram of four-point probe resistivity measurement.

Measurement of voltage and current was done using of Keithly SourceMeter which was configured to source current and measure voltage simultaneously on the thin film sample. A four wire remote sensing technique was adopted to minimize errors due to potential drops in the test leads when sourcing or reading voltages. Four wire remote sensing ensured that the programmed voltage was delivered to the thin film under test.

2.3. Determination of Activation Energy of Crystallization

For stoichiometric combination of $\text{In}_{60}\text{Se}_{40}$ under investigation different temperature dependence of sheet resistance curves were obtained. The heating rates were varied between 2.5K/min and 12.5K/min. For each run, fresh specimens of the film were used. The peak crystallization

temperature for each specific heating rate was obtained from the minimum of the first derivative of sheet resistance. The Kissinger plots were used in determining the activation energies for the sample.

2.4. Measurement of Film Thickness for as Deposited Films

The thickness of the as deposited films was determined using Alpha-Step IQ Surface profiler with a vertical resolution of 0.012 Å and vertical range of 100 Å-0.4 mm. The profiler compares the thickness of a blank glass slide with that having a film. The thickness was found to be 213.0 ± 0.1 nm.

2.5. Sheet Resistance Dependence on Temperature

Sheet resistance for as deposited and annealed films was measured using the four point probe following a procedure proposed by Van Dar Pauw and compared to those obtained for GST (Friendrich *et al.*, 2000). The sheet resistance of as deposited films was $1.696 \times 10^8 \pm 0.0005$ (Ω/Sq) which is higher compared to that of GST at $0.9 \times 10^8 \pm 0.0005$ (Ω/Sq) which is widely used for PCM applications.

The obtained values of sheet resistance for as deposited films are approximately twice the sheet resistance of the widely used GST. This is an advantage with respect to PCM applications as high crystalline resistance reduces reset operating power.

2.6. Variation of Sheet Resistance with Temperature for $\text{In}_{60}\text{Se}_{40}$

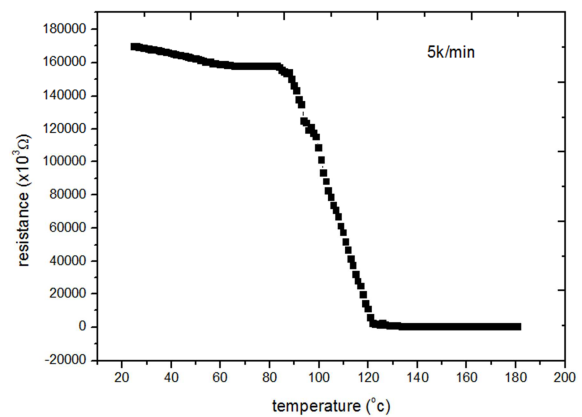


Fig. 2. The graph of sheet resistance dependence on temperature for $\text{In}_{60}\text{Se}_{40}$.

Figure 2 shows variation of sheet resistance upon annealing for $\text{In}_{60}\text{Se}_{40}$ thin film at a heating rate of 5k/min. Annealing was done at a temperature range between 25°C to 250°C. Initially the film had a resistance of 1.72×10^8 Ω/Sq which reduced to 1.71×10^6 Ω/Sq. after annealing. The drop in resistance shows that there was a change of phase from amorphous to crystalline, however the change was not abrupt. Transition took place at temperature range between 84°C to 122°C. Transition temperature was obtained by differentiating the results obtained. The differentiated curve is shown in figure 3.

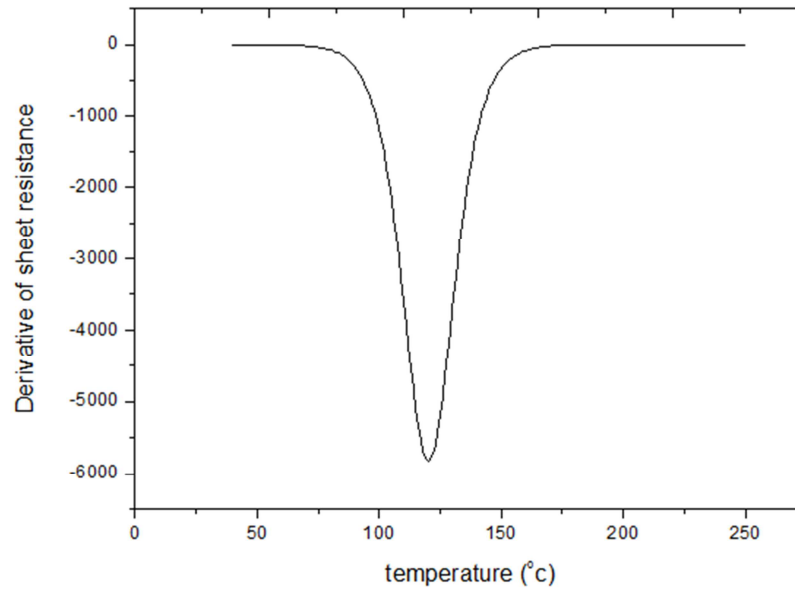


Fig. 3. Graph of derivative of Sheet resistance vs. Temperature.

From figure 3 transition temperature for $\text{In}_{60}\text{Se}_{40}$ was $105.38 \pm 0.54^\circ\text{C}$. The transition temperatures for $\text{In}_{60}\text{Se}_{40}$ was 105.38 ± 0.54 which imply that a PRAM from this alloy will be stable at room temperature since the value of transition temperature is above the room temperature.

2.7. Comparison of Sheet Resistance for as Deposited and as Annealed Films

Table 1. Sheet resistance for as deposited and as annealed films.

Sample	Sheet resistance ($\Omega/\text{Sq.}$) As deposited (± 0.0005) $\times 10^8$	Sheet Resistance ($\Omega/\text{Sq.}$) As annealed (± 0.005) $\times 10^2$
$\text{In}_{60}\text{Se}_{40}$	1.696	2.99
$\text{Ge}_2\text{Sb}_2\text{Te}_5$	0.900	44.00
(Friedrich et al., 2000)		

The table 1 give summary of sheet resistance for as deposited and annealed films. The values have also been compared to those of GST according to Friedrich *et al.* (2000). These values were used to compute sheet resistivity using the measured values of thickness.

Sheet resistivity for $\text{In}_{60}\text{Se}_{40}$ as deposited was $3.61 \times 10^3 \Omega\text{cm}$ and $6.37 \times 10^{-3} \Omega\text{cm}$ upon annealing showing an electrical contrast of six orders of magnitude. According to chung *et al.* (2008), an electrical contrast of at least three orders of magnitude is required for a phase change material. Therefore based on electrical contrast these alloys are suitable for PCM applications.

Table 2. Sheet resistivity for as deposited and as annealed films for different stoichiometry.

Sample	Sheet Resistivity (Ωcm) As deposited (± 0.005)	Sheet Resistivity (Ωcm) As annealed (± 0.005)	Sheet Resistivity (Ωcm) As annealed (± 0.005)
$\text{In}_{60}\text{Se}_{40}$	3.61×10^3	6.37×10^{-3}	6
$\text{Ge}_2\text{Sb}_2\text{Te}_5$	1.35×10^3	4.95×10^{-2}	6
(Friedrich et al., 2000)			

$\text{In}_{60}\text{Se}_{40}$ thin films were annealed at heating rates of 2.5, 5, 7.5, 10 and 12.5K/min within the temperature range of 25°C to 250°C .

2.8. The Activation Energy of Crystallization for $\text{In}_{60}\text{Se}_{40}$

The result for crystallization temperature dependence on heating rates for $\text{In}_{60}\text{Se}_{40}$ shows a positive shift in transition

as the heating rate is increased for the heating rates 2.5, 5, 7.5, 10 and 12.5k/min. Figure 4 shows the various shifts as the heating rates are increased.

Figure 4 show the variation of sheet resistance upon annealing at different heating rates (2.5, 5, 7.5, 10 and 12.5k/min). A positive shift in the transition temperature with increase in heating rates is also observed for this alloy. The crystallization parameters for this alloy are tabulated as shown in table 3.

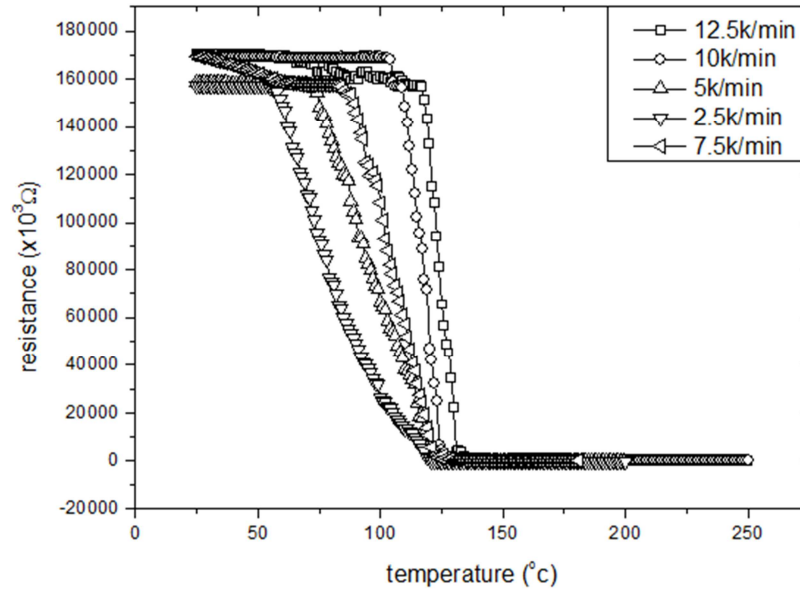


Fig. 4. Graph showing shifts in transition temperature with change in heating rates for $\text{In}_{60}\text{Se}_{40}$.

Table 3. Crystallization parameters for as deposited $\text{In}_{60}\text{Se}_{40}$.

Heating rate β ($\pm 0.05\text{k/min}$)	T_c ($^{\circ}\text{C}$)	T_c (K)	$1000T_c^{-1} \text{ K}^{-1}$	$\ln(\beta T_c^{-2})$
2.5	77.82 ± 0.78	350.82 ± 0.78	2.85046 ± 0.00634	-10.80426 ± 0.02445
5.0	96.89 ± 1.03	369.89 ± 1.03	2.70351 ± 0.00753	-10.21697 ± 0.01557
7.5	105.39 ± 0.55	378.39 ± 0.55	2.64278 ± 0.00384	-9.85695 ± 0.09570
10.0	117.38 ± 0.22	390.38 ± 0.22	2.56161 ± 0.00144	-9.63166 ± 0.00613
12.5	124.16 ± 0.19	397.16 ± 0.19	2.51788 ± 0.00120	-9.44295 ± 0.00496

Figure 5 shows the Kissinger plot for the alloy.

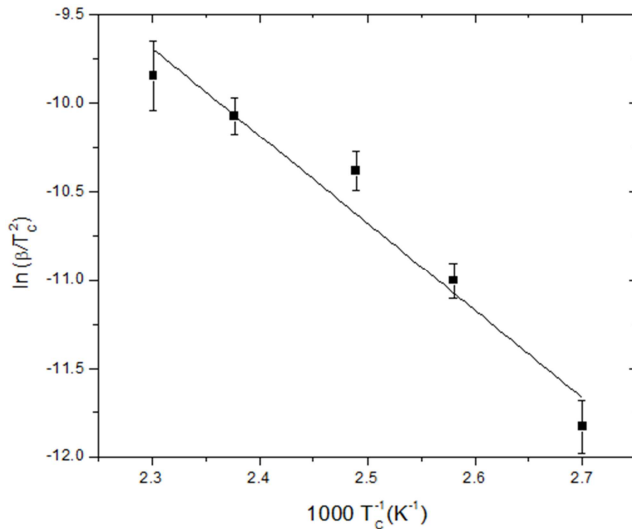


Fig. 5. The Kissinger plot for calculation of activation energy for $\text{In}_{60}\text{Se}_{40}$ film.

The activation energy for $\text{In}_{60}\text{Se}_{40}$ was found to be $0.354 \pm 0.018\text{eV}$.

The values of transition temperature of the alloys at all heating rates: 1, 2.5, 5, 7.5 and 10K/min were much higher than the room temperature. This is an advantage for these

alloys because it is essential to prevent self-transition of recording materials between the two phases. Hence one can expect the PCM made from this alloy to remain stable in its amorphous and crystalline states at the room temperature.

Since the crystalline SET state is a stable low resistance state, it is the stability of the quenched high resistance RESET phase which dominates retention issues (Burr *et al.*, 2010). The amorphous phase suffers from two independent resistance altering processes: resistance drift and spontaneous crystallization (Burr *et al.*, 2010). Although resistance drift does not cause any data loss, thermally activated crystallization leads to significant reduction in the resistance of the active layer, causing eventual retention failures for the binary storage.

3. Conclusion and Recommendation

Crystallization kinetics of $\text{In}_{60}\text{Se}_{40}$ thin films has been successfully investigated. The value of crystallization temperatures was much higher than room temperature. Therefore a PRAM cell from this material is stable and therefore this alloy is suitable for PRAM applications. These temperatures prevent self-transition of glassy alloys which is required for the application as stable glasses (shukla *et al.*, 2000). The films also showed high crystalline resistance which reduces reset operating power. An electrical contrast

of six orders of magnitude was also exhibited. According to chung *et al.* (2008) an electrical contrast of at least three orders of magnitude is required for a phase change material. A high activation energy of is 0.354 ± 0.018 eV was realised. Activation energy for crystallization is proportional to crystallization temperature and high crystallization temperature leads to high data stability.

References

- [1] Aggarwal I. D, and Sanghera J. S.(2002) Development and applications of chalcogenide glass optical fibers. *Journal of Optoelectronics and Advanced Materials* 4: 665-678.
- [2] Asokan, S. Prasad, M. V. N. Parthasarathy G and Gopal E. S. R. (1989), Mechanical and chemical thresholds in IV-VI chalcogenide glasses, *Physics Review Letters* 62: 808.
- [3] Balasubramanian S. and Rao, K. J. (1994). A molecular dynamics study of atomic correlations in glassy B_2S_3 , *Journal of Physical Chemistry* 98: 9216-9221.
- [4] Burr, G. W., Breitwisch, M. J., Francheschini, M., Garetto, D., Goparakrishna, K., Jackson, B., Kurdi, B., Lam, C., Lastras, L. A., Padilla, A., Rajidan, B., Raoux, S. and Shenoy, R. S. (2010). "Phase change memory technology". *Journal of Vacuum Science and Technology* 28: 223-262.
- [5] Chung, K. M., Wamwangi, D., Woda, M., Wuttig, M. and Bensch W. (2008). Investigation of $SnSe$, $SnSe_2$ and Sn_2Se_3 alloys for phase change memory application. *Journal of Applied Physics* 10 (8): 083523.
- [6] Friedrich, I., Weidenhof, V., Njoroge, W., Franz, P. and Wuttig, M., (2000). Structural transformation of $Ge_2Sb_2Te_5$ films studied by electrical resistance measurements. *Journal of applied physics* 87: 4130-4134.
- [7] Kolobov, A. V., Fons, P., Tominaga, J., Frenkel, A. I., Ankudinov, A. I., Yannopoulos, S. N., Andrikopoulos, K. S. and Uruga, p. (2005). Why phase media are fast and stable: A new approach to an old problem, *Japanese Journal of Applied Physics* 44: 3345-3349.
- [8] Kumar J, Ahmad M., Chander R, Thangaraj R, and Sathiaraj T. S. (2008) Phase segregation in Pb: $GeSbTe$ chalcogenide system *The European Physical Journal Applied Physics* 41: 13.
- [9] Lathrop D. and Eckert, H.(1989). Chemical Disorder in Non-Oxide Chalcogenide Glasses. Site Speciation in the System Phosphorus-Selenium by Magic Angle Spinning NMR at Very High Spinning Speeds *Journal of Physical Chemistry* 93: 7895-7902.
- [10] Rao K. J. and Mohan R.(1980) Glass transition in As-Se glasses, *Journal of Physical Chemistry* 84: 1917.
- [11] Shukla, R., Agarwal, P. and Kumar, A. (2010). Crystallization kinetics in glassy $Se_{100-x}In_x$ system using iso-conversional methods. *Chalcogenide letters*. 7: 249-255.
- [12] Suri N, Bindra K, and Thangaraj R. (2006) Electrical conduction and photoconduction in $Se_{80-x}Te_{20}Bi_x$ thin films *Journal of Physics: Condensed Matter* 18: 9129.
- [13] Tanaka K, (1989) Structural phase transitions in chalcogenide glasses. *Physical Review B* 39: 1270.