

SYNTHESIS AND CHARACTERIZATION OF Cu_2SnSe_3 THIN FILMS COMPOUND USED IN THE FABRICATION OF SOLAR CELLS

SÍNTESIS Y CARACTERIZACIÓN DEL COMPUESTO Cu_2SnSe_3 COMO PRECURSOR DE PELÍCULAS DELGADAS APLICADAS EN CELDAS SOLARES

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Abstract

The purpose of this paper is to contribute to the development of materials used in the fabrication of solar cells based on Kesterite type compounds which are being widely investigated because they possess excellent photovoltaic properties and their precursor elements are nontoxic, inexpensive and abundant in nature. We present details of the synthesis and optimization of optical and structural properties of the ternary Cu_2SnSe_3 (CTSe) compound which is used as a precursor in the synthesis of the $\text{Cu}_2\text{ZnSnSe}_4$. The CTSe compound is formed by a solid state reaction of the metal precursors sequentially evaporated in the presence of elemental selenium, in a two stage process. The optimization of the properties of the CTSe was achieved studying the effect of synthesis parameters on optical, electrical and structural properties through spectral transmittance, electrical conductivity and X-ray diffraction measurements. The results indicated that these compounds grow with cubic structure and have an optical bandgap of 1.6 eV.

Keywords: Cu_2SnSe_3 , Thin Film, Solar Cell, Structural and Optical Properties

Resumen

El propósito de este trabajo es contribuir al desarrollo de materiales usados en la fabricación de celdas solares basadas en películas en compuestos con estructura tipo kesterita que están siendo ampliamente investigadas debido a que poseen excelentes propiedades fotovoltaicas y sus elementos precursores son no tóxicos, de bajo costo y abundantes en la naturaleza. Se presentan detalles de la síntesis y optimización de las propiedades ópticas y estructurales del compuesto ternario Cu_2SnSe_3 (CTSe) que es empleado como precursor en la síntesis del compuesto $\text{Cu}_2\text{ZnSnSe}_4$. El compuesto CTSe es formado a través de una reacción en estado sólido de sus precursores metálicos evaporados secuencialmente en presencia de selenio elemental, en un proceso de dos etapas. La optimización de las propiedades del compuesto CTSe se realizó estudiando el efecto de los parámetros de síntesis sobre las propiedades ópticas, eléctricas y estructurales a través de medidas de transmitancia espectral, conductividad eléctrica y difracción de rayos-x. Los resultados indicaron que este tipo de compuestos crecen con estructura cúbica y presentan un gap óptico de 1,6 eV.

Palabras clave: Películas delgadas, Cu_2SnSe_3 , celdas solares, propiedades ópticas y estructurales

Introduction

Ternary and multinary compound semiconducting materials with direct optical band gap between 1.1 to 1.5 eV are being explored as candidates for absorb layer in thin film solar cells. CuInGaSe_2 thin film solar cells achieved at laboratory level and efficiency record of 20.3 % [1] laboratory level. However, the elements In and Ga present in this material are expensive and scarce. $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) have received much attention

in recent years as alternative solar cell absorb layers, owing to their suitable properties and non-toxic nature. CZTS based thin film solar cells with laboratory efficiency of 8.4 % [2] have been reported. $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ -based solar cells using hydrazine-based solution process have already reached an energy conversion efficiency as high as 11.1 % [3], which demonstrates the effectiveness of the solution process in CZTSe-based solar cells.

Because Cu_2SnSe_3 (CTSe) is an important precursor for the growth of CZTSe via solid state reaction with ZnSe [4], a thorough understanding of the growth and properties of these precursor layers is essential. Techniques like co-evaporation [5], DC sputtering [6, 7] have been earlier used to deposit CTSe thin films. The present paper describes the procedure to prepare CTSe 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 400°C. The optical, structural and electrical properties of CTSe thin films have also been investigated.

Experimental

Thin films of Cu_2SnSe_3 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. The synthesis of $\text{Cu}_2\text{ZnSnSe}_4$ is quite difficult to achieve, however considering the phase diagrams of binary and pseudo-binaries system from the ZnSe-SnSe₂-Cu₂Se primary sulfides, it is possible to find a route suitable for the synthesis of this compound. Figure 1 shows the phase diagram of the ternary pseudo-binary primary sulfide ZnSe-SnSe₂-Cu₂Se, where possible routes for obtaining the phase $\text{Cu}_2\text{ZnSnSe}_4$ are appreciated.

According to the phase diagram of the ternary pseudo-binary ZnSe-SnSe₂-Cu₂Se system, several routes can lead to the formation of $\text{Cu}_2\text{ZnSnSe}_4$ compound; however we have grown this compound by a solid state chemical reaction of the ZnSe and Cu_2SnSe_3

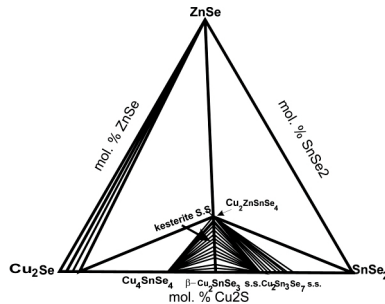


FIGURE 1. Phase diagram of the ternary pseudo-binary primary sulfide $\text{ZnSe} - \text{SnSe}_2 - \text{Cu}_2\text{Se}$, which provide information on the molar proportions required to obtain the $\text{Cu}_2\text{ZnSnSe}_4$ phase. [8]

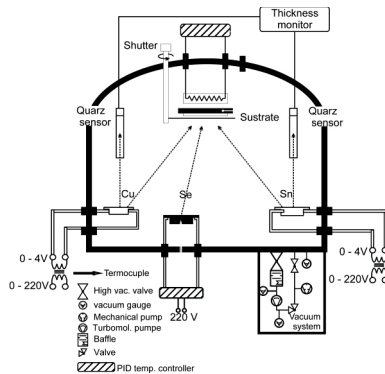


FIGURE 2. System used to prepare Cu_2SnSe_3 thin films by sequential deposition of CuSe/SnSe thin films followed by annealing in Se atmosphere.

precursors, where the ternary precursor is obtained by a solid state reaction of the binary Cu_2Se and SnSe_2 compounds sequentially deposited in a two stage process. This process was performed in a vacuum cabinet (Figure 2), in the first stage, the Cu_2Se and SnSe_2 layers are sequentially deposited by co-evaporation of its elemental precursors at 250°C . In the second stage the CTSe compound is formed by annealing the stacked CuSe/SnSe system at a temperature of 400°C , in a Se atmosphere to evaporate Cu and Sn , and an effusion cell to evaporate Se .

The background pressure of the vacuum chamber was around 1×10^{-5} mbar. The temperature of the effusion cell is controlled using PID temperature controller. The deposition rates were monitored with a thickness monitor which uses a quartz sensor.

In order to find the growth conditions of the CTSe films containing predominantly the Cu_2SnSe_3 phase, a broad number of samples were deposited on glass substrates under different sequences (CuS/SnSe, SnSe/CuSe) 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 Cu_2SnSe_3 thin films. The study revealed that CTSe films can be grown using the CuSe/SnSe sequence and the deposition routine displayed in Fig. 3.

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

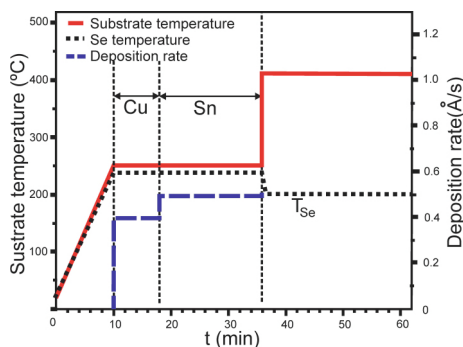


FIGURE 3. Routine used to prepare Cu_2SnSe_3 thin films

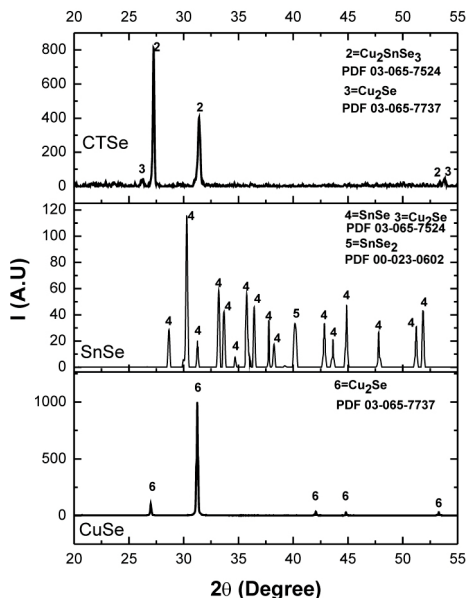


FIGURE 4. Comparison of the diffractogram of a Cu_2SnSe_3 thin film with those of thin films of CuSe , SnSe deposited under the conditions described previously

Results and Discussion

Structural characterization

Figure 4, shows the XRD pattern of a CTSe thin film prepared by sequential deposition of CuSe and SnSe thin films, using a preparation routine like that plotted in Fig. 3 and evaporated masses of Cu and Sn of 0.01 and 0.07 g respectively. The Figure 4 shows the XRD for films of CuSe and SnSe . These are compared with the CTSe diffractogram in order to identify with a greater degree of accuracy the reflections corresponding to secondary phases in the CTSe thin film.

It is observed that the diffractogram of the CTSe film shows reflections corresponding to the Cu_2SnSe_3 phase (PDF cart #03-065-7524) and to the Cu_2Se phase (PDF cart #03-065-7737). The diffractograms of copper selenide thin films present only the Cu_2Se phase (PDF cart #03-065-7737), whereas the diffractogram of tin selenide indicates a mixture of both SnSe_3 (PDF cart

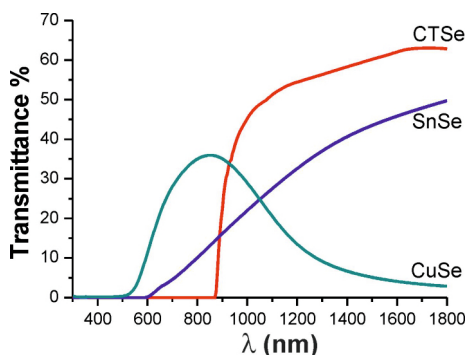


FIGURE 5. Comparison of the transmittance of a typical Cu_2SnSe_3 thin film with those of thin films of CuSe and SnSe

#03-065-7524) and SnSe_2 (PDF cart #00-23-0602) phases.

From this study can be established that the sequential evaporation of Cu and Sn at 250°C in presence of elemental selenium followed by annealing at 400°C results mainly in the formation of a mixture of Cu_2SnSe_3 and Cu_2Se . The XRD study also revealed that the co-evaporation of Cu and Se at 250°C followed by annealing at 400°C leads to the formation of a single phase of Cu_2Se , whereas the co-evaporation of Sn and Se at 250°C followed by annealing at 400°C leads to the formation of a mixture of SnSe_3 and SnSe_2 phases.

Optical characterization

In Fig. 5 is compared the transmission spectrum of a Cu_2SnSe_3 thin film with those of CuSe and SnSe thin films, which were prepared as described previously.

It is observed that the studied samples exhibit low transmittance at wavelengths longer than that corresponding to the cut-off wavelength, indicating that the CTSe, SnSe and CuSe films grow with a high density of native defects, that generate absorption centers within the energy gap which contribute to the photon absorption. The presence of native defects on $\text{Cu}_2\text{ZnSnSe}_4$ have been identified by other authors [9] on the basis of a structural analysis of neutron powder diffraction data. This compound was

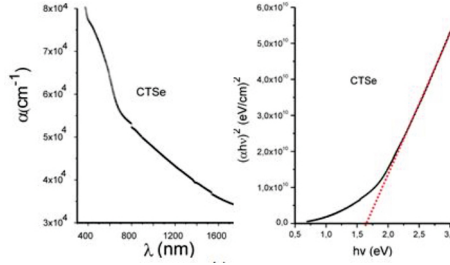


FIGURE 6. curves of α vs λ and $(\alpha h\nu)^2$ vs. $h\nu$, corresponding to the Cu_2SnSe_3 film.

found to crystallize in the kesterite type structure, but with a disorder within the Cu-Zn layers at z 1/4 and 3/4. The latter causes CuZn and ZnCu anti-site defects, whose concentration depends on the sample growth conditions.

In particular, the transmittance of the CuSe films decreases strongly near infrared (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 shallow centers generated by structural defects.

The optical gap of the CTSe thin film (Fig. 6) was determined by extrapolation of the $(\alpha h\nu)^2$ vs $h\nu$ curve with the $h\nu$ axis. The absorption coefficient α was estimated using the relation $T(\lambda) = (1 - R(\lambda))^2 \exp(-\alpha d)$ [10], where $T(\lambda)$ is the spectral transmittance, $R(\lambda)$ the spectral reflectance and d the film thickness which in this case corresponds to a sample $0.8\mu\text{m}$ thick. An E_g value of 1.6 eV was found for the CTSe films.

Electrical characterization

It is observed in Fig. 7 that the conductivity increases as the temperature increases indicating a typical behavior of semiconductor materials. The behavior of the $\ln \sigma$ vs $1000/T$ curve plotted in Fig. 8 indicates that the conductivity of the CTSe films can be expressed by the relation: $\sigma = \sigma_0 \cdot \exp[-\Delta E/kT]$ where E is the activation energy. This result shows that the conductivity

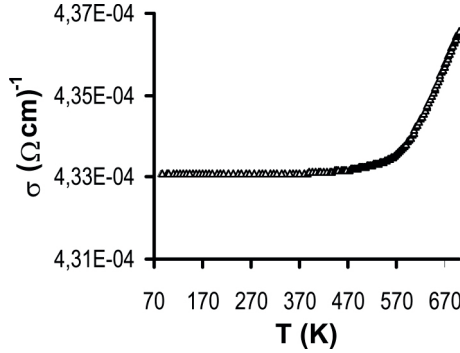


FIGURE 7. Curve of σ vs T for a CTSe film grown as described in section 2

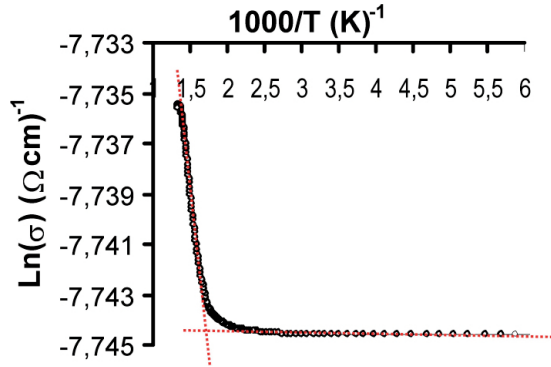


FIGURE 8. Curve of $\ln \sigma$ vs $1000/T$, for a CTSe film grown as described in section 2.

is predominantly affected by free carrier transport in states of the valence band [11]. Considering that the mobility decreases with increasing temperature (from 11 to 9.5 cm^2/Vs in the studied temperature range), the increase in conductivity with increasing temperature is mainly caused by an increase in the density of charge carriers apparently generated by native acceptor impurities.

Considering that the activation energy in the range of high temperatures $T > 550$ K is significantly higher than that observed in the low temperature range, the increase of σ at $T > 550$ K could be attributed to an increase of the carrier density coming from deep acceptor impurities presents in the Cu_2SnSe_3 compound, whereas the change of σ observed in the range of low temperatures

($T < 350K$) 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 indicates that the conductivity of the CZTS films is affected by two different types of impurities, which could be vacancies and antisite defects that have been reported elsewhere.[12]

Conclusions

Cu_2SnSe_3 thin films were grown using a method based on sequential evaporation of thin films of CuSe, and SnSe in a two stage process. Characterization performed by XRD gave evidence of the formation of a compound containing predominantly the Cu_2SnSe_3 phase; however the sequence in which the binary precursors are evaporated and the preparation parameters, significantly affects the phase as well as the structural, optical and electrical transport properties of the CTSe films. Optical characterization performed by spectral transmittance measurements revealed that the CTSe 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 CTSe films. The results also revealed that the Cu_2SnSe_3 films are characterized to get p-type conductivity and an energy band gap E_g of about 1.6 eV.

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

References

- [1] P. Jackson, D. Hariskos, E. Lotter, S. Paetel, R. Wuerz, R. Menner, W. Wischmann, and M. Powalla, *Prog. Photovoltaics* **19**, 894 (2011).
- [2] B. Shin, O. Gunawan, Y. Zhu, N. A. Bojarczuk, S. J. Chey, and S. Guha, *Prog. Photovoltaics* **21**, 72 (2013).
- [3] T. K. Todorov, J. Tang, S. Bag, O. Gunawan, T. Gokmen, Y. Zhu, and D. B. Mitzi, *Adv. Energy Mater.* **3**, 34 (2013).
- [4] P. U. Bhaskar, G. S. Babu, Y. K. Kumar, and V. S. Raja, *Appl. Surf. Sci.* **257**, 8529 (2011).
- [5] G. S. Babu, Y. K. Kumar, Y. B. K. Reddy, and V. S. Raja, *Mater. Chem. Phys.* **96**, 442 (2006).
- [6] H. Yoo, R. Wibowo, A. Holzing, R. Lechner, J. Palm, S. Jost, M. Gowtham, F. Sorin, B. Louis, and R. Hock, *Thin Solid Films* **535**, 73 (2013).
- [7] P. Salome, P. Fernandes, and A. da Cunha, *Thin Solid Films* **517**, 2531 (2009), thin Film Chalcogenide Photovoltaic Materials (EMRS, Symposium L).
- [8] H. Wang, *Int. J. Photoenergy* **2011**, 801292 (2011).
- [9] S. Schorr, *Sol. Energ. Mat. Sol. C.* **95**, 1482 (2011).
- [10] J. Pankove, *Optical Processes in Semiconductors*, Dover books in physics (Dover, 1971).
- [11] M. H. Brodsky, *Amorphous Semiconductors*, Topics in Applied Physics, Vol. 36 (Springer Berlin Heidelberg, 1986).
- [12] S. Chen, J.-H. Yang, X. G. Gong, A. Walsh, and S.-H. Wei, *Phys. Rev. B* **81**, 245204 (2010).