

PHOTO-CRYSTALLIZATION IN a- $\text{Se}_{1-x}\text{Sb}_x$ THIN FILMS

S. K. Dwivedi^a, V. S. Kushwaha^a, A. Kumar^{a*}

^a*Department of Physics, Kanpur Institute of Technology, Kanpur -208 001, India*

^b*Department of Physics, Harcourt Butler Technological Institute, Kanpur - 208002*

The present paper reports photo-crystallization in amorphous thin films of $\text{Se}_{1-x}\text{Sb}_x$ where x is varied from 0 to 0.04. It is observed that photocrystallization occurs in these films when light is shone for more than 6 hours. The d. c. conductivity of the films increases by 2-3 orders of magnitude on crystallization, which is taken as a characteristic quantity to measure the extent of crystallization. X-ray diffraction and electron microscopy have been used to confirm crystallization. The results indicate that the effect of photo-crystallization decreases as Sb concentration increases.

(Received August 7, 2008; accepted August 20, 2008)

Keywords: Se-Sb; Thin film; Photo-crystallization, XRD, TEM

1. Introduction

Photo-crystallization in amorphous semiconductors was first observed in amorphous selenium by Dresner and Stringfellow [1] and then by de Neufville [2], Clement et.al. [3] and Kim & Turnbull [4]. These authors showed that the photo-crystallization effects result from the generation of electron-hole pairs in the vitreous phase.

Kotkata et. al. [5] have studied the effect of light on crystallization kinetics in amorphous selenium which was doped with sulfur and showed that the exposure of light destroys the Se-Se bonds, reduces the length of Se chains and opposes the crystal growth.

The photo-crystallization in amorphous $\text{Ge}_x\text{Se}_{1-x}$ has been investigated by Matushita et.al. [6] and they have shown that for $x = 0.05$ only, the crystallization effect is enhanced over thermal effects. However, for other compositions the crystallization effect is suppressed.

In the case of amorphous $\text{Se}_{1-x}\text{Te}_x$ films, Okuda et al. [7] have shown that photo-crystallization is suppressed at $x = 0.04$ as compared to pure amorphous Se films, whereas for the composition $x > 0.1$, the photocrystallization was certainly enhanced over the case of pure Se films.

In the above cases, light was shone on the samples at temperatures much higher than room temperature where thermal crystallization can also occur. However, in some binary and ternary Se based glasses, Kumar and his co-workers [8-11] have reported that crystallization of the amorphous films can also occur at room temperature on prolonged exposure of the films to white light. The results are found to depend on the composition of the film.

From the above results, it is apparent that the results of crystallization in presence of light are highly intriguing. In some cases, the effect of shining light is to increase the rate of crystallization [7, 8-11]. However, in some cases, the crystallization rate is decreased in presence of light [5, 6].

Thus, more experimental work is required to understand the crystallization in presence of light. The present paper reports a study of photocrystallization in a- $\text{Se}_{1-x}\text{Sb}_x$ films with a view to see the effect of Sb addition on the photocrystallization in a-Se films.

*Corresponding author: dr_ashok_kumar@yahoo.com

For the above study, white light is shown on vacuum evaporated amorphous thin films of $\text{Se}_{1-x}\text{Sb}_x$ for different exposure times and d. c. conductivity is measured as a function of temperature after each exposure time.

As d. c. conductivity increases by several orders of magnitude on photocrystallization, this quantity is taken as a parameter to monitor the extent of crystallization in the present glassy system. X-ray diffraction and electron microscopy techniques are used to confirm the crystallization on light shining.

2. Experimental

Glassy alloys of a- $\text{Se}_{1-x}\text{Sb}_x$ were prepared by a quenching technique. Materials (99.999% pure) were weighed according to their atomic percentage and were sealed in quartz ampoules (length ~5 cm, internal dia ~8 mm) in a vacuum of 1 mPa. The ampoules were rocked for 10 hours at the temperature (600 °C) to make the melt homogeneous. The melts were quenched in ice water and the glassy nature of the alloys was ascertained by X-ray diffraction.

Thin films of the glassy alloys were prepared by the vacuum evaporation technique, keeping substrates at room temperature and at a base pressure of 1mPa, using Molybdenum boats. The thickness of the amorphous film was about 500 nm.

Well-degassed 7059 Corning glass was used as a substrate. In films pre-deposited on them in a coplanar geometry were used as electrodes. The planer geometry of amorphous films (length ~ 1.3 cm and electrode gap ~0.5 mm) was used for the electrical measurements.

For the measurements of d. c. conductivity, the thin film samples were mounted in a specially designed sample holder where a vacuum $\sim 10^{-2}$ Torr was maintained throughout the measurements using rotary vacuum pump. Current-Voltage (I-V) characteristics were measured and the samples were found to be ohmic up to 30 Volts. In the present case, however, a d. c. voltage of 10 Volts only was applied across the sample and the resulting current was measured by a digital electrometer (Keithley, model 614). The temperature was measured by mounting a copper- constantan thermocouple very near to the sample.

Photocrystallization was achieved by shining white light from a 200 W tungsten lamp (intensity~ 3000 lux) on the amorphous films mounted in the sample holder which had a transparent quartz window to shine light. A vacuum $\sim 10^{-2}$ Torr was maintained during the exposure of the films to white light. D.c. conductivity was measured as a function of temperature after each exposure of different duration. The d. c. conductivity at room temperature returned back to the original value after each cycle of heating. This ensured the absence of thermally induced crystallization during each set of measurement.

3. Results

The temperature dependence of d. c. conductivity (σ) is studied before and after exposing the films of a- $\text{Se}_{1-x}\text{Sb}_x$ to white light (intensity 3000 lux) for different exposure times. The results for various glassy alloys are shown in Fig 1-3. It is clear from the figures that $\ln \sigma$ vs $1000/T$ curves are straight lines before and after light exposure. This indicates that the conductivity is thermally activated with a single activation energy (ΔE) in the present temperature range of measurements.

No appreciable effect of exposure on σ and ΔE occurred after an exposure of films to white light up to 6 hours. However, when the films are exposed to higher exposure times, σ increases by many orders of magnitude with a decrease in ΔE (see Figs. 1-3)

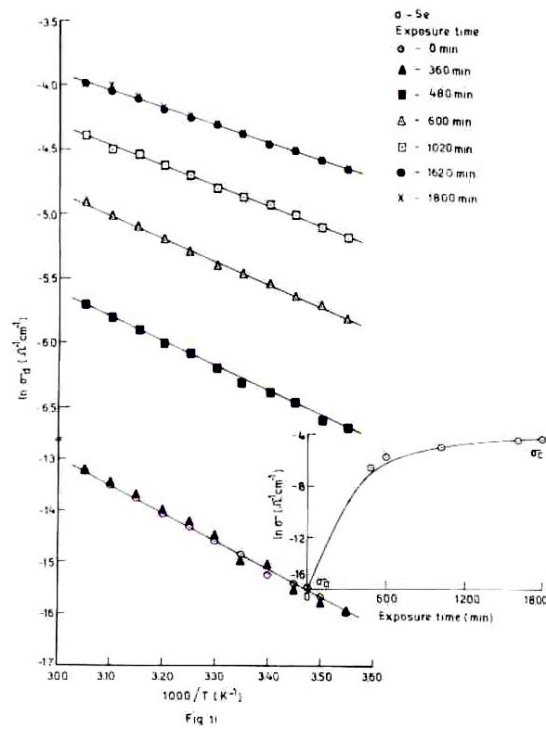


Fig. 1. Temperature dependence of d.c. conductivity in $a\text{-Se}$ films before and after exposure to white light for various exposure times. The inset shows d.c. conductivity as a function of exposure time.

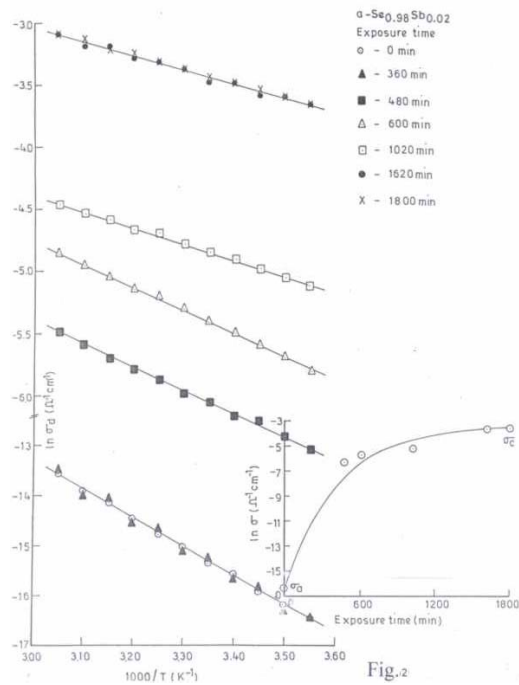


Fig. 2. Temperature dependence of d.c. conductivity in $a\text{-Se}_{0.98}\text{Sb}_{0.02}$ films before and after exposure to white light for various exposure times. The inset shows d.c. conductivity as a function of exposure time.

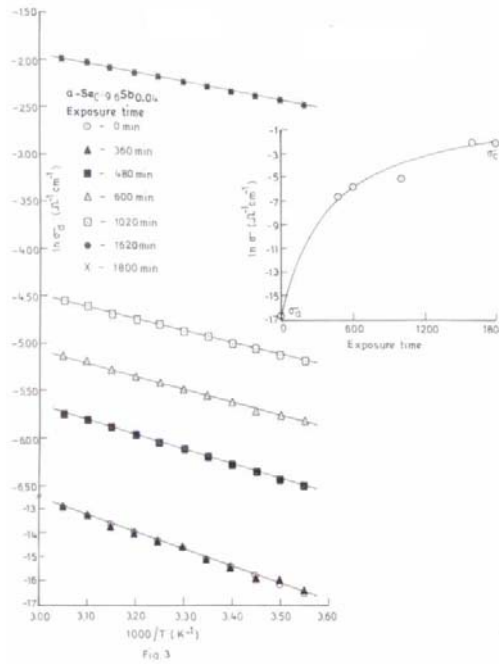


Fig. 3. Temperature dependence of d.c. conductivity in $a\text{-Se}_{0.96}\text{Sb}_{0.04}$ films before and after exposure to white light for various exposure times. The inset shows d. c. conductivity as a function of exposure time.

The insets of Figs. 1-3 plot the variation of conductivity at room temperature as a function of total exposure time. It is evident from the insets that σ increases with exposure time and then saturates, i.e., no further change in σ occurs after certain exposure time. This indicates complete crystallization and the conductivity at this stage (crystalline state) is designated by σ_c and the conductivity before exposure to light (amorphous state) is designated by σ_a . For any other exposure time, between 0 and maximum value, the conductivity is due to partially crystalline state and the measured conductivity (σ) may be written as [12]:

$$\ln \sigma = \alpha \ln \sigma_c + (1 - \alpha) \ln \sigma_a \quad (1)$$

where α represents the volume fraction of the crystalline phase and also called as the extent of crystallization.

The above relation is applicable when the conductivity increases by several orders of magnitude. Since, d. c. conductivity increases by several orders of magnitude on crystallization in chalcogenide glasses, this equation has widely used to calculate the crystallization kinetic parameters in chalcogenide glasses [13-16]. The crystallization kinetic parameters calculated using this equation match reasonably well with the values of the same parameters calculated from other techniques [16].

Using the values of σ_a , σ_c and σ measured at various exposure times, the values of α is calculated after each exposure in all the three glassy alloys studied in $\text{Se}_{1-x}\text{Sb}_x$ system.

The values of α thus calculated, are given in Table I and plotted as a function of Sb concentration in Fig. 4 for $\text{Se}_{1-x}\text{Sb}_x$ glassy system. It is clear from this figure that α , at a particular exposure time, decreases with Sb concentration which indicates that photocrystallization is suppressed on Sb addition to Se glass.

Table 1. Composition dependence of the extent of crystallization in a $Se_{1-x}Sb_x$.

| Sample No. | Sample | (α) light action for 8 hours | (α) light action for 10 hours | (α) light action for 27 hours |
|------------|-------------------------|-------------------------------------|--------------------------------------|--------------------------------------|
| 1 | a-Se | 0.82 | 0.90 | 0.96 |
| 2 | a- $Se_{0.98}Sb_{0.02}$ | 0.78 | 0.83 | 0.89 |
| 3 | a- $Se_{0.96}Sb_{0.04}$ | 0.74 | 0.81 | 0.86 |

Though proper care was taken to avoid thermal effects of light, there is still a possibility of an increase in temperature due to thermal heating of the films on shining light. However, it was confirmed that films kept for 2 hours in dark at a temperature (40 K higher than room temperature) did not produce any effect of crystallization. Therefore, the small change in temperature, due to light exposure, may not be responsible for crystallization in the present case. The increase in d.c conductivity on exposure to light in the present case may, therefore, be due to photocrystallization and not due to thermal heating on account of light exposure.

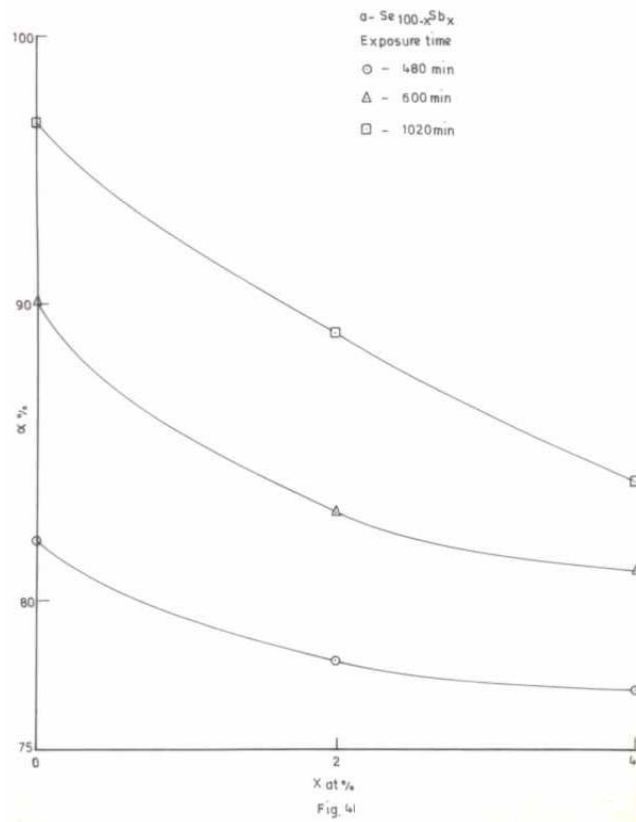


Fig. 4. The extent of crystallization (α) as a function of Sb concentration in a- $Se_{1-x}Sb_x$.

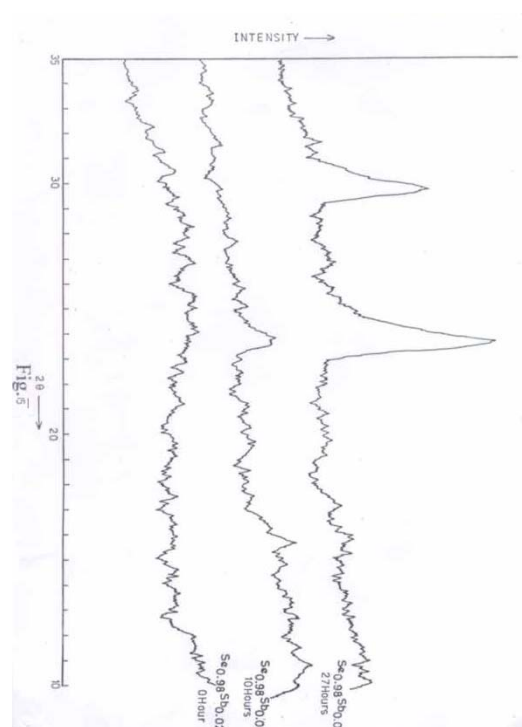


Fig. 5. X-ray diffractogram for $a\text{-Se}_{0.98}\text{Sb}_{0.02}$ films with and without light exposure.

To ascertain crystallization of the amorphous film, X-ray diffraction studies were performed on the films before and after light exposure in all these glasses studied here. It was found that no sharp diffraction peak occurs in the unexposed films except a broad halo in the X-ray diffraction pattern, confirming the amorphous nature of the film (see Fig. 5 in case of $\text{Se}_{0.98}\text{Sb}_{0.20}$). However, sharp diffraction peaks are observed in case of light exposed films. Results for two different exposure times in case of amorphous $\text{Se}_{0.98}\text{Sb}_{0.20}$ are shown in Fig.5. The peaks become sharper as the exposure time is increased. Similar results were obtained in other glasses also. The position of the peaks in $a\text{-Se}_{0.98}\text{Sb}_{0.20}$ and $a\text{-Se}_{0.96}\text{Sb}_{0.40}$ indicates the presence of crystallization Sb_2Se_3 compound on photo-crystallization.

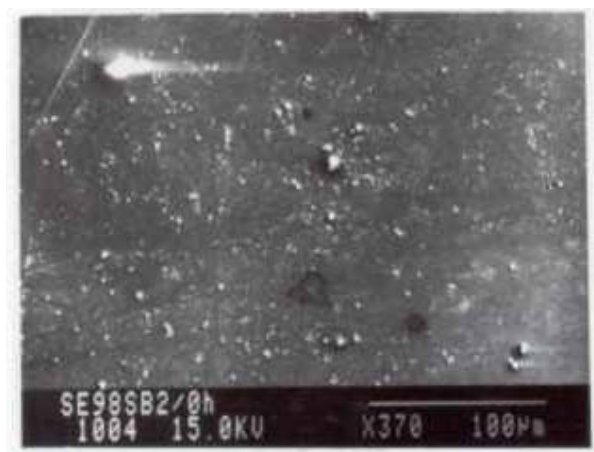


Fig. 6. Scanning electron micrograph for $a\text{-Se}_{0.98}\text{Sb}_{0.02}$ films without light exposure.

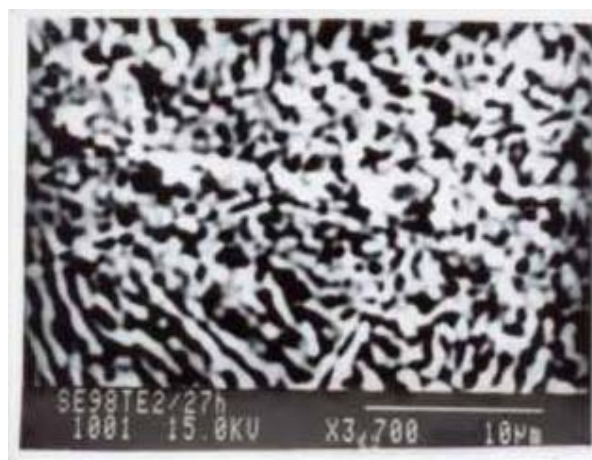


Fig. 7. Scanning electron micrograph for a- $\text{Se}_{0.98}\text{Sb}_{0.02}$ films on light exposure of 27 hours.

Figs. 6 and 7 show the scanning electron micrographs for light unexposed and exposed (for 27 hours) a- $\text{Se}_{0.98}\text{Sb}_{0.20}$ films, respectively. Crystallization of the films is evident from the micrographs in light exposed films. Similar results were also observed in case of other glasses studied here.

4. Discussion

The generally accepted structural model of amorphous Se [17] includes two molecular species; meandering chains, which contain helical chains of trigonal Se; and Se_8 ring molecules of monoclinic Se or linear polymeric chains of Se_n . Due to the large size than Se, Sb atoms are forced by the steric hindrance of end a-Se chain [18]. Around 1at % Sb, all Se chains ends have to be saturated. For compositions greater than 1 at % Sb start to be incorporated in Se-chains [18]. The incorporation of Sb into Se chains at concentrations above 1 at %Sb is a process, which partially destroys long Se- chain [18].

When Sb is incorporated in the binary $\text{Se}_{1-x}\text{Sb}_x$ system, the Sb atoms may interact with Se in the polymeric chains and form a cross-linked structure, which stabilizes the structure of $\text{Se}_{1-x}\text{Sb}_x$ system. This is probably the reason why photocrystallization is suppressed on increasing Sb concentration in $\text{Se}_{1-x}\text{Sb}_x$ glassy system.

Predeep et. al. [19] has performed Differential Scanning Calorimetric (DSC) studies in glassy $\text{Se}_{100-x}\text{Se}_x$ system where x is varied from 0 to 4 as in the present case. They have observed an increase in glass transition temperature (T_g). The crystallization temperature (T_c) is also measured for each glassy alloy. They have found that the difference between crystallization and glass transition temperatures (T_c-T_g) increases with Sb concentration in this glassy system. The increase in T_g along with the increase in T_c-T_g , is interpreted in terms of the increased thermal stability of the alloys containing Sb as compared to pure Se glass.

In the present case also, composition dependent photo-crystallization indicates more stability of the films containing Sb as α decreases on increasing Sb concentration in glassy $\text{Se}_{1-x}\text{Sb}_x$ system. This is consistent with the DSC studies mentioned above in the same glassy system.

5. Conclusions

Photo-crystallization in vacuum evaporated thin films of amorphous $\text{Se}_{1-x}\text{Sb}_x$ is studied by d. c. conductivity measurements before and after crystallization. Photo-crystallization is achieved

by shining with white light at room temperature in vacuum. Photo-crystallization is confirmed by X-ray diffraction and electron microscopy. Results indicate the formation of Sb_2Se_3 crystalline phase during photo-crystallization.

To monitor the extent of crystallization with exposure time, d. c. conductivity is taken as characteristic parameter to follow crystallization. We find that the extent of crystallization, at a particular exposure time, decreases with Sb concentration (x), which indicates that photo-crystallization, is suppressed on increasing Sb concentration in a- $\text{Se}_{1-x}\text{Sb}_x$ system. This is explained qualitatively in terms of the formation of relatively stabilized structure as compared to pure a-Se due to cross linking of Sb atoms in a-Se polymeric chains. This conclusion is in agreement with the conclusion drawn by Predeep et.al [17] from their DSC studies.

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