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EFFECT OF ANNEALING ON THE SWITCHING PROPERTIES OF CuInSeTe THIN FILMS

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The switching properties of amorphous CuInSeTe thin films have been investigated. The amorphous quaternary semiconductor CuInSeTe thin films ∼ 220 nm and ∼ 330 nm thick have been prepared by thermal evaporation of the bulk compound under vacuum of about 10^{-4} Pa and with deposition rate about 8 nm/s. The structure of the bulk and thin films were investigated by the X-ray diffraction technique. The compositional studies of CuInSeTe in both powder and thin films were carried out by Perkin Elmer Model 1100 atomic absorption spectrometer. The annealing of the films at different annealing temperatures (300, 350, 400, 450 and 500 K) improves the switching characteristics and decrease the threshold voltage V_{th}. The threshold switching voltage and the threshold activation energy E_{s} were found to decrease linearly with increasing annealing temperature. Moreover, the threshold switching voltage decreased exponentially with temperature.

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Keywords: amorphous CuInSeTe thin film, annealing, switching characteristics, threshold voltage, threshold activation energy

1. *Introduction*

The ternary chalcopyrite semiconductors of the type $\mathrm{A^I B^{III} C_2^{VI}}$ have been receiving a great deal of attention for their potential use in non-linear optics and solar cells. These compounds allow preparing quaternary systems in which the band gap of the alloy can be optimized by suitable compositions within the miscibility range. The properties of amorphous thin films of the quaternary semiconductor are of particular interest because of their applicability in semiconductor technology and switching devices [1].

In the amorphous semiconductor films, electric breakdown effects have drawn particular attention since the discovery that electrical breakdown can be a regenerative and non-destructive process [2 – 7]. However, the breakdown mechanism is still unclear. Various model based on thermal and mixed electro-thermal mechanisms have been proposed [4, 5, 8, 9]. Boer and Ovshinsky [9] have shown that the phenomenon of switching is limited by Joule heating of a current channel, which produces thermally stabilized high electric field effects close to the electrodes. These effects are responsible for starting the switching process. Few studies on the electrical and optical properties of CuInSeTe thin films have been reported [10 – 14]. There are no published studies, to our knowledge, on the switching phenomenon in CuInSeTe thin films. We also studied the electrical and optical properties of CuInSeTe thin films [15, 16].

This paper reports the results of study of the switching properties of thermally evaporated CuInSeTe thin films, which has led to the conclusion that the switching phenomenon is essentially thermal in nature.

2. *Experimental*

The investigated samples of CuInSeTe were prepared by the fusion method using spectroscopically pure Cu, In, Se and Te (99.999, Mathey Chemical Ltd.) in the proper ratio [15]. This method is simple and takes a short time. We describe it briefly as follows.

A furnace with a two-section tube was used for preparing the compounds because the melting points of the reactants differ largely.

The chalcogen (Se or Te) was held at a temperature not exceeding half of its boiling point to avoid explosion. The Cu and In elements were always placed in the hot part of the silica tube, and were maintained at a temperature 50°C above the melting point of Cu. In this way reaction took place between vapour of the chalcogen and the melted elements (Cu and In). After the reaction was completed (revealed by the disappearance of the chalcogen vapour), the temperature of the cold zone of the tube was raised to the temperature of the hot zone. To ensure homogeneity of the compound, the tube was carefully shaken several times. The temperature was kept constant for 2 hours to ensure completion of the reaction and homogeneity of the melt. The temperature of the furnace was then lowered slowly to a value equal to half the value of the melting point of the compound. The tube was then left in the furnace at this temperature for further homogenization and annealing for about four days. Finally, the sample was gradually cooled down to room temperature.

A Leybold Univex 300 coating unit equipped with a quartz thickness monitor was used for thin-film production in a vacuum around 10^{-4} Pa. The thin films were evaporated onto polished pyro-graphite substrates at room temperature (300 K) at a rate of 8 nm/s by heating the fine-grained CuInSeTe powder in a tungsten boat. The thickness of the produced films was also measured using an optical multiple-beam interferometer. The as-deposited thin films were annealed at different annealing temperatures (350, 400, 450 and 500 K) under vacuum of ~ 0.1 Pa for two hours.

The structure of the investigated samples in both powder and thin-film form were investigated by using the X-ray diffractometer Philips PW 1373. The compositional studies of CuInSeTe in both powder and thin films were carried out using Perkin Elmer Model 1100 atomic absorption spectrometer.

The current–voltage characteristics were measured through the CuInSeTe films (the current perpendicular to the film) in a two-electrode cell. The lower electrode, made of copper, was in good contact with the pyro-graphite substrate. The upper electrode was a movable platinum wire of diameter ~ 200 μm at its tip. This tip provided a good electrical contact with the upper film surface using a weak spring. The pressure exerted by the two electrodes on the film was kept constant throughout the measurements. A highly-stabilized power supply, a sensitive voltmeter and an electrometer capable of measuring down to 10^{-11} A were used in measuring the $I - V$ characteristics. A heater and a thermocouple were used for providing heat and to measure the temperature of the film during the experiment.

3. Results and discussion

Figure 1a shows the X-ray diffraction patterns of CuInSeTe in powder form which reveal a polycrystalline nature, while Fig. 1b shows the X-ray diffraction patterns of the as-deposited CuInSeTe thin films and those annealed at different annealing temperatures (350, 400, 450 and 500 K). It is clear that, after the films were annealed at different annealing temperatures, no significant change of their amorphous structure has been observed and all films retain their amorphous structure [16] (as shown in Fig. 1b).

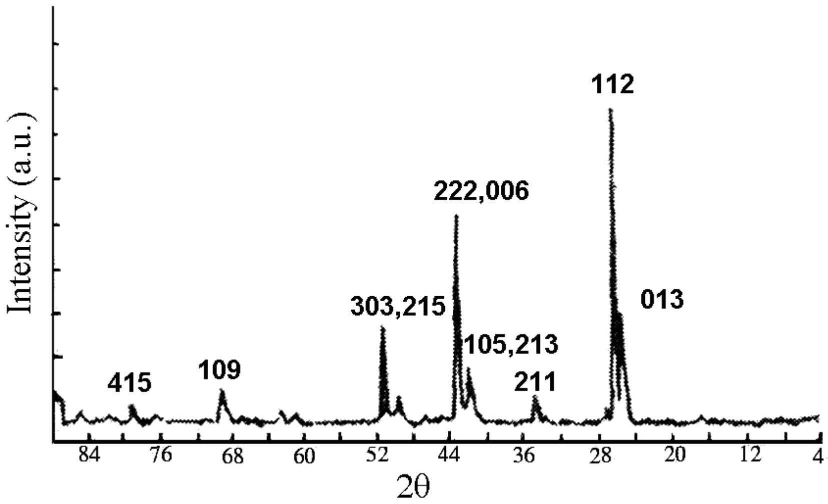


Fig. 1a. X-ray diffraction patterns of powder CuInSeTe.

The weight percentages of the elemental-composition analysis of the prepared CuInSeTe samples both in powder and thin films forms are given in Table 1. It

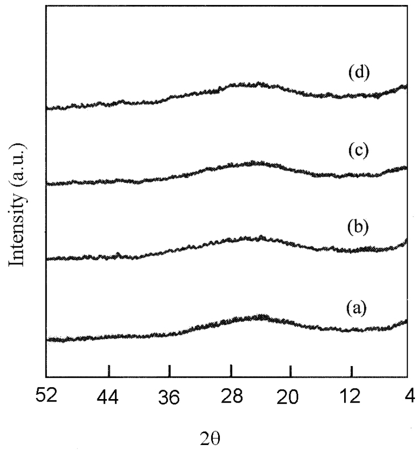


Fig. 1b. X-ray diffraction patterns of CuInSeTe *thin films annealed at different temperatures (a – 350* K*, b – 400* K*, c – 450* K *and d – 500* K*).*

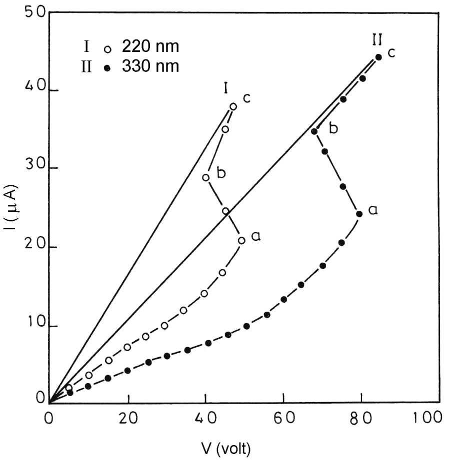
TABLE 1. Weight percentage of CuInSeTe *powder and thin films as-deposited and annealed at 500* K.

Elements	Powder	Thin films (as-deposited)	Thin films (annealed at 500 K)
Cu	22.101	22.052	21.979
In	39.511	39.481	39.502
Se	27.183	27.285	27.309
Te	11.205	11.182	11.210

is observed that these results confirm the nearly stoichiometric composition of the films.

Room temperature static $I-V$ characteristics for CuInSeTe thin films with samples of thickness $\sim$220 nm and 330 nm are shown in plots I and II of Fig. 2, respectively.

As shown in the plot I of Fig. 2, it is clear that the current is very weak and it increases with increasing applied voltage, as represented by the data along the line Oa (O stands for the origin) for samples of thickness $\sim$220 nm. This is called the off-state. This off-state can be divided into three parts: the first part is linear (O to 19 V), the second part (19 V to 50 V) follows the Pool-Frenkel relation [17], $I = I_{0\,\mathrm{exp}}(V/V_0)^{1/2}$, while in the third part (50 V to V_{th}), the current increases exponentially with the voltage according to [18] $I = I_0 \exp(V/V_0)$. At the threshold voltage, V_{th}, a switching process takes place after which further increase of the applied voltage causes the current to increase to the "on-state" as shown by line bc of the plot I in Fig. 2. Reducing the voltage to zero from its value in the on-state resulted in zero current (line cO). Changing to the film thickness



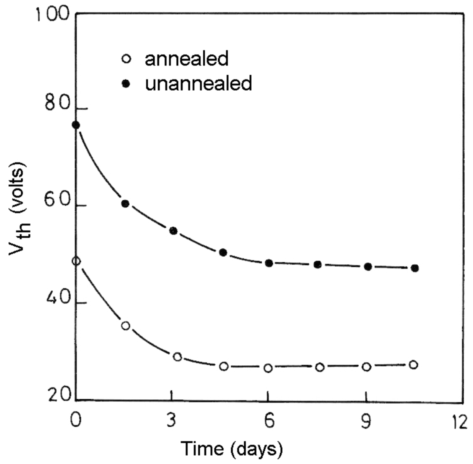


Fig. 2 (left). Current-voltage characteristics of the as deposited CuInSeTe *thin films of thickness* $\sim$ *220* nm *(I) and* $\sim$ *330* nm *(II).*

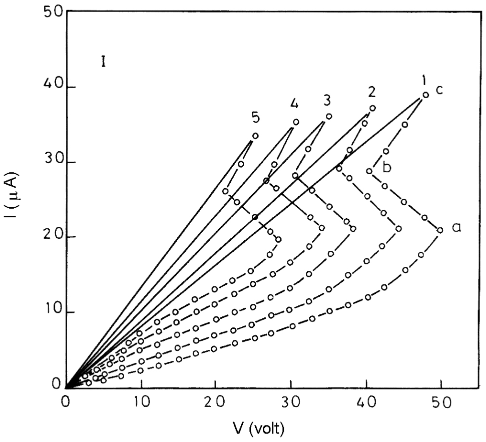
Fig. 3. Variation of the threshold voltage V_{th} *with ageing period of* CuInSeTe *thin films of thickness* $\sim$ *330 nm un-annealed and annealed at 400* K.

of $\sim$330 nm resulted in an increase of V_{th} as shown by the plot II of Fig. 2. This result is in agreement with previous observations for different amorphous semiconductors [19, 20].

Figure 3 shows the variation in V_{th} with the ageing time for the sample $\sim$330 nm thick (Fig.2-II) after and before annealing at 400 K for two hours. The threshold switching voltage decreases sharply during the first few days for both annealed and un-annealed samples. After about two days, V_{th} starts to saturate. The value of V_{th} for the un-annealed sample, however, was measured to be always higher than the corresponding value for the annealed films measured after the same ageing time. Similar behaviour was obtained for the other thickness. Thus we may conclude that either heat treatment or ageing for relatively long periods may stabilize and improve the switching properties.

Figure 4 shows the current–voltage characteristics for the evaporated CuInSeTe thin films of $\sim$220 nm thick, heat-treated at different annealing temperatures (300, 350, 400, 450 and 500 K). The curves are characteristic of threshold switching where transformation from a high-resistance off-state into a low-resistance on-state takes place as the voltage exceeds a threshold value V_{th}. Moreover, annealing the films at different annealing temperature improves the characteristics and results in decreasing V_{th} as shown in Fig. 4. Similar behaviour was obtained for films $\sim$330 nm thick as shown in Fig. 5. This decrease will be shown later to be exponential.

The dependence of the threshold voltage on the ambient temperature can be explained in terms of a thermal model in the pre-switching region. The conductivity process in semiconductor materials is well known to be of activated type. Therefore, increasing the temperature of a material in the Joule-heated regions provides a mechanism for the increase of the current.



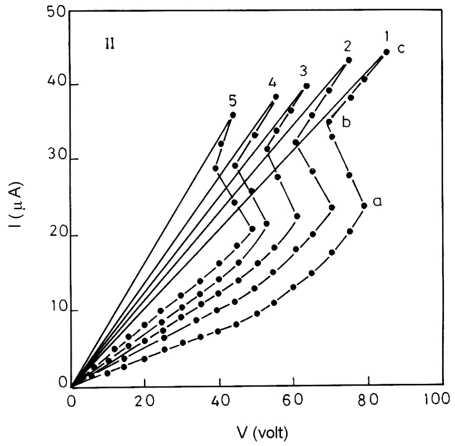
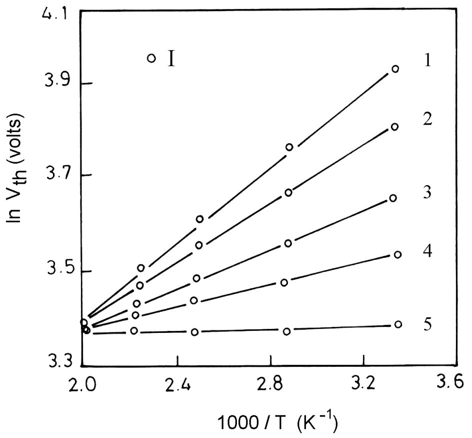


Fig. 4 (left). Current–voltage characteristics of the CuInSeTe *thin films of thickness* ~ 220 nm*, as-deposited and annealed at 350, 400, 450 and 500* K *(data denoted by 1, 2, 3, 4 and 5, respectively).*

Fig. 5. The same as in Fig. 4, but for the film thickness of ~ 330 nm.

The calculated temperature dependence of V_{th} for the as-deposited CuInSeTe thin films of thicknesses ~ 220 and ~ 330 nm and annealed at different annealing temperatures (300, 350, 400, 450, 500 K) are shown in Fig. 6 (data denoted 1, 2, 3, 4, 5, respectively) and Fig. 7 (data denoted 1, 2, 3, 4, 5, respectively). The relation between $\log V_{\mathrm{th}}$ versus $1000/T$ is linear and can be put in the form [6]



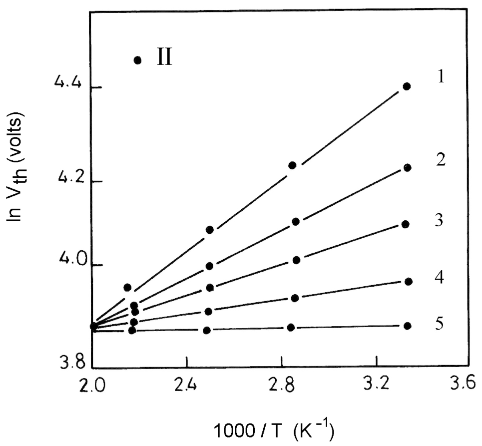
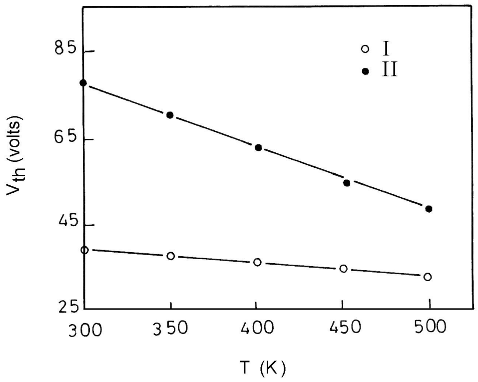


Fig. 6 (left). Logarithmic plot of the switching threshold voltage V_{th} *versus reciprocal temperature for the* CuInSeTe *thin films of thickness* ~ 220 nm*, as-deposited and annealed at 350, 400, 450 and 500* K*, respectively.*

Fig. 7. The same as in Fig. 6, but for the film thickness of ~ 330 nm.

$V_{th} = V_0 \exp(E_s/kT)$, where E_s is the threshold voltage activation energy and k is the Boltzman constant.

The calculated values of E_s for CuInSeTe thin films in comparison with the conductivity activation energy ΔE obtained from previous work [15] give the value of $E_s/\Delta E \approx 0.55$. This is in agreement with the observation of Shimakawa et al. [21] for the thermal breakdown process. The calculated values of V_{th} and E_s for samples of thickness ~ 220 nm and ~ 332 nm are plotted in Fig. 8 and Fig. 9 versus the annealing temperature, respectively. From the plots of Figs. 8 and 9, it is clear that both quantities, V_{th} and E_s, decrease linearly when increasing the annealing temperature.



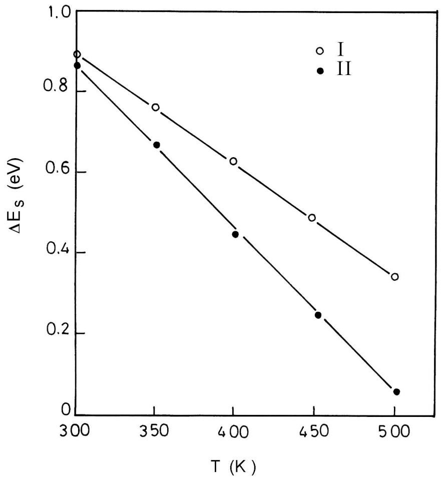


Fig. 8 (left). Threshold voltage V_{th} of the as-deposited CuInSeTe *thin films of thickness $\sim$ 220* nm *(I) and $\sim$ 330* nm *(II) as a function of the annealing temperatures.*

Fig. 9. Threshold voltage activation energy E_s of the as-deposited CuInSeTe *thin films of thickness $\sim$ 220* nm *(I) and $\sim$ 330* nm *(II) as a function of the annealing temperatures.*

4. Conclusion

The current–voltage characteristics of both as-deposited and annealed films of amorphous CuInSeTe thin films fit completely within the accepted picture of thermal breakdown. The annealing process improves the switching characteristics and decreases the threshold voltage V_{th}. Both the threshold switching voltage and threshold voltage activation energy E_s decrease linearly with increasing annealing temperature.

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UČINAK OPUŠTANJA NA PREKIDAČKA SVOJSTVA TANKIH SLOJEVA CuInSeTe

Istraživali smo prekidačka svojstva amorfnih tankih slojeva CuInSeTe. Tanke amorfne slojeve četiritvornog poluvodiča CuInSeTe debljine ~ 220 nm i ~ 330 nm pripremali smo naparavanjem spoja u vakuumu pri oko 10^{-4} Pa, brzinom naparavanja od oko 8 nm/s. Strukturu praha i tankih slojeva odredili smo rendgenskom difrakcijom. Sastav CuInSeTe u prahu i tankih slojeva ispitali smo pomoću Perkin Elmer-ovog (model 1100) apsorpcijskog spektrometra. Opuštanje tankih slojeva na nizu temperatura (300, 350, 400, 450 i 500 K) poboljšava njihova preklopna svojstva i smanjuje napon praga preklopnog napona $V_{\rm th}$. Našli smo da se prag preklopnog napona i prag aktivacijske energije $E_{\rm s}$ linearno smanjuju s povećanjem temperature opuštanja. K tome, prag preklopnog napona smanjuje se eksponencijalno s temperaturom opuštanja.