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CRYSTALLIZATION KINETICS OF $In_{40}Se_{60}$ THIN FILMS FOR PHASE CHANGE RANDOM ACCESS MEMORY (PRAM) APPLICATIONS

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Chalcogenide based semiconductors have attracted much attention recently due to their applications in solid state devices (SSD). Chalcogenide phase change memory is considered as a potential replacement of flash memory due to its high storage density and archival stability. Phase change non-volatile semiconductor memory technology is based on an electrically initiated, reversible rapid amorphous-to-crystalline phase change process in multicomponent chalcogenide alloy materials similar to those used in rewritable optical disks. In order to view the suitability of a material for PRAM applications, it is necessary to investigate the crystallization behaviour of the material concerned. In the present work, a systematic investigation of crystallization kinetics of $In_{40}Se_{60}$ alloy has been made. Thin films of $In_{40}Se_{60}$ 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 LabView 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 energy was determined to be 0.538±0.063eV.

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Keywords: Crystallization, Phase change memory material, Activation energy, Kissinger method

1. Introduction

Phase change memory (PRAM) exploits the large resistance contrast between the amorphous and crystalline states in so-called phase change materials. The amorphous phase tends to have high electrical resistivity, while the crystalline phase exhibits a low resistivity, sometimes 3 or 4 orders of magnitude lower or higher. To SET the cell into its low-resistance state, an electrical pulse is applied to heat a significant portion of the cell above the crystallization temperature of the phase change material. This SET operation tends to dictate the write speed performance of PCM technology, since the required duration of this pulse depends on the crystallization speed of the phase change material. SET pulses shorter than 10ns have been demonstrated (Wang *et al.,* 2008, Choi *et al*., 2009). Because the crystallization process is many orders of magnitude slower at low temperatures (< 120^{o}C), PRAM is a non-volatile memory technology that can offer years of data lifetime. In the RESET operation, a larger electrical current is applied in order to melt the central portion of the cell. If this pulse is cut off abruptly enough, the molten material quenches into the amorphous phase, producing a cell in the high-resistance state (Raoux *et al,* 2009). The RESET operation tends to be fairly current and power hungry, and thus care must be taken to choose an access device capable of delivering high current and power

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without requiring a significantly larger footprint than the PCM element itself. The read operation is performed by measuring the device resistance at low voltage, so that the device state is not perturbed. These operations are summarized in Figure 1.

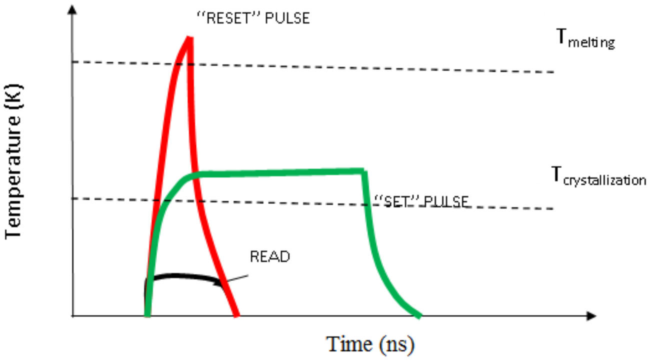

Fig.1: Read, Reset and Set operations of a PRAM. Burr et al.*, 2010*

2. Experimental procedure

2.1 Preparation of $In_{40}Se_{60}$ alloy

The glassy alloy used in the present study was prepared by melt-quenching technique. This alloy belongs to a class called amorphous semiconductors and has wide applications in electronics (Mehta *et al,* 2005, Agarwal *et al,* 1991, Ates *et al*, 2008, Kaur, G. and Komatsu, T. 2000). The exact proportions of high purity elements, in accordance with their atomic percentages, were weighed using an electronic balance with the least count of 10^{-4} grams. In preparing $In_{40}Se_{60}$ alloy, 1.23g of indium and 1.27g of selenium were used. Indium and selenium mixture was placed in a test tube and then heated to over $400^{o}C$ before quenching. The heating was continuous and gentle to prevent the glass from breaking. The temperature was measured using a thermocouple thermometer. The mixture was heated until the two materials melted and mixed evenly and then allowed to cool down to room temperature. The bulky material was separated from Pyrex test tube by breaking the tube. The ingots were ground into fine powder in a porcelain motor. For each of the samples, 0.1 g was measured and placed in a boat for evaporation.

2.2 Preparation of $In_{40}Se_{60}$ thin films

Thermal evaporation technique was employed in the preparation of thin films. This is the oldest and simplest method of depositing thin films (Poortmans and Arkhipov.,2006). Ordinary microscope slides having dimensions 2.54cm x 7.62cm were used as the substrate. The substrates were thoroughly cleaned as thin films readily adhere to a clean insulating surface. It has been reported that if the surface is contaminated with dirt like oil or grease, the adhesion of the film will be minimized and the film may crack or peel (Sharma, J. 2007). The cleaned substrates were placed on the substrate holder directly above the evaporation boat such that the vapours of the material were deposited on them. For each of the samples, 0.1g of the fine powder was placed on the molybdenum boat. Before deposition, the vacuum chamber was evacuated to a vacuum of 4.0 x 10^{-5} mbar. The thin films were prepared using resistive evaporation method in an Edwards vacuum deposition setup model type Auto 306. The Auto 306 uses a turbo molecular pump which is fully automatic in its pumping procedures. The pressure was monitored using a compact gauge capable of recording atmospheric to sub-atmospheric pressure. The sample holder was connected to a rotatilt, so that the substrates were rotated as the material was being deposited to ensure uniform coating. After attaining the right pressure the deposition process commenced by applying current gradually after which the shutter was removed to allow deposition. Thickness as well as rate of deposition was monitored. After deposition, the vacuum chamber was vented and the films removed.

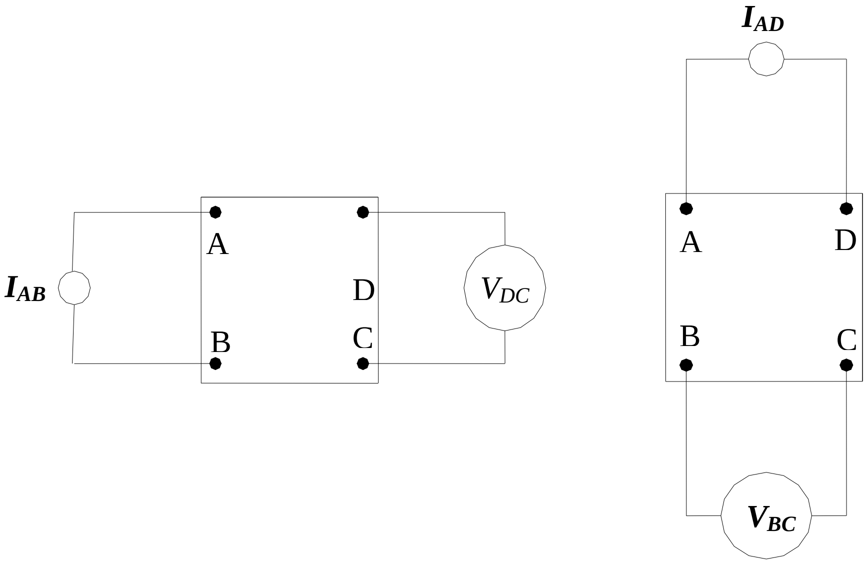

Fig. 2: A schematic diagram of four-point probe resistivity measurement

Electrical resistivity measurements of the 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. The keithly SourceMeter operate by both sourcing and measuring at the same time. Four wire remote sensing was adopted since this minimizes errors due to potential drops in the test leads when sourcing or reading voltages and it ensured that the programmed voltage was delivered to the thin film under test. Figure 2 shows a schematic diagram of four-point probe resistivity measurement. A current of 1.0×10^{-10} A was applied through the contacts A and B and the potential drop across D and C measured. Sheet resistance of the samples was measured upon annealing at constant rate. This was done by placing the samples in a quartz tube of the electric furnace in argon ambient. The temperature was varied in the range between 25°C to 250°C. The measured values of current, voltage drops and film thickness were used to compute sheet resistivity.

3. Result and discussions

The thickness of the films was determined using Alpha-Step IQ surface profiler with a vertical resolution of 0.012Å 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 film had a thickness of 185.0±0.05nm. Figure 3 shows the variation of sheet resistance vs. Temperature, upon annealing at a rate of 5K/min.

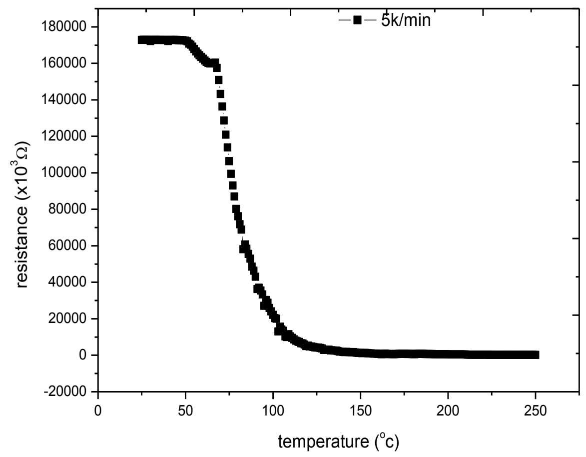

Fig.3: Graph of temperature dependence of sheet resistance of $In_{40}Se_{60}$ films

The as deposited sheet resistance was found to be 1.731 x 10^8 Ω/Sq, after annealing this value reduced to 2.08 x 10^2 Ω/Sq. At the beginning of the measurement, the films had high resistance because they were in the amorphous phase. With increase in temperature, the resistance decreased. A one sharp drop in resistance indicated a phase transition from amorphous to crystalline. Crystallization temperature was obtained by differentiating the curve as shown in figure 4.

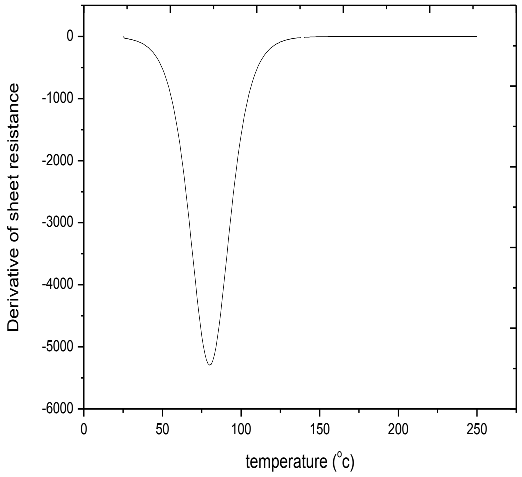

Fig.4: Derivative of sheet resistance vs. temperature for $In_{40}Se_{60}$

The transition temperature for $In_{40}Se_{60}$ was found to be 75.96±0.38°C. Although this value is lower than that obtained by Friedrich *et al.*, 2000 for the widely used GST which is 149°C, it was much higher than room temperature. This is an important advantage for this alloy because it is essential to prevent self-transition of recording materials between the two phases; amorphous and crystalline. Hence one can expect the PRAM made from this alloy to remain stable in its amorphous and crystalline states at room temperature.

Sheet resistivity for as deposited $In_{40}Se_{60}$ was 3.20 x 10^3 Ωcm and decreased to 3.85 x 10^{-3} Ωcm after annealing. This exhibited a high electrical contrast of six orders of magnitude as compared to GST which has a contrast of five orders of magnitude as reported by Friendrich *et al.*, 2000. Large electrical resistance change between two phases gives high signal to noise ratio.

According to Chung *et al*., 2008, an electrical contrast of at least three orders of magnitude is required for a phase change material to be used for memory applications.

3.1 Activation energy of crystallization

$In_{40}Se_{60}$ 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. Figure 5 shows the variation of sheet resistance versus temperature for samples annealed at different heating rates. There is a positive shift in transition temperature as the heating rates increase. The peak temperatures T_p at various heating rates were used to plot the Kissinger plots from where the activation energy of crystallization was determined. The value of the slope was used in the calculation of activation energy according to the following equation

$$\ln(\beta T_P^{-2}) = -\frac{\Delta E}{K_B}\left(\frac{1}{T_P}\right) + constant$$

Where β is the heating rate, T_P is peak crystallization temperature, ΔE is activation energy, K_B is Boltzmann constant. From the above equation, slope = - $\frac{\Delta E}{K_B}$ and therefore the activation energy ΔE= slope x $K_{B.}$

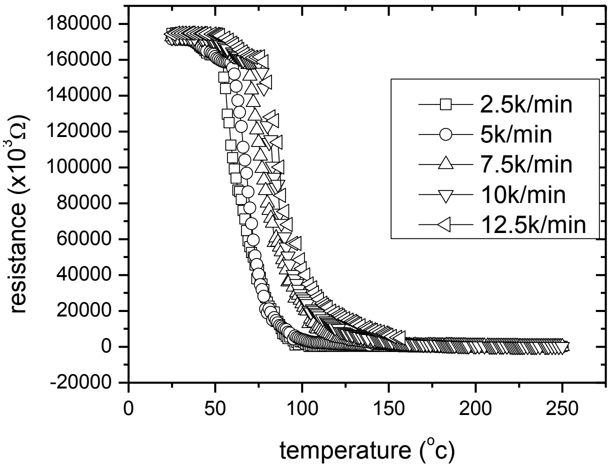

Fig.5: Shift in transition temperature with change in heating rates.

Figure 6 shows Kissinger plot for $In_{40}Se_{60}$ thin film. The activation energy was found to be 0.538 ± 0.063eV which is high compared to the value reported for GST (0.39 eV). The high obtained value of activation energy for $In_{40}Se_{60}$ alloy implies that PRAM cells made from this sample will have higher stability against recrystallization (Njoroge *et al.,* 2001).

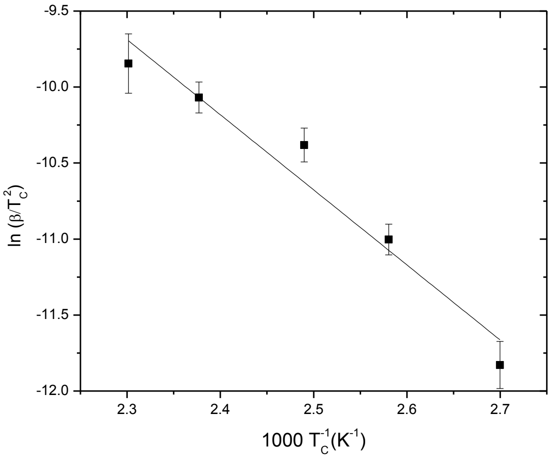

Fig.6: The Kissinger plots for calculation of activation energy for $In_{40}Se_{60}$ *film*

4. Conclusion

Crystallization kinetics of $In_{40}Se_{60}$ thin films has been successfully investigated. The crystallization temperatures were found to be much higher than room temperature and therefore a PRAM cell from this material will be stable at room temperature. High crystallization temperatures prevent self-transition of glassy alloys which is required for the application as stable glass. The film showed an electrical contrast of six orders of magnitude which is an advantage because an electrical contrast of at least three orders of magnitude is required for a phase change memory application. Activation energy of 0.538 ± 0.063eV was determined for $In_{40}Se_{60}$ alloy. This value is high implying high data stability for PCM devices employing $In_{40}Se_{60}$ alloy as the active layer.

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