

Preparation and characterization of $\text{Cu}_2\text{ZnSnSe}_4$ thin films grown from ZnSe and Cu_2SnS_3 precursors in a two stage process

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Abstract. Compound of the kesterite familie has been considered as an alternative absorber layer in the manufacture of thin film solar cells due to its earth abundant and environmental friendly constituents and high absorption coefficient. In this work we propose a new route to grow single phase $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) thin films with tetragonal-kesterite type structure; this consist in sequential evaporation of thin films of CuSe , SnSe and ZnSe in a two stage process. Measurements of X-ray diffraction (XRD) revealed the formation of the $\text{Cu}_2\text{ZnSnSe}_4$ compound, grown with tetragonal Kesterite type structure. Optical characterization performed through spectral transmittance measurements established that this compound has high absorption (absorption coefficient $> 10^4 \text{ cm}^{-1}$) and a forbidden energy gap of 1.46 eV; these results indicate that the CZTSe thin films we have prepared has properties suitable for later use as absorber layer in solar cells. Results regarding electrical transport properties determined from temperature dependent conductivity measurements are also reported

1. Introduction

Recent growth of the thin-film PV industry and champion cell efficiencies of 20% for $\text{Cu}(\text{InGa})\text{Se}_2$ [1], demonstrate that thin film photovoltaics (PV) is becoming a viable option for large-scale power generation. However, due to the limited availability of In, some concern exists that high material expenses restrict the capacity to lower production costs, especially in view of the desired industrial mass production. Kesterites used as thin film solar cell absorbers have attracted much attention in the past years [2-4] due to the fact that this material has several promising attributes for efficient, inexpensive solar cells made from abundant and nontoxic elements. Efficiencies of up to 11.1 % [5] have been reported for $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ -based photovoltaic devices. Clearly, CZTSe is a new material with very high potential for future PV industrial mass production, but advances in both material quality and device structures are needed.

Several groups have reported the fabrication of CZTSe thin films using a variety of methods such as co-evaporation [6,7] and selenization of elemental and binary chalcogenides precursors, deposited with different techniques such as, evaporation, sputtering and non-vacuum processes [8-12]. In this work, we report on studies performed to get conditions to grow $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) thin-films by means of a solid state chemical reaction between the binary chalcogenide precursors sequentially



deposited, followed by annealing in selenium atmosphere at temperatures around 500°C. The optical, structural and electrical properties of CZTSe thin films has also been investigated.

2. Experimental

Thin films of $\text{Cu}_2\text{ZnSnSe}_4$ were grown by means of a solid state chemical reaction between the binary chalcogenide precursors sequentially deposited on a soda lime glass substrate in a two stage process. In the first stage the binary CuSe, SnSe and ZnSe precursors are sequentially deposited in high vacuum environment; The CuSe and SnSe layers are deposited by co-evaporation of its elemental precursors and the ZnSe layer is deposited by evaporation of the compound. In the second stage the CZTSe compound is formed by annealing the stacked CuSe/SnS/ZnSe system at a temperature of 500 °C, under Se atmosphere.

In Fig.1 is shown the system used to prepare the CZTSe films This is equipped with two tungsten boats to evaporate Cu and Sn, and two effusion cells used to evaporate ZnSe and Se respectively. The background pressure of the vacuum chamber was around 1×10^{-5} mbar. The temperatures of each effusion cells are controlled using PID temperature controllers. The deposition rates were monitored with a thickness monitor which uses a quartz sensor as transducer.

To find conditions to grow single phase CZTSe films with kesterite structure, a broad number of samples were deposited on glass substrates under different sequences (CuSe/SnSe/ZnSe, SnSe/CuSe/ZnSe) and varying the main deposition parameters (post deposition annealing temperature, deposition rate, mass ratio of the elemental precursors) in a wide range. XRD measurements carried out to each one of the prepared samples allowed us to find the sequence and deposition parameters which lead to the growth of $\text{Cu}_2\text{ZnSnSe}_4$ thin films with kesterite structure. The study revealed that single phase CZTSe films can be grown using the CuSe/SnSe/ZnSe sequence and the deposition routine displayed in fig. 1b. Samples prepared using any other sequence and/or deposition routines, grow in general with a mixture of the CZTSe phase and secondary phases

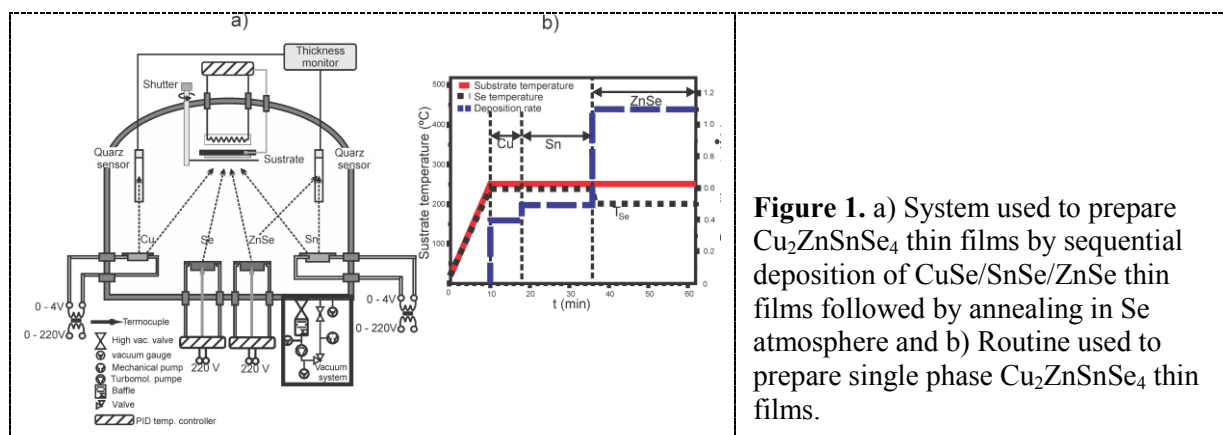


Figure 1. a) System used to prepare $\text{Cu}_2\text{ZnSnSe}_4$ thin films by sequential deposition of CuSe/SnSe/ZnSe thin films followed by annealing in Se atmosphere and b) Routine used to prepare single phase $\text{Cu}_2\text{ZnSnSe}_4$ thin films.

The electrical properties of the CZTSe films were studied through temperature dependent conductivity measurements and the optical properties through transmittance measurements carried out on a Oriel VIS-NIR spectrophotometer. Further characterization involved X-ray diffraction on a Shimadzu-6000 diffractometer. The film thickness was determined using a Veeco Dektak 150 surface profiler.

3. Results and Discussion

3.1. Structural characterization

Fig. 2, shows the XRD pattern of a CZTSe thin film prepared by sequential deposition of thin films of CuSe, SnSe and ZnSe, using a preparation routine like that plotted in Fig.1b and evaporated mass of Cu, Sn and ZnSe of 0.01 gr., 0.07 gr. and 0.15 gr. respectively. In order to identify with a greater degree of accuracy the reflexions corresponding to secondary phases that could be present in the

diffractogram of the CZTS films, this is compared with those of thin films of CuSe, SnS, ZnSe and ternary chalcogenides of Cu and Sn (CTSe). The CuSe and SnSe layers were deposited by co-evaporation of its elemental precursors at 250°C followed by annealing at 500° in Se atmosphere and the ZnSe layer was deposited by evaporation of the compound at 250°C followed by annealing at 500°C. The ternary CTSe layer was prepared by sequential deposition of CuSe/SnSe at 250°C followed by annealing at 500°C in Se atmosphere.

It is observed that the diffractogram of the CZTSe film shows only reflections corresponding to the Cu₂ZnSnSe₄ phase grown with tetragonal-kesterite type structure (PDF card #00-052-0868), oriented preferentially along the (112) plane. The diffractograms taken on thin films of binary chalcogenides show that these samples grow in the Cu₂Se (PDF card #03-065-7737), SnSe (PDF card # 00-032-1382), SnSe₂ (PDF card # 00-023-0602), and ZnSe PDF card #01-080-0021) phases respectively. The XRD pattern of the ternary compound shows that this compound grows with a mixture of the Cu₂SnSe₃ (PDF card #03-065-7524) and Cu₂Se phases being Cu₂SnSe₃ the majority phase.

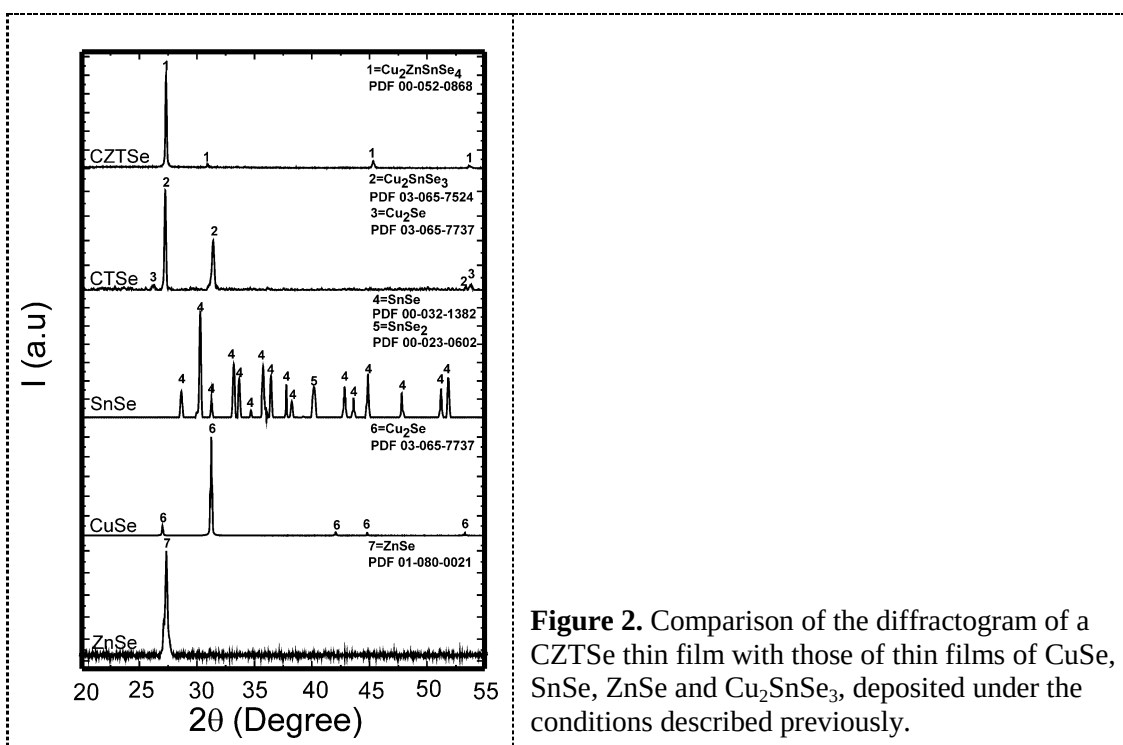
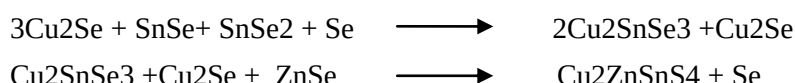


Figure 2. Comparison of the diffractogram of a CZTSe thin film with those of thin films of CuSe, SnSe, ZnSe and Cu₂SnSe₃, deposited under the conditions described previously.

From this study may be established that a possible route for the formation of the Cu₂ZnSnSe₄ compound is the following:

The sequential evaporation of Cu and Sn at 250°C in presence of elemental selenium followed by annealing at 500°C results in the formation of a mixture of Cu₂SnSe₃ and Cu₂Se. The subsequent evaporation of ZnSe at 250°C and further annealing at 500°C leads to the formation of a single phase Cu₂ZnSnSe₄ film, according to the following reaction.



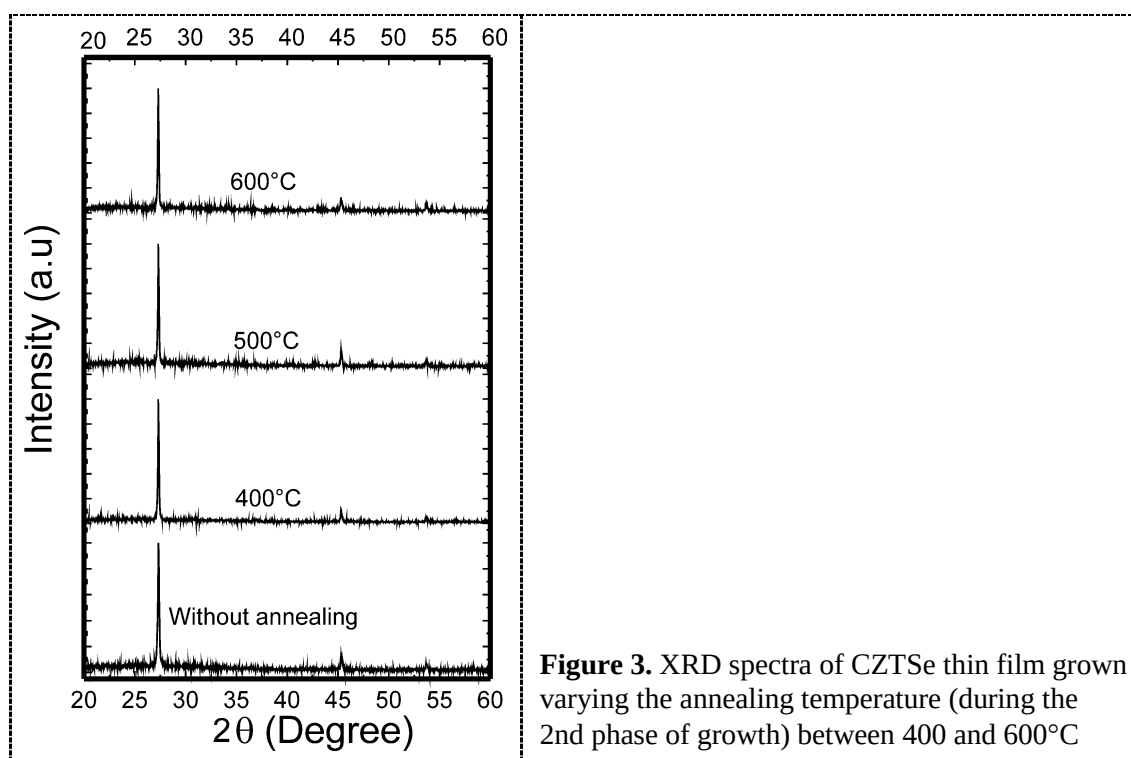


Figure 3. XRD spectra of CZTSe thin film grown varying the annealing temperature (during the 2nd phase of growth) between 400 and 600°C

The effect of annealing temperature of the CuSe/SnS/ZnSe system (during and growth phase), on the structural properties of CZTSe films was also studied. Figure 3 shows XRD spectra corresponding to a CZTSe thin film formed by annealing at temperatures ranging between 400 and 600 °C. This results indicates that in the range studied, the annealing temperature does not affect the phase in which the CZTSe films grow, probably because the thin films obtained at the end of the sequential deposition of precursors at 250°C exhibit a stable $\text{Cu}_2\text{ZnSnS}_4$ phase; the subsequent annealing not affect either the phase or the lattice constants, only affects the density of native and structural defects.

3.2. Optical characterization

In Fig.4 is compared the transmission spectrum of a single phase $\text{Cu}_2\text{ZnSnS}_4$ thin film with those of thin films of CuSe, SnSe, ZnSe and ternary chalcogenides of Cu and Sn. The samples were prepared as described previously. It is observed that with the exception of ZnSe films, all other studied samples exhibit low transmittance values, indicating that the CZTSe, SnSe and CuSe films grow with a high density of native defects (vacancies, interstitial and antisite).

These defects generate absorption centers within the energy gap which contribute to the photon absorption. In particular, the transmittance of the CuSe films decreases strongly in the NIR region apparently due to the formation of a very high density of shallow defects. It is also observed that the transmittance curve of the SnSe film has a very small slope. This behavior seems to be caused by absorption of photons in deep centers generated by structural defects.

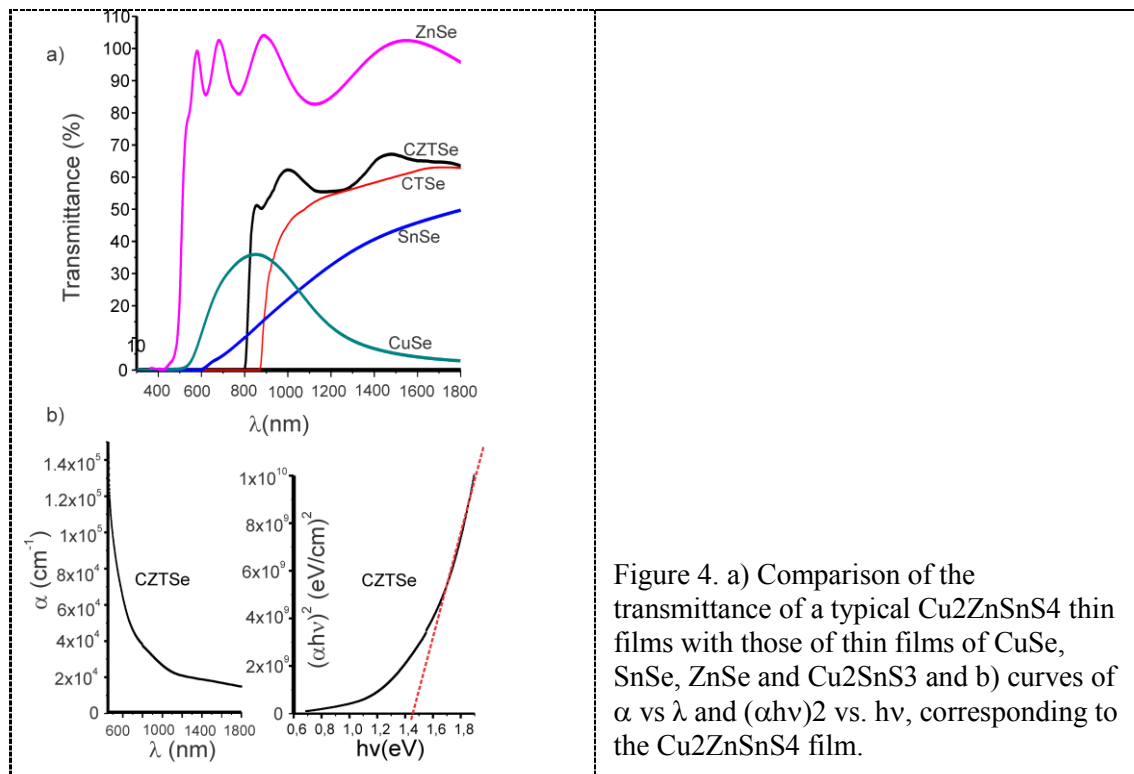


Figure 4. a) Comparison of the transmittance of a typical Cu₂ZnSnS₄ thin films with those of thin films of CuSe, SnSe, ZnSe and Cu₂SnS₃ and b) curves of α vs λ and $(\alpha hv)^2$ vs. $h\nu$, corresponding to the Cu₂ZnSnS₄ film.

The optical gap of the CZTSe thin film was determined by extrapolation of the $(\alpha hv)^2$ vs. $h\nu$ curve with the $h\nu$ axis. The absorption coefficient α was estimated using the relation $T(\lambda) \approx (1-R(\lambda)) \exp(-\alpha d)$, where $T(\lambda)$ is the spectral transmittance, $R(\lambda)$ the spectral reflectance and d the film thickness. An E_g value of 1.45 eV was found for the CZTSe films.

The effect of annealing temperature during 2nd growth phase, on the optical properties of CZTSe films was also studied through transmittance measurements. Fig. 5 shows transmittance spectra corresponding to a CZTSe thin film grown at annealing at temperatures varying between 400 and 600 °C. This results indicates that in the range studied, the annealing temperature significantly affect the transmittance of the CZTSe films. It is observed that not annealed samples or annealed at temperatures less than 500°C have both, low transmittance as small slope compared with samples annealed at temperatures around 500°C and higher. This behavior indicates that the annealing at high temperatures reduces the density of both, native defects and structural defects. Shifting of cutoff wavelength to lower wavelength values observed in samples annealed at 500°C is apparently due to increased grain size.

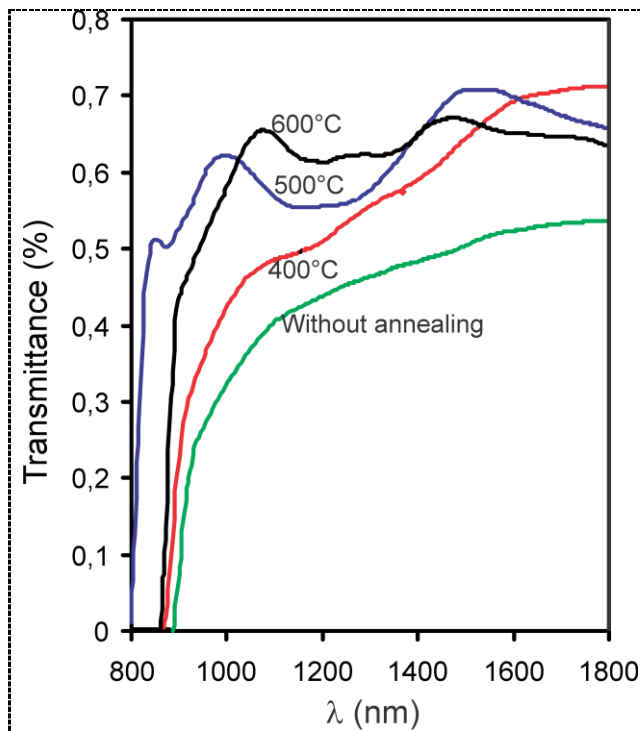


Figure 5: Transmittance spectra of CZTSe thin film grown varying the annealing temperature during the 2nd phase of growth, between 400 and 600°C

3.3. Electrical characterization

Fig. 6 shows curves of both, σ vs T and $\ln\sigma$ vs $1000/T$, obtained with a CZTSe film grown in the $\text{Cu}_2\text{ZnSnS}_4$ phase as described in section 2.

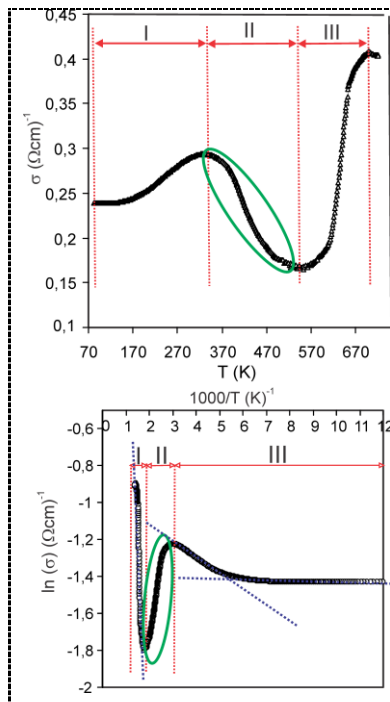


Figure 6: Curves of σ vs. T and $\ln(\sigma)$ vs. $1000/T$ corresponding to a typical $\text{Cu}_2\text{ZnSnS}_4$ thin film

It is observed in Fig.6 that in the regions designated as I and III, the conductivity increases as the temperature increases indicating a typical behaviour of semiconductor materials; however it is observed that in the region II the conductivity decreases with increasing temperature. The abnormal

behavior in the region II is caused by a phase change of the CZTS compound induced by the sample heating and not by an effect of temperature on the transport properties; this was verified by XRD measurements in dependence of the temperature, which indicated that these samples grow preferentially in the Cu₂ZnSnS₄ phase with the presence of Cu and Sn selenides in small proportions; however, when the sample is heated above 350K, begins a transformation of binary phases into the Cu₂ZnSnS₄ phase. At temperatures of the order of 550K the sample only contains the Cu₂ZnSnS₄ phase, which is stable as the temperature continues to increase.

The behavior of the $\ln\sigma$ vs. $1000/T$ curve plotted in Fig. 6b indicates that in the regions I and III, the conductivity of the CZTSe films can be expressed by the relation: $\sigma = \sigma_0 \exp[-(E_C - E_F)/(kT)]$ indicating that the conductivity is predominantly affected by free carrier transport in states of the valence band. The increase in conductivity with increasing temperature is apparently caused by an increase in the density of charge carriers generated by native acceptor impurities. In the range of high temperatures ($T > 550$ K), the increase of σ could be attributed to an increase of the carrier density coming from deep acceptor impurities presents in the Cu₂ZnSnS₄ compound, whereas the change of σ observed in the range of low temperatures ($T < 350$ K) can be attributed to a change of the carrier density coming from shallow acceptor impurities associated to the binary phases. The two slopes identified in the $\ln\sigma$ vs. $1000/T$ curve (high temperature region) indicates that the conductivity of the CZTS films is affected by two different types of impurities (probably vacancies and antisite defects). At temperatures greater than 700K, the conductivity begins to decrease with increasing temperature indicating a saturation of the thermal excitation of free carriers from the impurities. The decrease in conductivity with increasing temperature could be then attributed to an increased mobility with temperature. The results also revealed that the Cu₂ZnSnS₄ films are characterized to get high absorption and an energy band gap of about 1.45 eV, indicating that this compound is suitable to perform as absorbent layer in thin film solar cells.

Conductivity measurements on temperature dependence revealed that conductivity of the CZTSe films is predominantly affected by free carrier transport in states of the valence band. In the range of high temperatures ($T > 550$ K), the increase of σ could be attributed to an increase of the carrier density coming from deep acceptor impurities, whereas the change of σ observed in the range of low temperatures ($T < 350$ K) can be attributed to a change of the carrier density coming from shallow acceptor impurities associated to secondary phases.

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4. Conclusions

CZTSe thin films with tetragonal-kesterite type structure were grown using a method based on sequential evaporation of thin films of CuSe, SnSe and ZnSe in a two stage process. Characterization performed by XRD gave evidence of the formation of single phase CZTSe films with kesterite structure using optimized growth parameters; however the sequence in which the binary precursors are evaporated and the preparation parameters, significantly affects the phase and morphology, as well as the structural, optical and electrical transport properties of the CZTS films. Optical characterization performed by spectral transmittance measurements revealed that the CZTSe films have low transmittance and poor crystallographic quality, probably associated to structural and native defects, indicating that further studies must be done to improve the properties of the CZTSe films.

5. References

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