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ELECTRICAL AND SWITCHING PROPERTIES OF $ZnIn_2Se_4$ AMORPHOUS THIN FILMS

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In this work electrical and switching properties of amorphous $ZnIn_2Se_4$ thin films have been studied. The amorphous films were obtained by thermal evaporation in vacuum, of polycrystalline materials, on glass or pyrographite substrates. From electrical measurements, it was found that for all films the dark electrical resistivity decreases with an increase of film thickness and temperature. The $ZnIn_2Se_4$ films exhibit nonlinear $I-V$ characteristics and switching phenomena. The threshold voltage decreases with increasing temperature and increases with increasing film thickness.

1. *Introduction*

The properties of amorphous thin films of semiconductors and their transition to the crystalline phase is of particular interest because of their applicability in semiconductor technology and switching devices [1].

Memory switching has been reported in a wide range of materials, including chalcogenide semiconductors, organic semiconductors, oxides, single crystals and amorphous thin films of semicondctors [2]. The switching process can be attained in several ways, including electrical and thermal mechanisms [3].

$ZnIn_2Se_4$ is a tetrahedrally coordinated semiconductor which crystallizes in the uniaxial defect chalcopyrite structure of space group S_414 [4]. Up to now, it has been the subject of relatively little interest. Only some fundamental properties such as photononductivity and optical absorption have been investigated. The photoconductivity of $ZnIn_2Se_4$ was first studied by Benn et al. [5] and later this work was extended by others [6–8]. The residual conductivity [9] inherent to $ZnIn_2Se_4$ has been used to develop memory cells. To our knowledge, no work concerning electrical and switching properties of $ZnIn_2Se_4$ thin film has been reported. In this paper, the electrical and switching properties of $ZnIn_2Se_4$ films deposited by thermal evaporation technique on glass and pyrographite substrates are studied.

Previously, one of the authors [10] has studied the preparation of polycristalline $ZnIn_2Se_4$, using diffusion method. Also, the crystal structure of both the powder and the thin films (as prepared, and annealed) of $ZnIn_2Se_4$ has been examined. In addition, the optical properties of these films were reported [10].

2. *Experimental techniques*

Polycrystalline $ZnIn_2Se_4$ was prepared by the difussion method [10]. For electrical resistivity measurement, amorphous thin films of $ZnIn_2Se_4$ were obtained in vacuum by thermal evaporation (at about 10^{-6} mbar) on clean thin glass substrates. Ohmic contacts were obtained by evaporation of indium. To measure the $I-V$ characteristics, thin films of $ZnIn_2Se_4$ were obtained by evaporation on clean highly polished substrates of pyrographite. The thin film sample was sandwiched between two electrodes, the lower electrode being a circular brass disc.

3. *Results and discussion*

3.1. *Electrical properties of* $ZnIn_2Se_4$ *thin films*

Analysis of X–ray diffraction patterns of the prepared $ZnIn_2Se_4$ in powder form, Fig. 1(A), reveals a polycrystalline nature while Fig. 1(B) shows that the thin films were completely amorphous for different thicknesses.

Figure 2, curve 1, shows the variation of dark electrical resistivity, ρ, with the corresponding values of the film thickness, t, of the $ZnIn_2Se_4$ films. From this figure, it was found that ρ decreases with increasing film thickness; this could be due to lattice defects such as vacancies and dislocations which might appear throught the first stage of the film growth. These defects diffuse as the film thickness increasses, thus reducing the resistivity. The increase in grain size also plays a role in decreasing the resistivity. This was confirmed by structural investigations using both X–ray and electron microscopy diffraction techniques. The thermal activation energy, ΔE, of the free charge carriers for $ZnIn_2Se_4$ thin films was calculated from the slopes of straight lines representing the temperature dependence of the electrical resistivity for various thicknesses. It was found that ΔE decreases with increasing film thickness, as can be seen in Fig. 2 curve II. For thicknesses greater than 400 nm, the results for ΔE attain a constant value of 0.95 eV. This value is in harmony with the expected value of the optical energy gap (1.9 eV) for $ZnIn_2Se_4$, as $\Delta E = E^{opt}/2$.

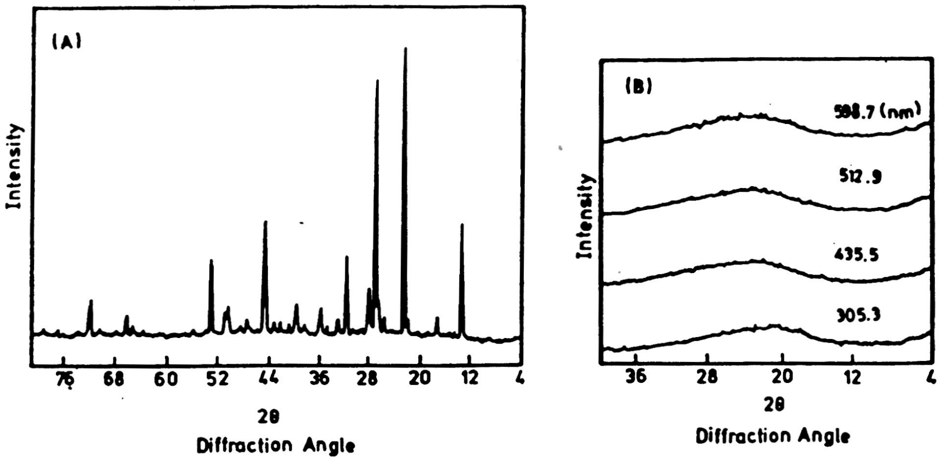

Fig. 1. X–ray diffraction pattern (A) powder form, (B) thin films.

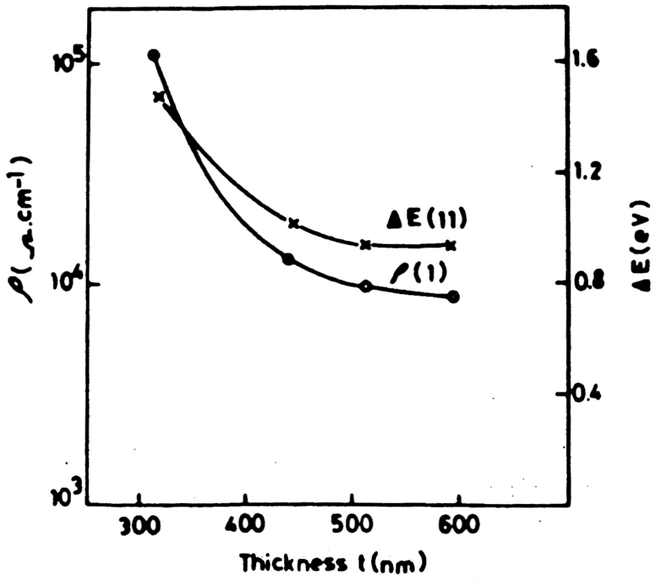

Fig. 2. Variation of ρ and ΔE with film thickness.

3.2. *Switching properties of* $ZnIn_2Se_4$ *thin films*

3.2.1. *Static* $I - V$ *characteristic curve of* $ZnIn_2Se_4$ *thin films*

The room–temperature static $I - V$ characteristic for a thin film sample (435.5 nm) of $ZnIn_2Se_4$ is presented in Fig. 3. It is clear that the current is very small and it increases with increasing applied voltage (part 0a of the curve, the OFF state). The OFF state can be divided into three regions, a linear region (0 − 13.5 V), an exponential region (13.5 − 30 V) following the Pool–Frenkel relation $I = I_0 \exp(V/V_0)^{1/2}$ and a third region ($30 - V_{th}$) where the current increases exponentially with voltage according to the formula $I = I_0 \exp(V/V_0)$. At the threshold voltage V_{th}, a switching process takes place. A further incerase in the applied voltage increases the current without significant increase in the potential drop (part bc of the curve in Fig. 3, the ON state). On decreasing the voltage in this state, the current decreases until finally both become zero (part c0 of the curve). The obtained curve is a typical $I - V$ characteristic for a memory switch.

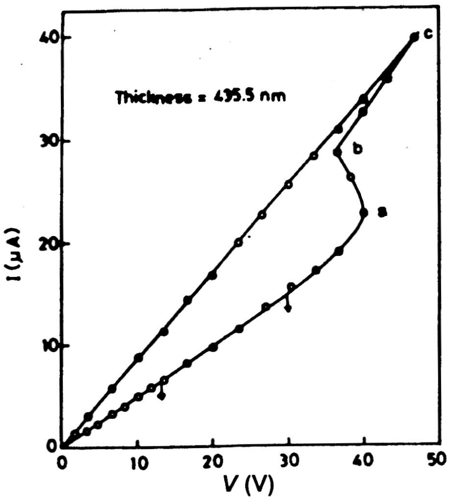

Fig. 3. Static $I - V$ *characteristic curve for* $ZnIn_2Se_4$ *thin film of thickness* 435.5 nm.

3.2.2. *Effect of heat treatment and aging on* V_{th}

20 runs were carried out with each specimen in order to chek reproducibility of the results. Initial fluctuation of the value of V_{th} was observed after which the devices become more stable. Thermally evaporated samples (305.5 − 598.7 nm) were isothermally annealed in vacuum for 1 hour at 50°C and then cooled gradually to room temperature. Figure 4, curves 1 and 2, represent the variation in V_{th} with aging time for a sample 435.5 nm thick, as an example, before and after annealing, respectivelly. As can be seen from the figure, V_{th} decreases sharply in first few days for both annealed and unannealed samples. Similar behaviour was obtained

for different film thicknesses. Thus, we may conclude that either heat treatment or aging for a relatively long period may stabilize and improve switching properties.

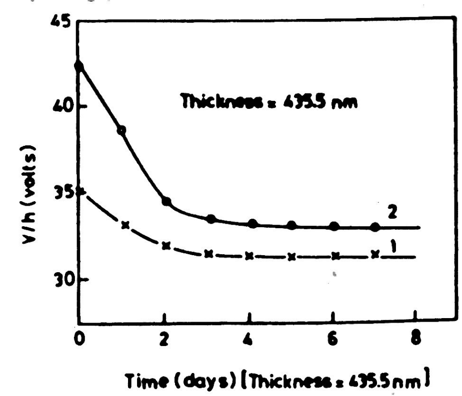

Fig. 4. Variation of threshold voltage, V_{th}, with aging period for $ZnIn_2Se_4$ *thin film: curve 1 after annealing, curve 2 before annealing.*

The activation energy for electric conduction in the OFF state was calculated from linear part of the $I-V$ curve and it was found to be 1.14 eV.

3.2.3. Threshold voltage and sample thickness

The treshold voltage was determined from the $I-V$ characteristic in Fig. 5 for preannealed films of different thicknesses. The obtained results are presented in Fig. 6, from which we observe a linear relationship between V_{th} and film thickness. This result is in agreement with previous observation for various amorphous semiconductors [11,12].

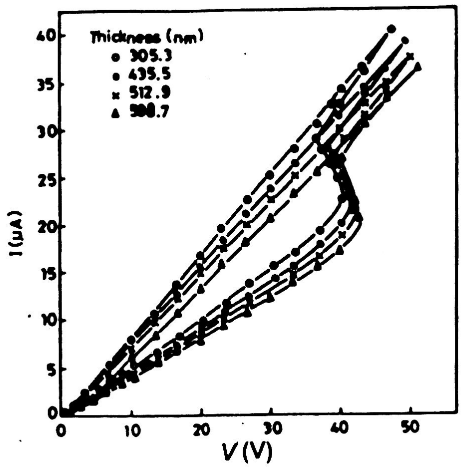

Fig. 5. Static $I-V$ characteristic curve for $ZnIn_2Se_4$ *thin films of different thickness.*

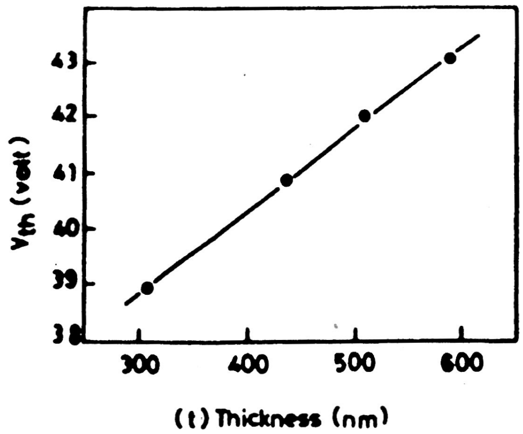

Fig. 6. The dependence of the mean value of the threshold voltage, V_{th}, on the sample thickness (t).

3.2.4. Threshold voltage and temperature

To investigate the variation of V_{th} with temperature for amorphous $ZnIn_2Se_4$ films of different thickness, V_{th} was determined at room temperature and at different elevated temperatures. The obtained results are shown in Fig. 7. It was found that V_{th} decreases exponentially with increasing temperature. The threshold–voltage activation energy was calculated for samples of different thickness and ilustrated in Fig. 8. Our results show that $ZnIn_2Se_4$ thin films display the behaviour of a negative–resistance device with memory.

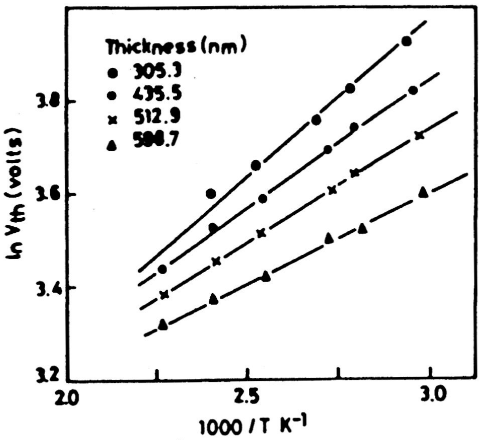

Fig. 7. Variation of threshold voltage V_{th} with temperature for $ZnIn_2Se_4$ thim films of different thickness.

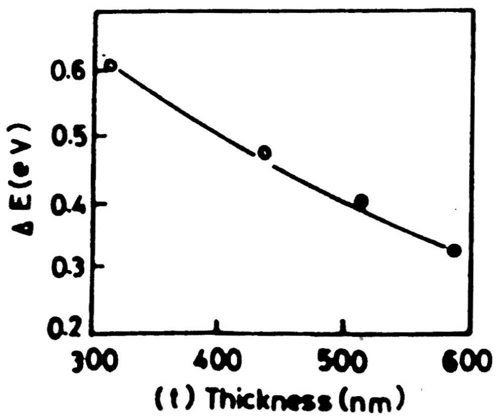

Fig. 8. Variation of the threshold voltage activation energy ΔE with the film thickness.

4. Conclusion

One can conclude that for all $ZnIn_2Se_4$ thin films, ρ and ΔE decrease with increasing film thickness, t, while the threshold voltage increases with sample thickness, and decreases exponentially with temperature, which could be understood in terms of a thermal model for the pre–switching region.

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ELEKTRIČNA I PREKLOPNA SVOJSTVA TANKIH AMORFNIH SLOJEVA $ZnIn_2Se_4$

Istraživala su se električna i preklopna svojstva tankih amorfnih slojeva $ZnIn_2Se_4$. Amorfni su slojevi pripremljeni naparavanjem polikristaliničnih materijala na staklene ili pirografitne podloge u vakuumu. Električna mjerenja pokazuju da se za sve slojeve električni otpor u tami smanjuje s povećanjem debljine sloja i temperature. Slojevi $ZnIn_2Se_4$ pokazuju nelinearnu ovisnost $I - V$ i preklopna svojstva. Napon praga preklopa smanjuje se s povećanjem temperature i povećava za veće debljine slojeva.