

Optical and structural characterization of CuInSe₂ (CIS) thin films grown by means of process in two stages

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CuInSe₂ thin films grown on soda lime glass substrate through a process which includes the chemical reaction between Cu and In_xSe_y (IS) thin films deposited sequentially by evaporation, followed by annealing in Se atmosphere at 550 °C, were characterized through spectral transmittance and XRD measurements. From the transmittance measurements the absorption coefficient and energy band gap was determined and the XRD measurements allowed us to identify the structure and phases present in the CIS compounds. Through a parameter study, the conditions to grow CIS thin film in chalcopyrite phase were found; this type of films presents good properties to be used as absorber layer in solar cells. The results revealed that the CIS films have an energy band gap of about 1.1 eV and absorption coefficient of the order of 10⁵ cm⁻¹ by wave lengths close to the cut off wavelength.

The x-ray spectra were analyzed with the help of the Powder Cell simulation program in order to get information regarding the influence of the preferential growth and to improve the reliability of the phases identification.

Keywords: Thin films; Solar cells; Lattice parameters; Optical constants

1. Introduction

Several semiconductor materials have been investigated for the fabrication of thin film solar cells. The best results however, have been obtained using CdTe CuInSe₂ (CIS) and Cu(In,Ga)Se₂ (CIGS) as absorber layer, CdS as buffer layer and SnO₂ or ZnO as transparent conductor [1,2]. The world record in conversion efficiency reported for thin films solar cells is 18.8%; this was obtained with a cell fabricated with the structure Mo/CIGS/CdS/ZnO [3]. The highest efficiency obtained with CdTe based solar cells is 16% which was obtained using the structure SnO₂/CdS/CdTe/C [4].

In this work, the deposition conditions were investigated to get CuInSe₂ thin film with adequate properties to be used as absorber layer of solar cells fabricated with the structure Mo/CuInSe₂/buffer/ZnO. The CuInSe₂ films were grown through a chemical reaction between the Cu and the IS film in a two stage process [5]. Following this procedure, CIS films were grown in the chalcopyrite phase which presents good properties for the fabrication of solar cells.

2. Deposition of the CuInSe₂ thin films

The preparation of the CIS layers was accomplished in a two stages process: In the first stage, the stacked Cu/(IS+Se) system is

sequentially deposited by evaporation. The Cu layer is deposited on soda lime glass substrate at room temperature and the IS + Se layer is deposited under a substrate temperature which vary linearly between 500 and 550 °C. In the second stage, the CuInSe₂ absorber is formed; for that, the Cu/(IS+Se) bilayer system is annealed in selenium environment at 550 °C during about 10 minutes. The last process is called selenization.

Fig.1 shows the system used to grow the CIS films by means of a two stages process and the substrate temperature routine typically followed during the formation of the CIS films. The temperature profile, shown in Fig 1b was achieved using a PID Eurotherm 9100 temperature controller. The Cu/In ratio was controlled by controlling the mass of Cu and In₂Se₃ which are evaporated during the first stage. The selenium flux during the selenization process is controlled through the evaporation temperature; temperatures ranging between 220 and 260 °C are typically used.

3. Result and discussion

3.1. Optical characterization

CIS samples deposited under different conditions were optically characterized through spectral transmittance measurements in the range between 1000 and 1800 nm. This measurements were carried out using a

Table 1. Values of the parameters used to deposit the CIS film whose transmittances are depicted in Fig. 3.

Sample	Structure	Thickness (μm)			Selenization time (min.)
		Cu-Layer	IS-Layer	CIS-Layer	
CIS-25	Cu/IS	1.3	1.5	3.2	0
CIS-26	Cu/IS+Se/Se	1.3	1.5	3.4	5
CIS-27	Cu/IS+Se/Se	1.3	1.5	3.4	10

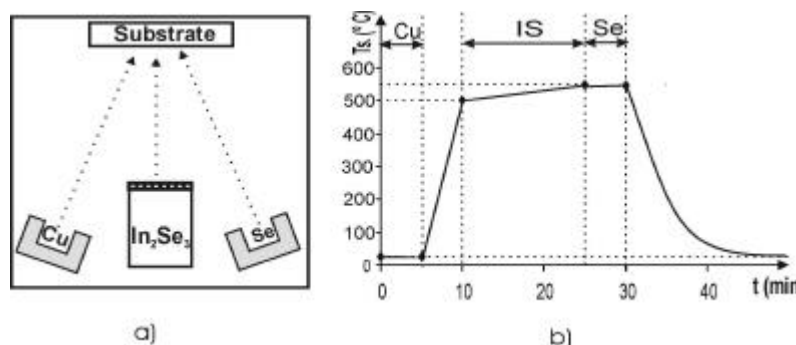


Figure 1. a) Schematic diagram of the system used to prepare CIS thin films and b) Substrate temperature routine followed during the formation of the CIS films.

spectrophotometer Oriel model 77200. The monochromator was calibrated with a multiband calibration filter (Didymium) in order to improve the wavelength measurements accuracy. Fig. 2 shows typical transmittance curves of CIS films deposited under the conditions indicated in table .1

It is observed that the cut off wavelength λ_c of the studied CIS samples differ each other, indicating that the optical gap and hence the chemical composition of the CIS films are influenced by the structure of the stacked layers used as precursors and by the selenization conditions. On the other hand, the transmittance of the samples is strongly influenced by the preparation conditions. This behavior seems to be related with an increase of absorption of light via states placed within the gap. This behavior is markedly observed in stoichiometric CIS samples, like the CIS-27.

Fig. 3a shows the variation of the absorption coefficient α as a function of the λ , and Fig. 3b depicts curves of $(\alpha h\nu)^2$ vs $h\nu$. The absorption coefficient was calculated using the transmission spectrum and calculations based on a model described in detail in the Ref. [6].

The results of Fig.3b show that at wavelength around the absorption edge, the absorption coefficient can be expressed by the relation $\alpha(h\nu)=A(h\nu-E_g)^{1/2}$, indicating that the CIS films present direct band gap. For these type of semiconductors the optical gap E_g can be determined by extrapolating the curve of $(\alpha h\nu)^2$ vs $h\nu$ to $\alpha=0$ in the spectral region close to λ_c . The intercept with the $h\nu$ axis gives the E_g value. The E_g values found for the samples CIS-25, CIS-26 and CIS-27 were 1.19, 1.07 y 1.01 eV

respectively.

3.2. XRD characterization

The phases of the CIS samples listed in Table 1 were identified though x-ray diffraction (XRD) measurements and theoretical simulation of the corresponding spectra. The measurements were made using the K_α line of the Cu ($\lambda=1.5406 \text{ \AA}$), a voltage of 40 kV and current of 30 mA.

Fig. 4 compares experimental XRD spectra correspondent to the samples CIS-25, CIS-26 and CIS-27 with those obtained theoretically using the Powder Cell simulation program.

In Table 2 are listed the phases, structure and values of lattice constants obtained from analysis of the XRD spectra depicted in Fig. 4, and in Table 3 are shown the composition percentages for each compound.

The results revealed that the $\alpha - \text{CIS}$ phase is formed in samples submitted to selenization after the deposition of the Cu/IS system. In no selenized samples (like the CIS-25) reflections were identified corresponding to the In_2Se_3 and CuIn_3Se_5 phases, indicating that the chemical reaction leading to the formation of the CIS phase is incomplete in this case. In samples selenized during a short time (less than 5 min) reflections were observed associated to the phases $\alpha - \text{CIS}$, Cu_2Se and InSe . Increasing the selenization time of the Cu/IS+Se system to about 10 - 15 minutes, the chemical reaction leads to samples which

Table 2. Spatial group, structure, lattices constants y preferential orientation corresponding to the phases found in the films deposited. It also shows the Wyckoff positions to carry out the simulation.

	CuInSe ₂			InSe		In ₂ Se ₃		Cu ₂ Se		CuIn ₃ Se ₅				
Spatial group	122 (T)			167 (H)		177 (H)		225 (C)		121 (T)				
Lattice constants (Å)	A	c		A	c	A	c	A		a		c		
	5.78	11.61		8.31	11.27	4.84	6.50	5.83		5.75		11.61		
Preferential orientation (plane)	112			11,0		00,2		111		112				
Wyckoff positions	Cu	In	Se	In	Se	In	Se	Cu	Se	Cu	In	Se*		
	4a	4b	8d	18d	18e	2c	3f	8c	4a	2a	2b	4d	4c	8h

(T)=tetragonal, (H)=hexagonal, (C)=cubic.

* Two atoms were eliminated from the structure

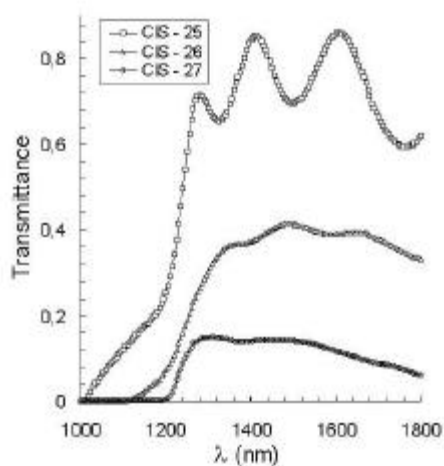


Figure 2. Transmittance curves of CIS films prepared under different conditions.

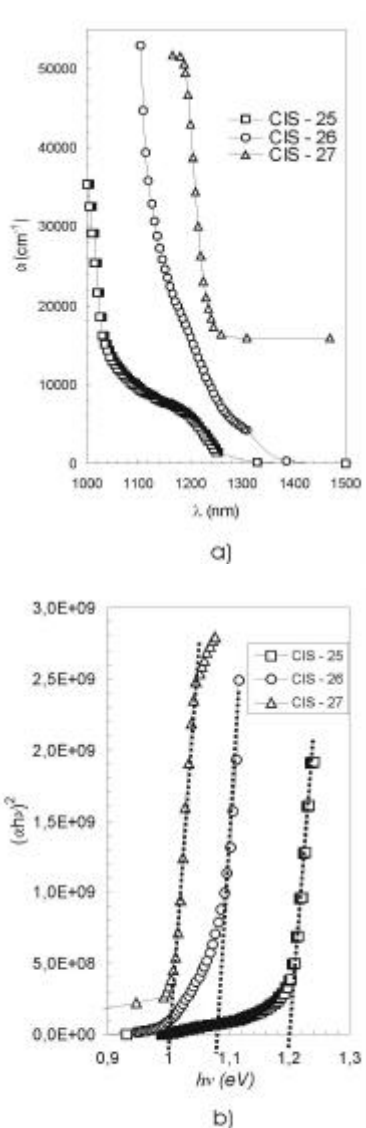


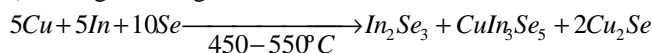
Figure 3. Variation of a) absorption coefficient α and b) $(\alpha h\nu)^2$ values as a function of $h\nu$, for the CIS samples deposited under the conditions indicated in table 1.

present only the α -CIS phase which is the phase usually used for solar cell fabrication.

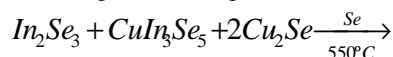
Since the In-rich phase CuIn_3Se_5 (known as the ordered vacancy compound (OVC)) grows with the same structure than the CIS and lattice constants slightly smaller than those of CIS, the resulting x-ray spectrum is quite similar to that of the CIS. Therefore, from only XRD measurements is not possible to know if the spectrum correspond to CIS or CuIn_3Se_5 . A reliable identification of the phases corresponding to the XRD spectra showed in Fig. 4, was achieved with the help of the Powder Cell simulation program and take into account the E_g values obtained from transmittance measurements. It is well known that the CIS have an optical gap of about 1 eV, which is significantly smaller than that of the CuIn_3Se_5 (about 1.2 eV) [7].

We propose as probably chemical reactions occurred during the two stages the following:

a) During first stage:



b) During second stage:



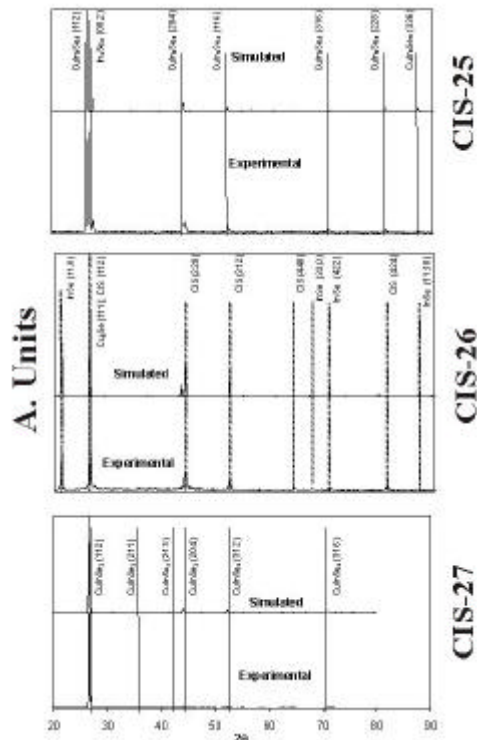
These reactions agree with the predictions of Cu, In and Se ternary compounds composition diagram [8], and the XRD results.

Correlating the E_g values obtained from transmittance measurements with the results obtained from XRD measurements, it can be concluded that the CuInSe_2 thin films grown in the chalcopyrite phase present an E_g value of 1.01 eV.

4. Conclusions

Through an exhaustive parameter study, the conditions to deposit CuInSe_2 thin films in the chalcopyrite phase were found; this type of compounds have demonstrated to have good properties for solar cells fabrication. The CuInSe_2 films were grown by a two stage process which includes deposition of the $\text{Cu}/\text{In}_x\text{Se}_y$ system followed by selenization at 550°C . However, in samples grown under inadequate selenization time, additionally to the CIS phase, secondary phases like CuIn_3Se_5 , InSe and Cu_2Se were found.

A reliable identification of the phases present in the studied samples was achieved through XRD measurements and theoretical simulation of the experimental XRD spectra performed with the help of the Powder Cell simulation program. Data of the E_g values obtained from transmittance measurements were also very useful to the phase identification.



In general, the CuInSe₂ films present high absorption coefficient at wavelengths greater than the cut off wavelength, indicating that additionally to the fundamental absorption, absorption via states within the gap also contributes.

Acknowledgements

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References

- [1] W. Jeong, G. Park, H. Chunk, CH. King and H.R. Park, Proc. 2nd World PVSE Conference, Vienna (1998) 747.
- [2] J. Britt and C. Ferekides, Appl. Phys. Lett. 62 (22) (1993) 2851.
- [3] M. A. Contreras, B. Egaas, J. Hiltner, A. Zwartlander, F. Hasoon and R. Nuofi, Progress in Photovoltaics: Research and Applications, Vol. 7 (1999) 311.
- [4] H. Ohyama, T. Aramoto, H. Higuchi, T. Arita, T. Nishio, M. Tsuji, A. Hanafusa and M. Murozono, Proc. 26th IEEE PVSC, Anaheim (1997) 343.
- [5] U.S. Patent No. 5, 441, 897 (August 15 1995).
- [6] R. Swanepoel, J. Phys. E: Sci. Instrum., 16 (1983) 1214.
- [7] S. H. Kwon, S. Ch. Park, K.H. Yoon and J. Song, Solar Energy, Vol.64, Nos. 1-3 (1998) 55.
- [8] B.J. Stanbery, A. Davydov, C.H. Chang and T.J. Anderson, Proceedings of the 14th NREL PV Program Review, AIP Press, New York (1997) 579.

Table 3. Composition percentages for each compound found in the samples CIS-25, CIS-26 and CIS-27.

Sample	Composition (%)				
	CuInSe ₂	InSe	Cu ₂ Se	In ₂ Se ₃	CuIn ₃ Se ₅
CIS-25	-	-	-	3.57	96.43
CIS-26	90.50	9.05	0.45	-	-
CIS-27	100	-	-	-	-