Light Induced Defects in $Se_{90}Sb_8Ag_2$ Thin Film

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ABSTRACT

The present work focuses on the determination of light induced defects by using thermally stimulated currents (TSC) technique in glassy alloy of $Se_{90}Sb_8Ag_2$, prepared by conventional melt quenching technique. Amorphous nature of sample was verified by XRD. Thin films of the present sample were prepared by vacuum thermal evaporation technique. For this, amorphous thin films are exposed to white light of intensity 15000 Lux at room temperature in the presence of vacuum ($\sim 10^{-2}$ Torr). TSC have been measured, before and after exposure of light in the temperature range 308 K to 378 K. From these measurements, the density of traps (N_t) has been calculated in exposed and unexposed samples. Results indicate that the density of traps increases with the increase of exposure time. The defect density increase with exposure time indicates that more and more defects are created as exposure time increases. Due to light soaking, number of dangling bonds may increase due to breaking of covalent bonds which increases the density of defect states.

Key words: Thin films, light induced defects, thermally stimulated currents, trap density.
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INTRODUCTION

A good amount of work has been reported in chalcogenide materials, related to their light induced phenomenon, during the past few years [1-3]. Chalcogenide materials reveal extensive variety of light induced changes in structural and electronic properties during band gap illumination, as optical imaging, photo-induced volume change, photodarkening, photo-induced change in the phase state (photo-crystallization and photo-amorphization), micro optical fabrication, etc [4-7]. The mechanism of the photo-structural changes on exposure of light in chalcogenides is due to the formation of several types of defects in the glassy structures is induces due to excitation of electrons from spatially localized states in the band tail. Structural defects such as transient bonds, ESR active sites and valance alternation pairs (VAP) may be play a key role in the photo induced modifications [8, 9]. The investigation of light induced defects in chalcogenide glasses is a special area of interest for researchers, in the field of amorphous materials and is also important for potential applications in optoelectronics [10]. It is well known that the internal or surface structure is changed by prolonged exposure of band gap light in amorphous chalcogenides and the optical absorption edge shifts towards lower energy side or higher energy side [11] depending upon the material. Drenser and Stringfellow first observed another photo induced phenomena in a-Se films in which films get crystallized and is called photo crystallization [12]. The phenomena of photoinduced defects creation in chalcogenide materials have been studied using ac transport [13-14], xerography [15-16], light induced electron spin resonance [17-18] and also photo current measurements [19].

The present paper is an attempt to measure the density of defects, created by light exposure, using thermally stimulated currents (TSC) measurements. TSC is a well known technique for the estimation of density of traps in semiconducting materials [20]. In this technique, traps are filled by shining light for short time at low temperature and when electric field is applied, the librated carriers produce an extra current and finally when they recombine with the carriers of the opposite type, the extra current becomes zero. This extra current when measured as a function of temperature during heating, is called TSC curve. The area of this curve is a measure of density of traps. Using above technique, we have calculated the density of traps (N_t) before and after light exposure for different exposure times.

EXPERIMENTAL PROCEDURE

The glassy alloy of $Se_{90}Sb_8Ag_2$ is prepared by quenching technique. The exact proportions of high purity (99.999%) Se, Sb and Ag elements in accordance their atomic percentages, are sealed in quartz ampoules (length~5 cm and internal diameter~ 8mm) with a vacuum ~ 10^{-5} Torr. The ampoule containing material is held at 900 ^{o}C for a period of 10 hrs and the ampoules are constantly rocked to make the melt homogeneous. Then the melt is cooled rapidly in ice cooled water. The quenched sample is then taken out by breaking these ampoules. The glassy nature of the alloy is confirmed by X-ray diffraction pattern as shown in Fig. 1. No sharp diffraction peaks in diffraction pattern indicates the amorphous nature of the prepared material. Amorphous thin films of $Se_{90}Sb_8Ag_2$ are prepared by vacuum evaporation technique, using indium electrodes for the electrical contacts. The thickness of the film was ~500 nm. The coplanar structure (length~12 mm and electrode separation~0.5mm) was used for the present measurements.
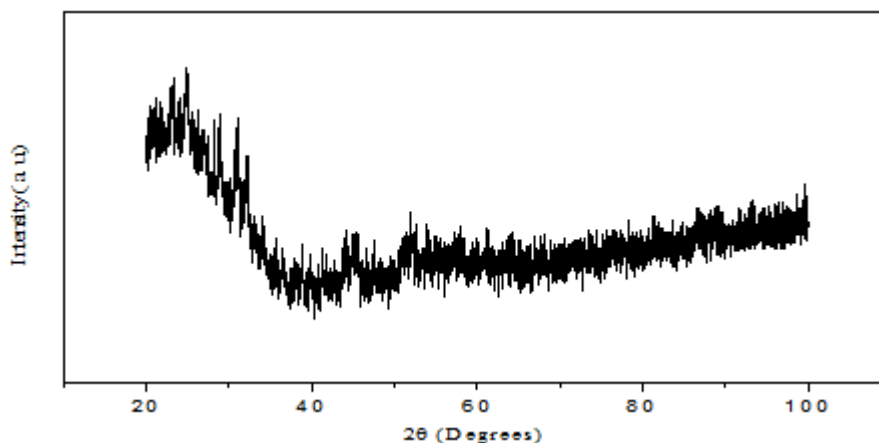

Fig. 1 X-ray diffraction pattern of a-$Se_{90}Sb_8Ag_2$ glassy alloy

For TSC measurements, thin films are mounted in a specially designed sample holder containing a transparent window for shining light and a vacuum of 10^{-2} Torr is maintained throughout the measurements. The temperature of the respective film was measured by a calibrated a copper constantan thermocouple mounted very near to the film. The films were annealed first at approximately 400 K for one hour in a vacuum of 10^{-2} Torr before the measurements. The films were exposed to white light of intensity 15000 Lux by mounting them in the sample holder for different exposure times and measurements were repeated after each exposure.

RESULTS AND DISCUSSION

For the measurements of TSC, temperature dependence of current has been measured in two states. In state I, the sample is heated at a constant heating rate from room temperature 308 K to 378 K without any light exposure and current is measured during heating. However, in the state II, light is incident on the sample for two minutes at room temperature through the transparent window of the sample holder. The decay of photoconductivity was allowed for 10 minutes after switching off the light. The sample was again heated from 308 K to 378 K at the same heating rate. The difference of conductivity at a particular temperature in these two states is calculated and plotted as a function of temperature to obtain TSC curve.

The experimental TSC curves for a- $Se_{90}Sb_8Ag_2$ thin films at different heating rates are shown in Fig. 2. From this graph it is clear that the TSC peaks shifts to the higher temperatures as the heating rates increases. Shift of this peak with heating rate confirms the observation of TSC [21-22] and as observed by various workers [23-26] in chalcogenide glasses. To study the effect of prolonged exposure to light, TSC measurements have been made before and after exposing the samples for different exposure times. This was done to see the changes in the density of defect states due to light exposure. The trap density has been calculated by calculating the area of TSC curve using the following relation [20]:

$$N_t = \frac{Q}{ALeG} \ (cm^{-3}) \tag{1}$$

Here Q represents the quantity of the charge released during TSC experiment. This can be calculated from the area under TSC peak. L and A are the thickness and area of the sample respectively, e is the electronic charge and G represents the photoconductivity gain and is estimated using the expression [27]:

$$G = \frac{\tau}{t_{tr}} \tag{2}$$

where τ represents the carrier life time and t_{tr} represents the carrier transit time between electrodes.
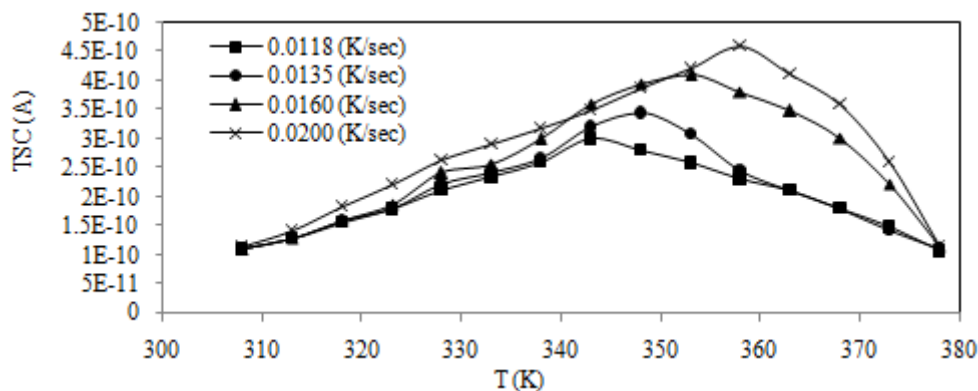
Fig. 2 Experimental TSC curve of a-Se$_{90}$Sb$_8$Ag$_2$ thin films at various heating rates

TSC curves in case of a- Se$_{90}$Sb$_8$Ag$_2$ thin films for different exposure times (0, 2, 4, 6 hours) are given in Fig. 3. Trap density has also been evaluated by using the relation (1) and results are given in Table - 1. Fig. 4 shows the concentration of trap density as a function of exposure time. From this figure it is clear that trap density increases with the increase of exposure time of light. On prolonged exposure of band gap light, Staebler and Wronski observed that hydrogenated amorphous silicon degrades upon light soaking and goes in to a metastable state [28] which was explained due to the creation of light induced defects in this material. In chalcogenide glasses also, light induced defects were observed by Biegelsen and Street [18]. These defects are also known as light induced metastable – defects [28-32].
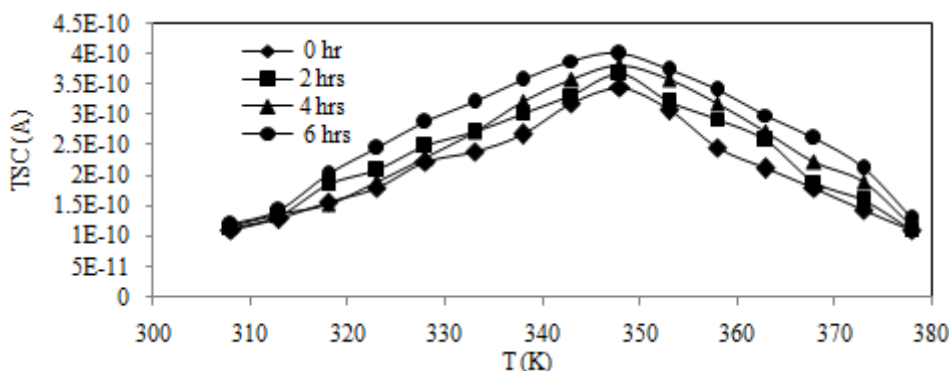

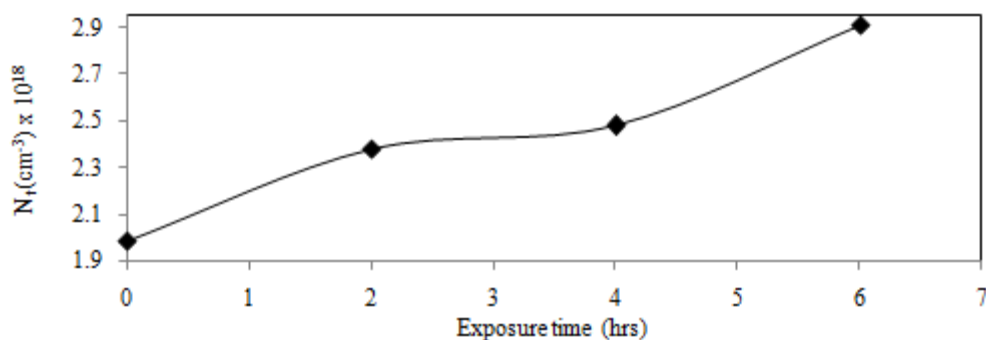**Fig. 3 TSC curve of a-Se$_{90}$Sb$_8$Ag$_2$ thin films at various exposure times (0, 2, 4, 6 hrs)**

Fig. 4 Variation of trap density as a function of exposure time for a-Se$_{90}$Sb$_8$Ag$_2$ thin films

Table -1 Values of Trap Density for Various Exposure Times at Constant Heating Rate 0.0135 (K/sec) in a-Se$_{90}$Sb$_8$Ag$_2$ Thin Films

Exposure time (in hours)	Trapping density (N_t) (in cm^{-3}) x 10^{18}
0	1.99
2	2.38
4	2.48
6	2.91

Shimakawa et al [33] have observed time dependent decreasing photocurrent during illumination in a-Si:H and As_2S_3 chalcogenide films. They have explained their results in terms of photo induced metastable defects created during illumination. They have also reported that common kinetics dominate for the creation of such defects in both the cases. A model has also been proposed for the common features between both the materials. Shimakawa et al [34] have also reported the effect of prolonged exposure of band gap light on chalcogenide thin films of As_2S_3, As_2S_7, AsS, As_2Se_3 , GeS_2, $GeSe_2$ and GeSe and found that photoconductivity decreases on light exposure. They also explained this decrease in terms of photoinduced metastable defects as these defects act as additional trapping and / or recombination centers.

Biegelsen and Street [18] have studied light induced ESR signal, extrinsic absorption below the band gap energy and non radiative recombination in chalcogenide glasses. They have explained these results in terms of the creation of large density of metastable defects in these glasses. A model has also been suggested for optically induced defects pairs. Freitas et al [35] have argued that thermal energy as well as photon energy is incorporated in photoinduced defect creation. Anisimova et al [36] have studied the a.c. conductivity of chalcogenide glasses and relaxation maximum of dielectric losses was observed. They explained their results in terms of defect structure model.

The present study could make a quantitative evaluation of the increase in defect density on light exposure. The defect density increase with exposure time indicates that more and more defects are created as exposure time increases. Due to light soaking, number of dangling bonds may increase due to breaking of covalent bonds which increases the density of defect states as observed in the present study. Vanderbilt et al [37] have also argued that light induced defects may be considered due to breaking of covalent bonds on light soaking when amorphous films are exposed to band gap light for longer times (a few hours).

CONCLUSION

Amorphous thin films of $Se_{90}Sb_8Ag_2$ are prepared by vacuum thermal evaporation technique. These amorphous thin films are exposed to white light of intensity 15000 Lux at room temperature in a vacuum ~ 10^{-2} Torr. Effect of prolonged exposure to light on the defect density is studied in this material using TSC technique. The results indicate that the density of defect states increases with the increase of exposure times. Due to light soaking, number of dangling bonds may increase due to breaking of covalent bonds which increases the density of defect states as observed in the present study.

REFERENCES

[1] M L Trunov, S N Dub and R S Shmegera, Light-induced structural relaxation and the photoplastic effect in chalcogenide glasses, *Solid State Phenomena,* **2006**, 115, 245-250.

[2] R Chauhan, A K Srivastava, A Tripathi and K K Srivastava, Photo-induced optical changes in $Ge_xAs_{40}Se_{60-x}$ thin films, *Progr. Nat. Sci.*, **2010**, 20, 54–60.

[3] Michal Piasecki, *Transactions of the Indian Ceramic Society,* **2012**, *71*, 211-214.

[4] M Frumar, A P Firth and A E Owen, Optically induced crystal-to-amorphous-state transition in As_2S_3, *J. Non Cryst. Sol.*, **1995**, 192-193, 447-450.

[5] K Tanaka, Nanostructured chalcogenide glasses, *J. Non Cryst. Sol.*, **2003,** 326, 21-28.

[6] V Lyubin, M Klebanov, B Sfez and B Ashkinadze, Photoluminescence and photodarkening effect in erbium-doped chalcogenide glassy films, *Mat. Lett.*, **2004**, 58, 1706-1708.

[7] M A Alvi, Shamshad A Khan and A A Al- Ghamdi, Photo-induced effects on electrical properties of $Ga_{15}Se_{81}Ag_4$ chalcogenide thin films, *Mat. Lett.*, **2012**, 66, 273-275.

[8] A V Kolobov, M Kondo, H Oyanagi, A Matsuda and K Tanaka, Negative correlation energy and valence alternation in amorphous selenium: An in situ optically induced ESR study, *Phys. Rev. B,* **1998**, 58, 12004-12010.

[9] P Lucas, A Doraiswamy and E A King, Photoinduced structural relaxation in chalcogenide glasses, *J. Non-Cryst. Solids,* **2003**, 332, 35-42.

[10] A V Kolobov, H Oyanagi, Ka Tanaka and K Tanaka, Photostructural changes in amorphous selenium: an in situ EXAFS study at low temperature, *J. Non-Cryst. Sol.,* **1996**, 198, 709-713.

[11] J P de Neufville, S C Moss and S R Ovshinsky, Photostructural transformations in amorphous As_2Se_3 and As_2S_3 films, *J. Non Cryst. Sol.*, **1974**, 13, 191-223.

[12] J Dresner and G B Stringfellow, Electronic processes in the photo-crystallization of vitreous selenium, J. Phy. Chem. Sol., **1968**, 29, 303-304.

[13] K Shimakawa, K Hattorri and S R Elliott, Photoinduced changes of ac transport in amorphous As_2S, *Phy. Rev. B,* **1987**, 36, 7741-7743.

[14] K Shimakawa and S R Elliott, Reversible photoinduced change of ac conduction in amorphous As_2S_3 films, *Phy. Rev. B,* **1988**, 38, 12479-12482.

[15] M Abkowitz, G M T Foley, J M Maerkovics and A C Palumbo, Optical Effects in Amorphous Semiconductors, AIP Conf. Proc., No. 120, AIP, New York, **1984,** p. 117.

[16] M Abkowitz and R C Enck, Photoenhanced metastable deep trapping in amorphous chalcogenides near room temperature, *Phy. Rev. B*, 1983, 27, 7402-411.

[17] J Hautala, W D Ohlsen and P C Taylor, Optically induced electron-spin resonance in As_xS_{1-x}, *Phy. Rev.* B, **1988**, 38, 11048-11060.

[18] D K Biegelsen and R A Street, Photoinduced defects in chalcogenide glasses, *Phys. Rev. Lett.*, **1980**, 44, 803-806.

[19] K Shimakawa, S Inami and S R Elliot, Reversible photoinduced change of photoconductivity in amorphous chalcogenide films, *Phys. Rev. B,* **1990**, 42, 11857-11861.

[20] C Manfredotti, R Murri, A Quirini and L Vasanelli, Photoelectronic properties of n-GaSe, *Phys. Stat. Sol.,* **1976**, 38, 685-693.

[21] J G Simmons and G W Taylor, Nonequilibrium Steady-State statistics and associated effects for insulators and semiconductors containing an arbitrary distribution of traps, *Phys. Rev. B,* **1971**, 4, 502-511.

[22] J G Simmons, G W Taylor and M C Tam, Thermally stimulated currents in semiconductors and insulators having arbitrary trap distributions, *Phys. Rev. B,* **1973**, 7, 3714-3719.

[23] D Kumar and S Kumar, Thermally stimulated currents in amorphous $Se_{60}Te_{20}Ge_{20}$, *J. Opt. Elect. Adv. Mat.*, **2004**, 6, 413-420.

[24] V S Kushwaha, D Kumar and A Kumar, Localized states in $a-Se_{98}Sb_2$ determined by thermally stimulated current measurements, *J. Opt. Adv. Mat.*, **2006**, 8, 1356-1358.

[25] S Yadav, R K Pal, S K Sharma and A Kumar, Determination of trap depth and trap density in $Se_{70}Te_{30-x}Zn_x$ thin films using thermally stimulated current measurements, *Physica B*, **2009**, 404, 2225-2228.

[26] S Yadav, D Kumar, R K Pal, S K Sharma and A Kumar, TSC measurements in $a-Ge_{22}Se_{78-x}Bi_x$ thin films, *Physica B,* **2010**, 405, 4982-4985.

[27] R H Bube, Photoelectronic properties of semiconductors, vol. 20, Cambridge: Cambridge Press, **1992**.

[28] D L Staebler and C R Wronski, Reversible conductivity changes in discharge-produced amorphous Si, *Appl. Phys. Lett.,* **1977**, 31, 292-294.

[29] D Redfield and R H Bube, Photoinduced Defects in Semiconductors, (Cambridge Uni. Press, Cambridge) **1996**.

[30] K Tanaka, Photoexpansion in As_2S_3 glass, *Phys. Rev B*, **1998**, 57, 5163-5167.

[31] K Morigaki, Physics of Amorphous Semiconductors (World Scientific, London), **1999**.

[32] J Singh and K Shimakawa, Advances in Amorphous Semiconductors (Taylor and Francis, London), **2003**.

[33] K Shimakawa, A Kondo, K Hayashi, S A Kahori, T Kato and S R Elliot, Photoinduced metastable defects in amorphous semiconductors: communality between hydrogenated amorphous silicon and chalcogenides, *J. Non-cryst. Sol.*, **1993**, 164, 387-390.

[34] K Shimakawa, S Inami, T Kato and S R Elliot, Origin of photoinduced metastable defects in amorphous chalcogenides, *Phys. Rev. B,* **1992**, 46, 10062-10069.

[35] R J Freitas, K Shimakawa and T Wagner, The dynamics of photoinduced defect creation in amorphous chalcogenides: The origin of the stretched exponential function, *J. Appl. Phys.,* **2014**, 115, 013704.

[36] N I Anisimova, G A Bordovsky, V A Bordovsky and R A Castro, Defect influence on charge transport in chalcogenide glasses, *Rad. Eff. Def. Sol.,* **2001**, 156, 359-363.

[37] D Vanderbilt and J D Joannopoulos, Theory of defect states in glassy As_2Se_3, *Phys. Rev. B,* **1981**, 23, 2596-2606.