Journal of Ovonic Research Vol. 5, No. 4, August 2009, p. 95 - 105

SWITCHING PHENOMENON IN Cd- Se- S THIN FILMS OF AMORPHOUS CHALCOGENIDE GLASS

S.El-Sayed[*], A. A. Abou Shama[a], N. H. Mousa, K. A. Sharaf,
A. A. Abd El-Ghany, H.M.Elwaraky
Physics Department, Faculty of Science for Girls, Al-Azhar University, Nasr City, Cairo, Egypt
[a]*Physics Department, Faculty of Science, Ain Shams University, 11566 Abbassia, Cairo, Egypt*

Current voltage characteristics were measured for Cd_3Se_{97} and $Cd_3Se_{76}S_{21}$ thin film samples as a function of temperature and thickness. Static I-V curves of the investigated samples are typical for a memory switch. The mean value of the threshold voltage $\overline{V_{th}}$ increases with film thickness (in the range ≈ (200 – 700nm)) and decreases with increasing temperature (in the range (303 – 365k)) and increases with the addition of sulfur S . The obtained mean value ≈ 0.48 of the ratio $\varepsilon/\Delta E_\sigma$ (where ε is the threshold voltage activation energy & ΔE_σ, the conduction activation energy) for the investigated compositions agree with the value of 0.5 obtained theoretically on the basis of an electrothermal model. Moreover, the obtained value of $\Delta T_{breakdown}$ for most of the investigated compositions are in the same order with those obtained before. Therefore the switching phenomenon in the investigated compositions can be explained according to the electrothermal model.

(Received August 6, 2009; Accepted August 28, 2009)

Keywords: Thin films; I-V characteristic; temperature dependence; Chalcogenide, Cd_3Se_{97}, $Cd_3Se_{76}S_{21}$.

1. Introduction

Chalcogenide glasses have recently attracted the attention of solid-state physicists, chemists and electronic engineers on account of their potential application in various solid state devices. The effect of impurities on the transport and structural properties has been an important issue since the discovery of these glasses [1]. Many studies have been devoted to the switching phenomena in various types of discovered materials, particularly in amorphous Chalcogenide glass [2-7].

Electronic switching is a rapid and reversible transition between a highly resistive OFF state and a conductive ON state, driven by an external electric field and characterized by a threshold voltage . Primarily, there are two types of electrical switching observed in Chalcogenide glasses, namely, threshold and memory types [8]. In threshold type, the ON state persists only while a current flows down to a certain holding voltage, whereas in memory type, the ON state is permanent until a suitable reset current pulse is applied across the sample [9]. Different mechanisms have been proposed to explain the phenomenon of electrical switching in

---

[*] Corresponding author: sozannasser3@yahoo.com

chalcogenide glasses. These include electronic [10], thermal [11] and electrothermal [12, 13] mechanisms.

In the present work the switching properties of thin films of amorphous Chalcogenide glasses of Cd_3Se_{97} and $Cd_3Se_{76}S_{21}$ were investigated for various sample thicknesses and at different temperatures.

2. Experimental

Cd_3 Se_{97} and Cd_3 Se_{76} S_{21} compositions were synthesized as follows: the elementary constituents of each composition of purity 99.999% were weighed in accordance with their atomic percentage and loaded in silica tube, which was then sealed under vacuum (10^{-5} torr). The content of each tube was heated gradually in an oscillatory furnace to 119°C (m.p. of S) and kept constant for 2h, then it was raised to 220°C (m.p. of Se) and kept constant for 2h, also it was raised to 320°C (m.p. of Cd) and kept constant for 2h and finally it was raised to 700°C and kept constant for 6h. The oscillation of the tube was necessary to ensure homogenization of the compositions obtained. The melt was quenched in ice. Thin film sample from the various compositions by thermal evaporation under vacuum (10^{-6} torr using coating unit) for switching measurements were prepared on a high polished pyrographite substrates for switching measurements. The film thickness was determined[*] by the Tolansky interference method [14].

X-ray analysis was used to investigate the structure of the obtained material in film form whose chemical composition was checked by energy dispersive analysis of X-ray (EDAX)[**].

Measurements of the current-voltage characteristics were carried out in a measuring cell fitted with two electrodes [5]. The lower one was made of copper in contact with the pyrographite substrate with dimensions ($1.5\times0.8\times0.1$ cm^3). The upper electrode was a movable platinum wire a thin circular and its diameter ≈ 200 μm. Measurements were carried out using highly stabilized power supply (0-400 Volt), a digital electrometer (Keithley type E617A) was used for the potential drop measurements and sensitive multimeter was used for the current measurements.

3. Results and discussion

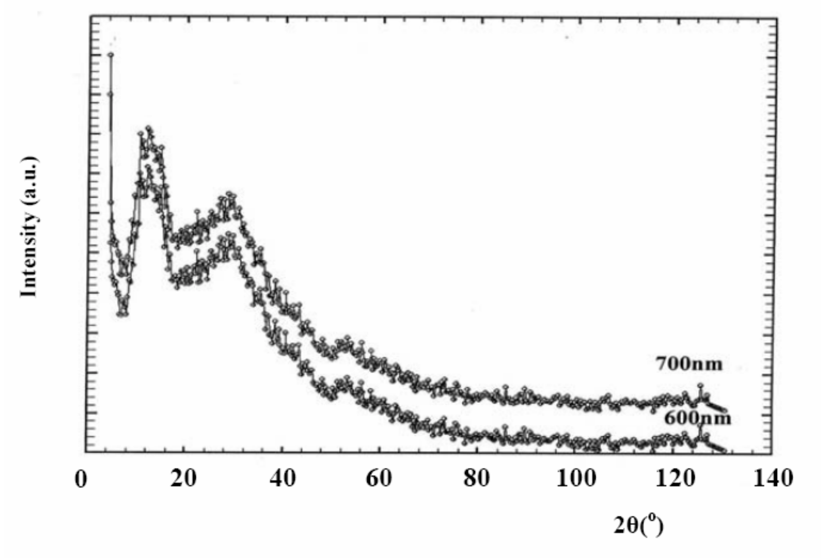
3.1 Structural identification

Fig. (1a, b) shows the X-ray diffraction patterns for the films of the compositions Cd_3Se_{97} and $Cd_3Se_{76}S_{21}$ for thickness 600,700 nm as representative example. Detailed examinations of the X-ray patterns indicate that all the films are amorphous with two main diffraction humps located at the same positions. This finding means that the basic structural units are similar in two samples.

---

[*] At the National Institute for standards (NIs), El Haram, El Giza, Cairo, Egypt

[**] At National Center for Radiation Research and Technology, Cairo, Egypt



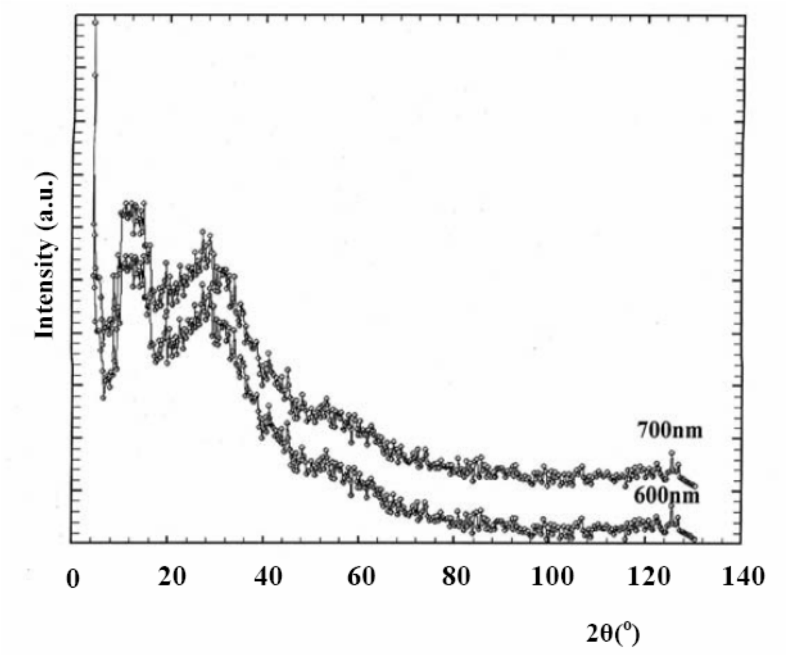
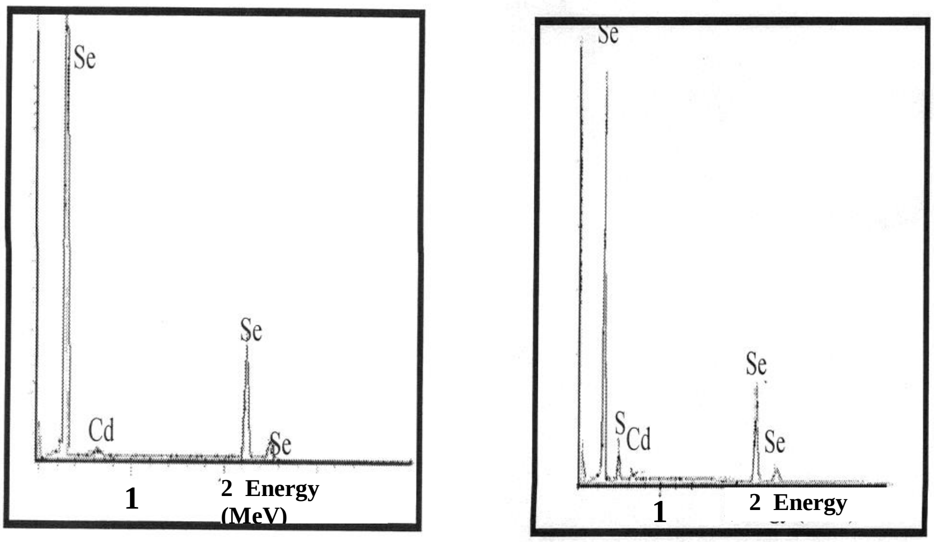


Fig. (1a,b): Total scattered intensity versus (2θ)of (a) Cd_3Se_{97} *and (b)*$Cd_3Se_{76}S_{21}$ *thin films.*

The composition of the investigated films was checked using energy dispersive X-ray analysis (EDAX). The obtained percentages of their constituent elements are illustrated in Fig (2a, b). They are close to the prepared compositions. Moreover, EDAX analysis indicates the absence of impurities elements in the studied compositions.



(a) **(b)**

Fig. (2a,b): The chemical composition of the obtained films is checked by (EDAX) energy dispersive analysis of X-ray (a) Cd_3Se_{97} and (b) $Cd_3Se_{76}S_{21}$.

3.2 Static I-V characteristic

A room temperature static I-V characteristic curve for a Cd_3Se_{97} film sample of thickness 700nm is shown in Fig (3) as a representative example.

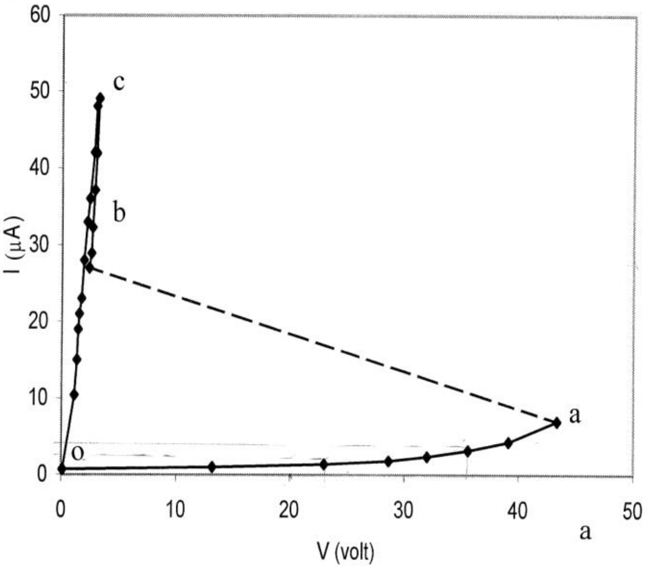


Fig. (3): Static I-V characteristic curve of Cd_3 Se_{97} thin film thickness (700nm).

It is observed that an increase in the applied voltage produces a very small current (the first branch oa of the curve which is illustrated in the inset of Fig (3)), representing the OFF state (with high resistance) of the switch. At point a, a sudden increase in current and drop in voltage to the point b takes place in a very short time of the order 10^{-9} s [9], i.e. switching occurs through the load line ab (negative resistance region). Therefore, it is impossible to record any reading in this range. A further increase in the applied voltage increases the current without any significant increase in the potential drop across the sample (part bc). This part of the curve represents the ON state with low resistance. On decreasing the applied voltage in this state, the current decreases until finally become zero (part co). The obtained I-V curve is a typical I-V characteristic for a memory switch [1].

3.3 Thickness dependence of threshold voltage:

The dependence on mean value for threshold voltage $\overline{V_{th}}$ on the sample thickness is also investigated. Figure (4 a, b) shows current-voltage curves at room temperature for evaporated films of Cd_3Se_{97} and $Cd_3Se_{76}S_{21}$ at different thicknesses ≈200-700 nm.

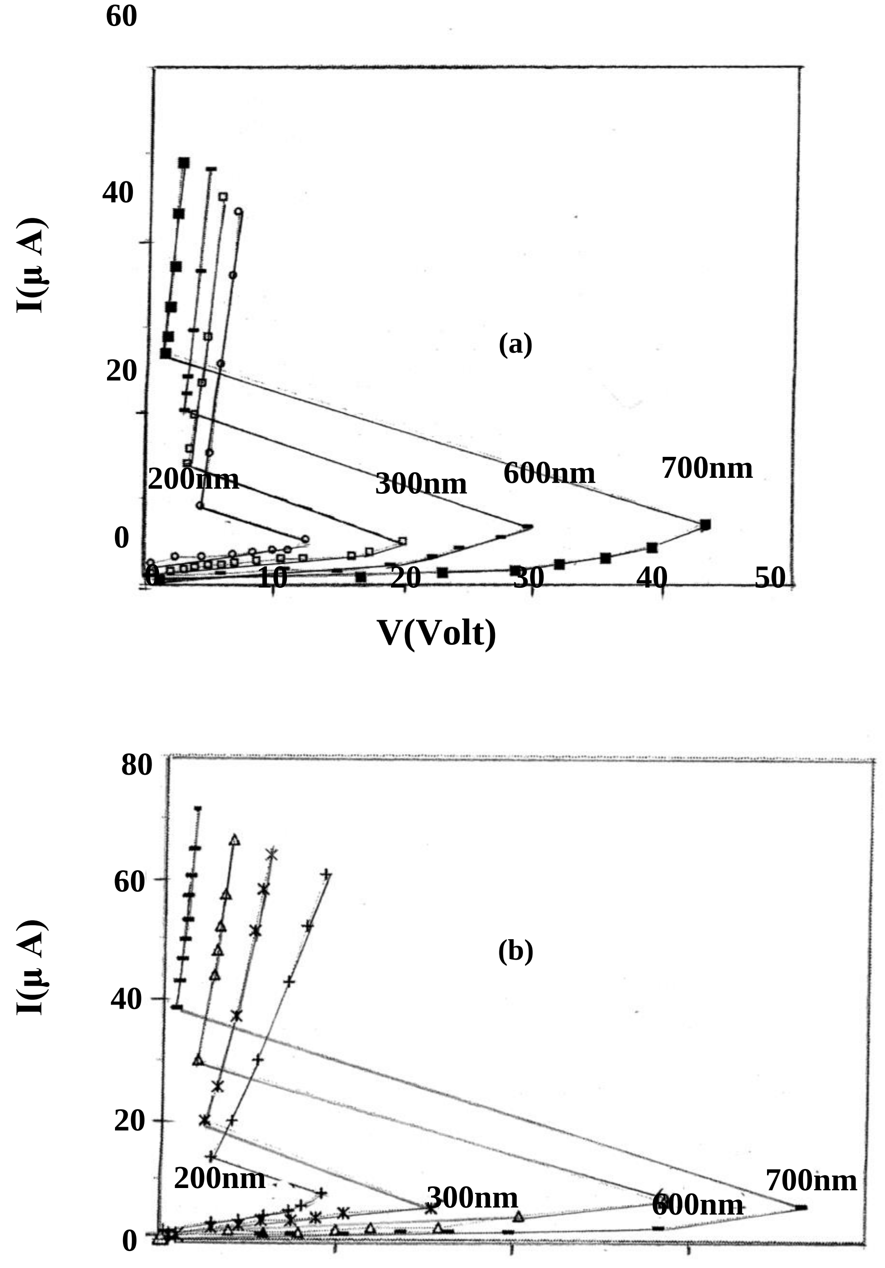
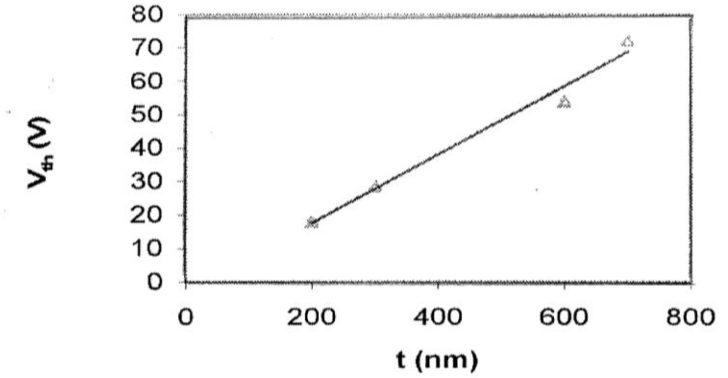
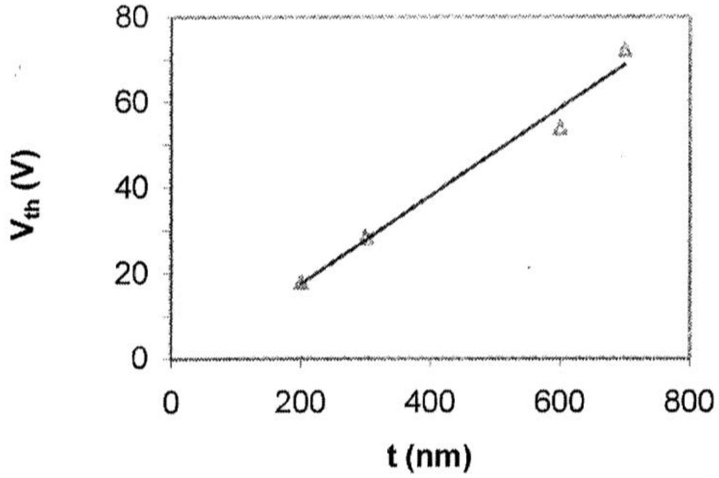


Fig. (4 a,b): Static I-V characteristic curves at different thickness for the composition (a)Cd_3 Se_{97} and (b)$Cd_3Se_{76}S_{21}$.

The curves show typical threshold switching, with a transformation from highly resistive state to a low resistive state. Figure (5 a,b). show that $\overline{V_{th}}$ increases linearly with the thickness of the film .



(a)



(b)

Fig. (5a,b): The thickness dependence of V_{th} *of the composition (a)*Cd_3Se_{97} *and (b)*$Cd_3Se_{76}S_{21}$.

This behavior is similar to the experimental results reported for other chalcogenide glasses [3, 7, 15, 16, 17]. From figure(5 a, b) it is observed that for a given film thickness, $\overline{V_{th}}$ increases with S content.

3.4 Temperature dependence of threshold voltage

Fig. (6 a, b) depicts the I-V characteristics obtained at different temperatures in the range (303-365 K) for Cd_3Se_{97} and $Cd_3Se_{76}S_{21}$ thin films.

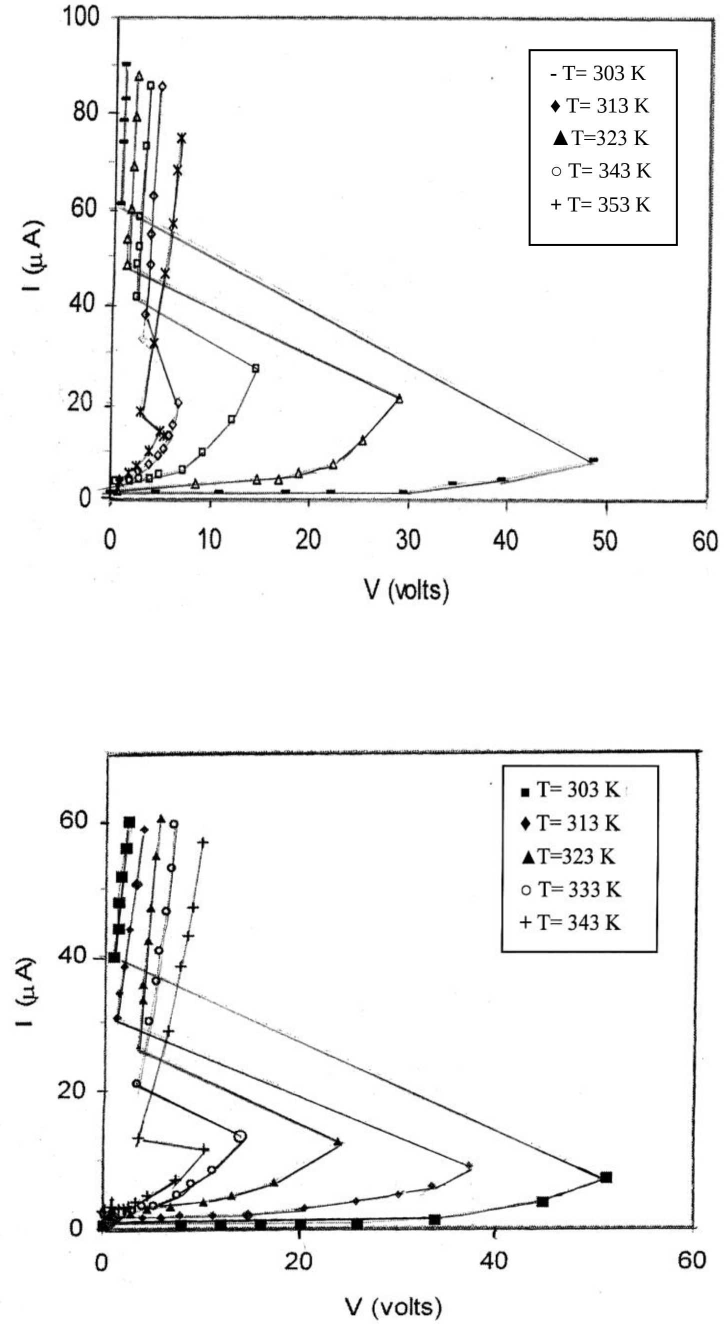
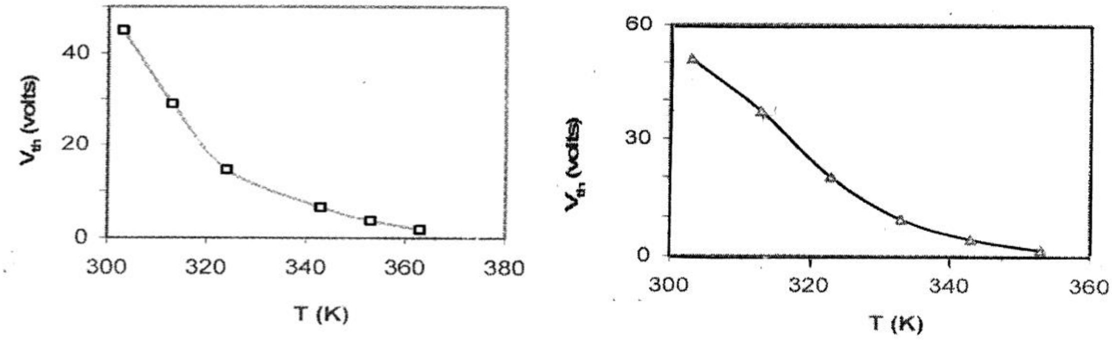


Fig. (6a,b): Static I-V characteristic curves at different elevated temperature for the composition (a)Cd_3 Se_{97} and (b)$Cd_3Se_{76}S_{21}$ at thickness 600 nm.

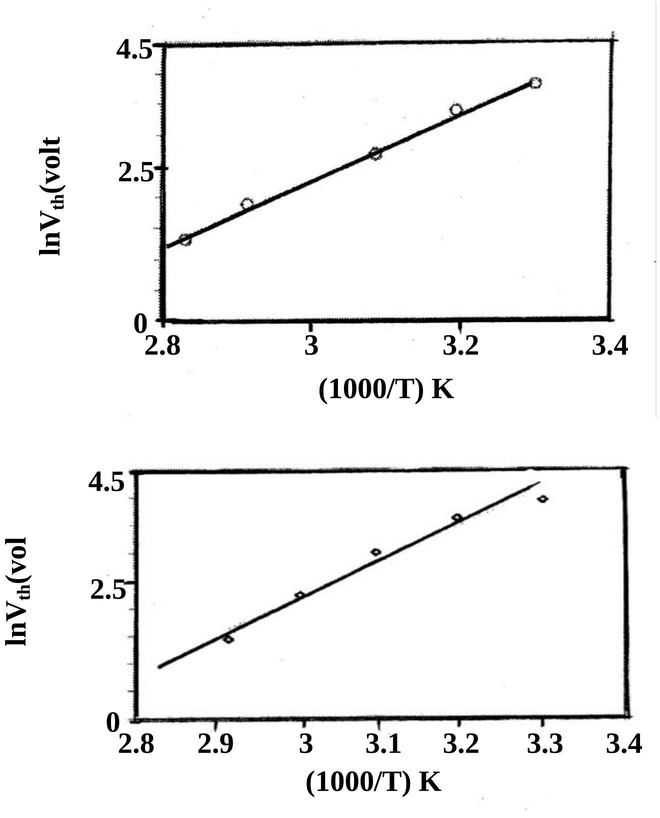
Fig. (7a, b) represents the variation of $\overline{V_{th}}$ with temperature for Cd_3 Se_{97} and $Cd_3Se_{76}S_{21}$ films of thickness 600 nm. It is clear that $\overline{V_{th}}$ seems to decrease exponentially with temperature.



(a) (b)

Fig. (7a, b): Temperature dependence of V_{th} *of the composition (a)*$Cd_3\,Se_{97}$ *and (b)*$Cd_3Se_{76}S_{21}$.

The dependence of $\overline{V_{th}}$ was plotted as $\ell n\,\overline{V_{th}}$ versus $1/T$ as shown in fig. (8 a, b) for thickness 600 nm as a representative curve.



b-($Cd_3\,Se_{76}\,S_{21}$)

Fig. (8a,b): Plot of $\ln V_{th}$ *vs. (1000/T) for the composition of (*$Cd_3\,Se_{97}$*) and (*$Cd_3Se_{76}S_{21}$*).*

The obtained relation yielded a straight line satisfying the following equation [13].

$$\overline{V_{th}} = V_o \exp\left(\varepsilon / K_B T\right) \quad (1)$$

where V_o is constant , ε the threshold voltage activation energy , K_B Boltzmann's constant and T absolute temperature . The mean value of ε obtained from the slopes of the straight lines (shown in Fig. 8a, b) given in table (1). We show that the obtained straight lines are parallel, indicating that the threshold voltage activation energy is single valued and independent of sample thickness in the investigated range.

Table 1. Values of E_σ , ε , ε/ E_σ and $\Delta T_{breakdown}$.

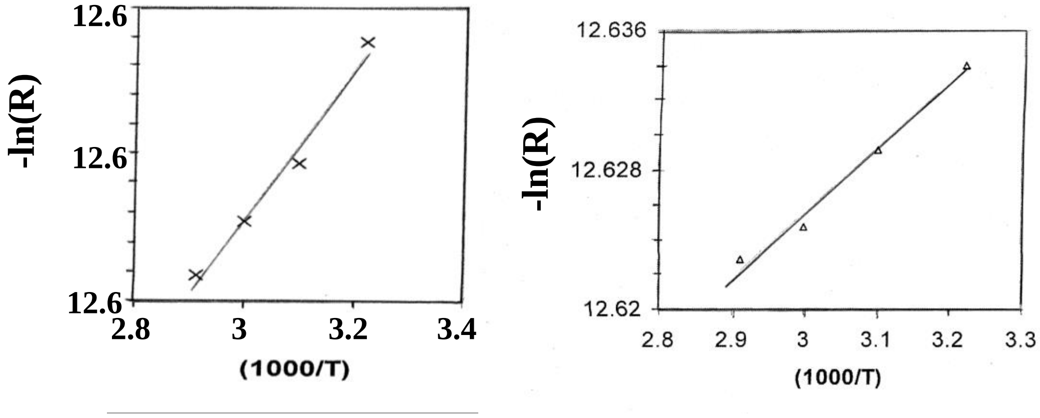
Composition	E_σ (eV)	ε (eV)	ε/ E_σ	$\Delta T_{breakdown}$
Cd_3Se_{97}	0.923	0.440	0.477	8.55
$Cd_3Se_{76}S_{21}$	0.953	0.460	0.483	8.31

The resistance (R)of thin film samples was calculated from the linear region of the OFF-state of the corresponding static I-V curve for different thickness ~ 200-700 nm at both room and elevated temperature. The resistance (R) of a semiconductor is usually given by the formula

$$R = c \exp\left(E_\sigma / K_B T\right) \quad (2)$$

where c is constant and E_σ is the conduction activation energy .

As representative example, the relation between ℓnR versus $1/T$ for thickness 600 nm in the temperature range (303 – 365K) for two compositions are illustrated in Fig (9 a,b).



(a) (b)

Fig. (9a,b): Plot of In(R) vs. (1000/T) for the composition of (a)Cd_3 Se_{97} and(b)$Cd_3Se_{76}S_{21}$.

We show that the straight lines are parallel, indicating that the conduction activation energy E_σ is independent of the sample thickness. The values obtained for E_σ are given in table (1) together with those of ε for the two compositions. This agrees with other work on Chalcogenide glasses [7]. The rations of ε/ E_σ ≈0.5 are given in table (1). This value is in agreement with that derived theoretically on the basis of an electrothermal model [12, 13] for the switching process.

So the observed temperature dependence of the threshold voltage for the pre-switching region can be explained in terms of an electrothermal model. The temperature of semiconductor is raised due to Joule heating. Since the conduction process in an amorphous material is of an activated type [18] the conduction of the sample is thus, increased when heated. This will allow more current flow through the heated region and allow more Joule-heating resulting in further increase in the current density. Stationary state is reached when the heat lost by conduction from the current filament becomes equal to the Joule-heat generated in that region.

The electrothermal model can be solved to a certain extent by finding a stationary state solution for the heat transport equation.

$$C(dT/dt)=\sigma E^2+\nabla(\psi\nabla T), \tag{3}$$

where C is the heat capacity, ψ is the thermal conductivity, E is the electrical field intensity ($E=V_{th}/t$,where t the film thickness) and σ the electrical conductivity of the samples, which is given by :

$$\sigma = \sigma_0 \exp(-E_\sigma/K_BT) \tag{4}$$

.

In the case of steady state breakdown, the time derivative of temperature (dT/dt) can be neglected for the solution of Eq. (3). Hence, the heat conduction equation for a small difference ($\Delta T=T_m-T_s$) between the temperature at the middle of specimen T_m and that of the surface T_s gives [19].

$$8\,\psi(\Delta T/t^2)+\sigma E^2=0. \tag{5}$$

The steady state breakdown occurs when the amount of heat generated by Joule-heating cannot be removed by thermal conduction and the temperature difference necessary for breakdown can be obtained from Eqs. (4) and (5) in the form [13,19].

$$\Delta T_{breakdown}=T^2k_B/E_\sigma \tag{5}$$

According to this equation $\Delta T_{breakdown}$ was calculated for the two compositions Cd_3Se_{97}, $Cd_3Se_{76}S_{21}$ films at room temperatures, and the obtained values are given in Table 1.This result is in agreement with previous observation for different amorphous system [5, 17, 20] .From the above results, it can be concluded that the observed memory type switching observed in two films could be satisfactory explained according to electorthermal breakdown process.

4. Conclusion

The most important conclusions of this study may be stated as follows:

- X-ray diffraction XRD results for Cd_3Se_{97}, $Cd_3Se_{76}S_{21}$ in thin film form have an amorphous structure.
- Static I-V characteristics curves for films under test are typical for a memory switch.
- The mean value of the threshold voltage $\overline{V_{th}}$ increases linearly with film thickness and with the addition of S, while it decreases exponentially while increasing temperature.
- The obtained mean value of the ratio $\varepsilon/E_\sigma \approx 0.5$ for two compositions under test and is attributed to electrothermal model based on Joule heating.
- Values of the temperature difference between that inside the film and that of its surface $\Delta T_{breakdown}$ calculated on the basis of the electrothermal breakdown process are in the same order with those obtained previously for other chalcogenide glasses.

References

[1] M.A. Afifi, M. Fadel, E.G. Metwally, A.M. Shakra, Vacuum **77,**259(2005).
[2] K.W. Boer, S.R Ovshinsky, J. Appl. Phys. **41,** 2675(1970).
[3] M. Fadel, H.T. Shair, Vacuum **43**,253(1992).
[4] M.J Zope, J.K. Zope, J. Master. Sci. Lett. **3**,850(1984).
[5] M.A. Afifi, H.H.A. Labib, A.H. Abou El-Ela and K.A. Sharaf, Appl. Phys. **A 46,**113(1988).
[6] F.M .Collins, J. Non-Cryst. Solids **2,**496(1970).
[7] M. Fadel, A. Negem, H. Metwally and M.A Afifi, J. Appl. Phys. **A 54**,288(1992).
[8] R .Landauer, JWF .Woo, Comments Solid State Phys. **4,**139(1972).
[9] S.R. Ovshinsky, Phys. Rev. Lett. **21,**1450(1968).
[10] D. Adler, Ms. Shur, , M. Silver, S.R. Ovshinsky, J. Appl. Phys, **51**,3289(1980).
[11] D. Adler, Sci. Am. **36**,236(1977).
[12] H. Fritzsche, S.R .Ovshinsky, J. Non-Cryst. Solids **4**,464(1970).
[13] R. Mehra, R. Shyam and P.C. Mathur, J. Non-Cryst. Solids **31**,435(1979).
[14] S. Tolansky, Multiple-beam Interference Microscopy of Metals, Academic Press, London(1970)
[15] K.H. Amirkhanov, Ya.B Magomedov, M.A. Aidamirov, L.G. Aio, Kh.O. Alieva, and Sh. M. Ismailov, Sov.J. Glass Phys. Chem. (USA) **6**,312(1980).
[16] S.R. Ovshinsky, and H. Fritzsche, IEEE Trans. Electron Devices **20**,91(1973).
[17] M.A. Afifi, A.E. Bekheet, N.N. Hegab, L.A. Wahab, H.A. Shehata, J. Appl. Phys. **40**, 133(2007).
[18] A.H. Abou El-Ela, N. Abdelmohsen, H.H. Labib, Appl. Phys. **A 26,**171(1981).
[19] K. Shimakawa, Y. Inagaki, T. Arizami, Jpn. J. Appl. Phs. **12,** 1043(1973).
[20] H. E. Atyia, Physica **B 403,**16(2008).