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EFFECT OF AIR ANNEALING ON $CuSbS_2$ THIN FILM GROWN BY VACUUM THERMAL EVAPORATION

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The effect of air annealing on the structural, optical and electrical properties of $CuSbS_2$ thin films prepared by the single source thermal evaporation method has been studied. The films were annealed in air atmosphere for 2h in the temperature range 100 - 300°C. X-ray diffraction (XRD) patterns indicated that the films showed an amorphous structure for annealing temperature below 200°C. For the films annealed at temperatures below 200°C one direct optical transition in the range 1,19 – 1,89 eV was found. For higher annealing temperatures two optical direct transitions at 0,87 and 3.7 eV corresponding respectively to the $CuSbS_2$ and Sb_2O_3 phases were found. A decrease in optical band gap Eg with increasing the annealing temperature was observed. Absorption coefficients higher than $10^5 cm^{-1}$ were found in the spectral range 1,2 - 3 eV. All the films present p-type conductivity after annealing for all the annealing temperature. The resistance values of the annealed $CuSbS_2$ thin films are in good correlation with annealing temperature.

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1. Introduction

The Optical properties of some I–III–VI_2 compounds (I–Cu, Ag; III–Sb, Bi; VI–S, Se) are also promising, but so far less investigated. Copper antimony sulfide ($CuSbS_2$) is one of the important semiconductors with narrow band gap showing potential applications invarious optoelectronic devices such as infrared detectors and solar cells [1]. The optical properties revealed the presence of direct band gaps with energies in the 1.30 to 2.30eV range [2]. $CuSbS_2$ polycristalline thin films have been deposited by techniques, combination of physical and chemical deposition [3]. Chemically desposited, near intrinsic Sb_2S_3 thin films and p–$CuSbS_2$ thin films obtained through heating Sb_2S_3–CuS thin films have been integrated in to a p-i-n structure [4]. Recently, considerable efforts have been done to gain a better understanding of structural, electrical and optical properties of ternary chalocogenide semiconductors because of their possible applications such as linear, non linear and thermoelectric devices and optical recording media [5]. Large area thin film semiconductor materials have been found useful generally in the areas of microelectronics, surface engineering, integrated circuits, etc [6]. So far, no works reported the effect of the air annealing on the $CuSbS_2$ properties. In previous studies we showed that the air annealing of the $CuInS_2$ films converts the films on to n-type conductivity [7]. Therefore if we would like to substitute indium by antimony it is important to study the effect of the air annealing on the $CuSbS_2$ properties, especially optical and the electrical.

In this paper, we report the effect of air annealing on the structural, optical and electrical properties of $CuSbS_2$ thin films deposited by single source vacuum thermal evaporation.

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2. Experimental procedures

2.1 Thin film preparation

Stoichiometric amounts of the elements of 99.999% purity Cu, Sb and S were used to prepare the initial ingot of $CuSbS_2$. $CuSbS_2$ thin films were prepared by the evaporation of the $CuSbS_2$ powder in a high-vacuum system with a base pressure of 10^{-5} Torr. A molybdenum crucible was used. Thermal evaporation source were used which can be controlled either by the crucible temperature or by the source power. Corning 7059 glasses substrates were used. The as-deposited films were annealed in air atmosphere for 2 h in the temperature range 100-300°C.

2.2 Characterization of the films

Optical transmittance (Texp) and reflectance (R_{exp}) were measured at normal incidence, in the wavelength range 300-1800 nm, with an UV-visible-NIR Shimadzu 3100S spectrophotometer equipped with an integrated sphere. The films thicknesses were calculated from the positions of the interference maxima and minima of reflectance spectra using a standard method [8]. The films thicknesses were found to be in the range of 160 – 290 nm. The absorption coefficients were deduced from transmittance and reflectance spectra [9]. The structural properties were determined by the X-ray diffraction technique using $CuK_{\alpha 1}$ radiation (λ =1.5418 Å). The film resistances were measured between two gold ohmic electrodes previously deposied by thermal evoparation. The type of conductivity of the layers was determined by the hot probe method.

3. Results and discussion

3.1 Structural properties

X-ray analysis Fig.1 (a) and (b) showed that the crystallinity of the films increases by increasing the annealing air temperature. The films annealed at temperatures below 200°C are amorphous. It may be noted that from the annealing tempearture 200°C, peaks assigned to (113), (109) and (213) planes appear which attributed to the $CuSbS_2$ phase.

Beyond 200°C, more peaks attributed to the $CuSbS_2$ phase appear. In addition, the films annealed at the temperatures 250°C and 300°C show additional peaks, which can be assigned to the oxyde compound Sb_2O_3. Consequently, only antimony oxides phases were formed and no copper oxides phases were detected. By comparaison, it is obvious that for the homologue amorphous $CuInS_2$ material (by replacing Sb by In), crystalline phase appears only by annealing the layers in air at temperatures higher than 200°C and we note the presence of the CuO and In_2O_3 as secondary phases[7]. So, annealing $CuSbS_2$ in air does not leads to the formation of copper oxide phases as the $CuInS_2$ material and probably could explain its p-type conductivity. The $CuInS_2$ after annealing in air exhibits a n-type conductivity. In the other hand and from the relationship between crystal grain size and X-ray line broadening, described by Scherer's equation $D = \frac{0.9\lambda}{\beta \cos\theta}$ (D = average crystallite dimension, λ is the X-ray wavelength, β = the full-width at half-maximum (FWHM), and θ the Bragg angle [10]). The average grain sizes of the air annealed $CuSbS_2$ thin films were found to be in the range 22 - 52 nm by using the diffraction line 111 of the $CuSbS_2$ film.

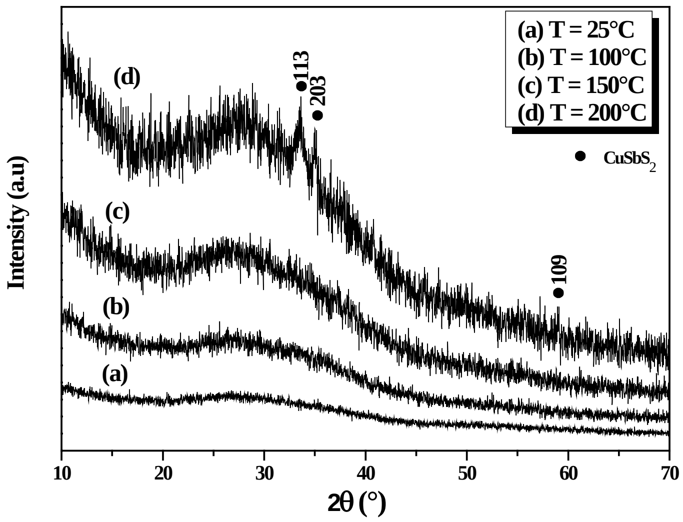

Fig.1(a): X-ray diffraction patterns of $CuSbS_2$ thin films annealed at different temperatures: (a) as-deposited , (b) 100°C, (c) 150°C and (d) 200°C.

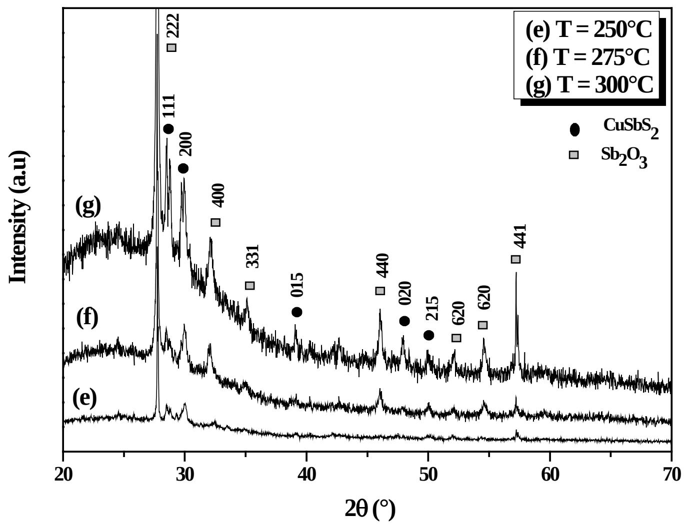

Fig.1(b): X-ray diffraction patterns of $CuSbS_2$ thin films annealed at different temperatures: (e) 250°C, (f) 275°C and (g) 300°C.

3.2. Optical properties

Optical transmittance (T) and reflectance (R) spectra of the $CuSbS_2$ thin films were recorded at different annealing air temperatures in the spectral range 300 – 1800 nm. This range covers the fundamental optical absorption edge and the transition regions of the semiconductor materials. The obtained spectra are shown in Figs (2) and (3). The transmittance and the reflectance spectra show interference patterns with sharp fall of the transmission at the band edge, which is an indication of good homogeneity of the films. The averages of the transmittance and the reflectance values of all the layers in the transparency region (600 - 1800 nm) are 50% and 25 % respectively.

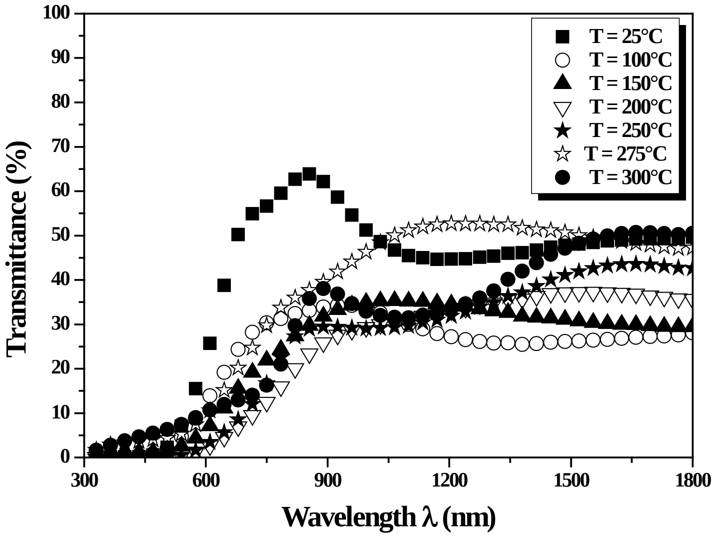

Fig.2: Optical transmittance spectra of $CuSbS_2$ thin films annealed at different temperatures.

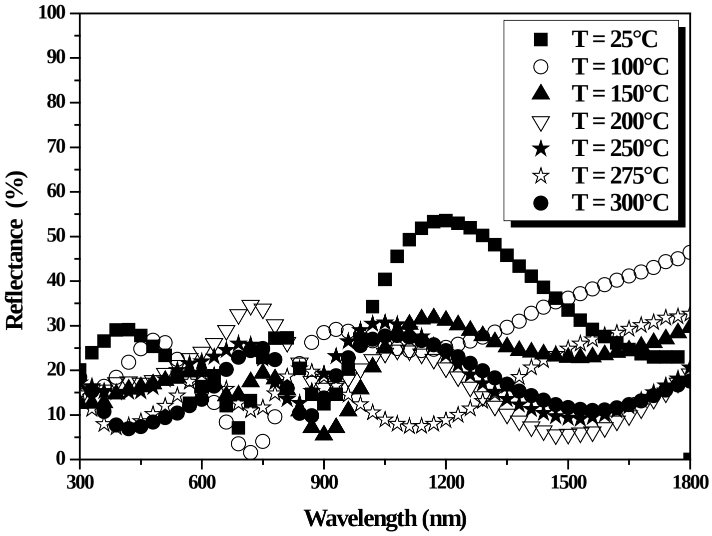

Fig.3: Optical reflectance spectra of $CuSbS_2$ thin films annealed at different temperatures.

The dependence of transmittance (T) and reflectance (R) on the wavelength in the spectral range from 300 - 1800 nm for the different films were used to calculate the absorption coefficient (Fig. 4) using the équation [11].

$$\alpha = \frac{1}{d}.Ln\left[\frac{(1-R)^2}{T}\right]$$

Where d is the the film thickness.

All films have relativety high absorption coefficients between $10^5 cm^{-1}$ and $4.10^5 cm^{-1}$ in the visible and the near-IR spectral range.

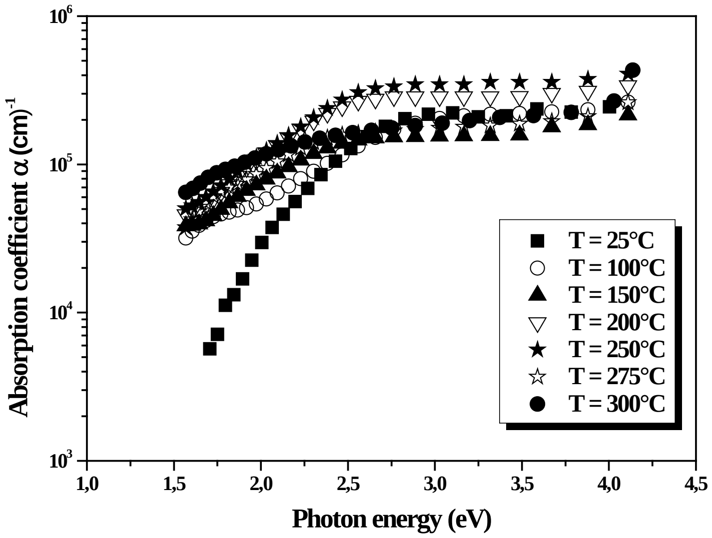

Fig.4: Absorption coefficients of $CuSbS_2$ thin films annealed at different temperatures.

It is well known that $CuSbS_2$ material is a direct gap semiconductor [12] with a band gap of about 1,53 eV [4]**.** Plotting $(\alpha h\nu)^2$ versus photon energy, hν, yields a straight line indicating direct optical transition (Fig. 5). The direct band gap energy decrases from 1,89 to 0,87 eV by increasing the annealing temperature from 100 to 300°C. For the annealing temperature in the range 250 – 300°C, a second optical direct transition was found at 3.7eV wich corresponding to the Sb_2O_3 phase [13].

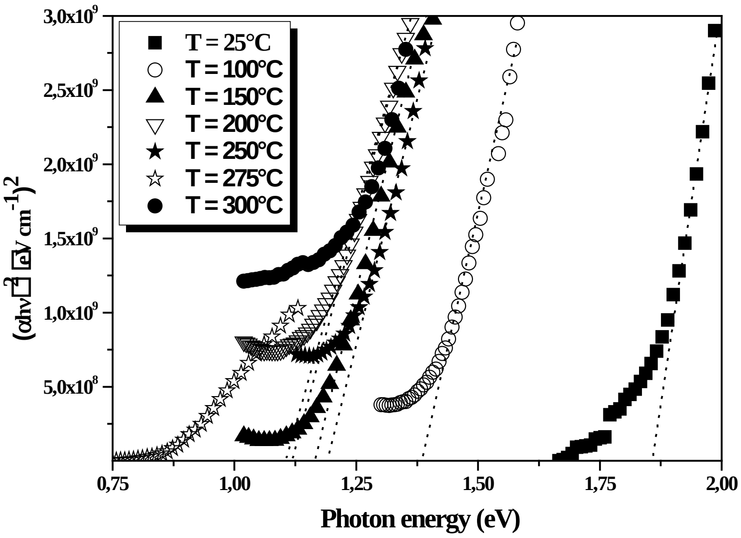

Fig.5: Plots of $(\alpha h\nu)^2$ versus hν for the $CuSbS_2$ thin films annealed at different temperatures.

3.3. Electrical properties

Fig. 6 shows the variation of the electrical resistance versus the annealing temperature T for the as-deposited layer, submitted to a thermal cycling for different annealing temperature values from 100 to 275°C. We note that from the annealing temprature 300°C, the layers start to degrade by the detachment of the films. However, the values of the resistances in the cooling cycle are higher than the resistances in the heating cycle.

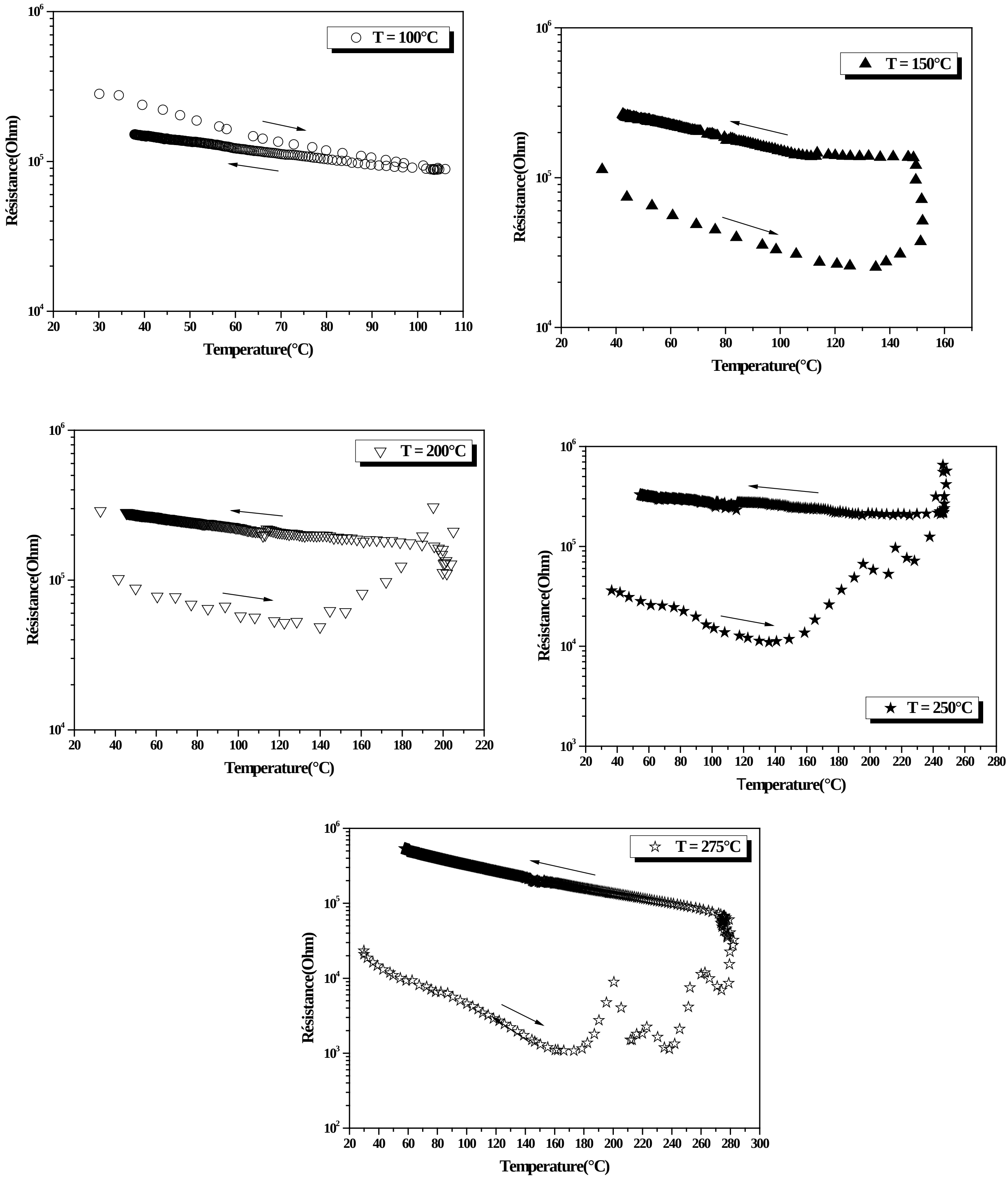

Fig.6: Variation of electrical resistance with annealing temperatures for the $CuSbS_2$ layers (→ heat cycle and ← cool cycle).

In the other hand, the dc conductivity σ (T) exhibits an activated temperature dependence, in accordance with the Arrhenius relation [14]: $\sigma (T) = \sigma_0 \exp(-E_a / k T)$

Here, σ_0 the pre-exponential factor. On the other hand the variations of Log (R) versus $10^3/T$ for all the $CuSbS_2$ layers are shown in (Fig. 7). It was observed that for all the layers, R (T) varied linearly with $10^3/T$ in accordance with the relation [15]:

$$R(T) = R_0(T)\exp(-E_a / k\,T)$$

Where, E_a is the corresponding activation energy and k the Boltzmann constant.

The observed linear behaviors in the studied temperature range imply thermally activated conduction. There is a monotonic dependence of both film resistance R (T) and activation energy for conduction E_a on chalcostibite films. It was observed that activation energy E_a and film resistivity at room temperature R decrease continuously with increasing the annealing temperature. Hot-probe measurement confirmed that the conductivity is p-type for all the layers, in agreement with that reported in Refs. [4]. In previous works [7], we have been shown that after annealing in air the $CuInS_2$ material exhibits an n-type conductivity. So when we substitute Indium by Antimony and after annealing in air, $CuInS_2$ compound exhibits n-type conductivity where $CuSbS_2$ compound exhibits p-type conductivity.

Consequently an heterojunction $CuInS_2$ (n)/ $CuSbS_2$ (p) is possible to develop. In this case $CuSbS_2$ with its high absorption coefficient offers perspective as an interest absorber material in solar cells applications.

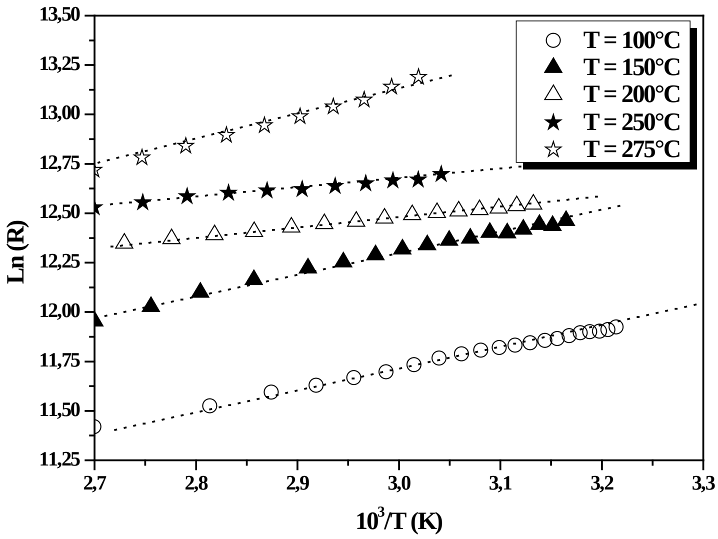

Fig.7: Plots of Ln(R) versus $\frac{10^3}{T}$ for the $CuSbS_2$ thin films annealed at different temperatures.

4. Conclusions

Amorphous $CuSbS_2$ thin films were prepared by vaccum thermal evaporation technique. The effect of post-growth treatments in air atmosphere on the structural, optical and electrical properties of the as-deposited $CuSbS_2$ thin films is studied. The air annealing temperatures were taken in the range 100-300°C. It has been shown that the annealing temperature must be grater than 200°C to obtain crystallizes material. All films have relativety high absorption coefficients between $10^5 cm^{-1}$ and $4.10^5 cm^{-1}$ in the visible and the near-IR spectral range.The optical gap energy (E_g) decreases by increasing the air annealing temperature from 1.89 eV to 0.87 eV and the films become more opaque. A second direct energy gap at 3.7 eV was also found for the layers annealed at temperatures higher than 200 °C which attributated to the Sb_2O_3 phase. After annealing all the films exhibit p-type conductivity and the air annealing consolidates this p-type conductuivity. On the contrary, its homologue $CuInS_2$ exhibits n-type conductivity after air annealing. So, these characteristics reported in this work offer perspective for $CuSbS_2$ as a stable p-type material may be after air annealing. And can be a good candidate as an absorber material in solar cells applications.

References

[1] J. Zhou, G. Bian, Q. Zhu, Y. Zhang, C. Li, J. Dai, Solvothermal crystal growth of $CuSbQ_2$ (Q = S, Se) and the correlation between macroscopic morphology and microscopic structure, Jounral of Solid State Chemistry **182**, 259 (2009).
[2] S. C. Ezugwu, F. I. Ezema, P. U. Asogwa, Chalcogenide Letters **7,** 369 (2010).
[3] P.U. Asogwa, Ph. D. The Pacific Journal of Science and Technology **10**, 812 (2009).
[4] Y. Rodríguez-Lazcano, M. T. S. Nair, P. K. Nair, J. Electrochem. Soc. **152**, 635 (2005).
[5] L.K. Samanta, S. Chatterjee, Phys. Stat. Sol. B **182**, 85 (1994).
[6] D. Avellaneda, M. T. S. Nair, P. K. Nair, Mater. Res. Soc. Symp. Proc. **12**, 1012 (2007).
[7] M. Ben Rabeh, M. Kanzari, B. Rezig, Thin Solid Films **515**, 5943 (2007).
[8] L. Vriens, W. Rippens, Appl. Opt. **22**, 4105 (1983).
[9] A. Rabhi, M. Kanzari, B. Rezig, Materials Letters **62**, 3576 (2008).
[10] V.K. Gandotra, K.V. Ferdinand, C. Jagadish, A. Kumar, P.C. Mathur, Phys. Stat. Sol. A **98**, 595 (1986).
[11] D.E. Milovzorov, A.M. Ali, T. Inkuma, Y. Kurata, T. Suzuki, S. Hasegawa, Thin Solid Films **382**, 47 (2001).
[12] M. Modreanu, M. Gartner, N.Tomozeiu, A. Szekeres, J. Optoelectron. Adv. Mater. **3**, 575 (2001).
[13] N. Tigau, Rom. J. Phys. **53**, 203 (2008).
[14] A. F. Qasrawi, N. M. Gasanly, Semicond. Sci. Technol. **20**, 446 (2005).
[15] M. Dongol, M. Abou Zied, G.A. Gamal, A. El-Denglawey, Appl. Surf. Sci. **161**, 365 (2000).