Cu(In,Ga)Se$_2$ thin films processed by co-evaporation and their application into solar cells

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Polycrystalline Cu(In,Ga)Se$_2$ (CIGS) solar cells are attractive because low cost techniques can be used to obtain high efficiency thin film photovoltaic devices. Several research groups around the world have developed CIGS/CdS solar cells with efficiencies larger than 15% [1] using evaporation, making it an attractive and reliable technique for thin film deposition. Our PVD system is provided with MBE-type Knudsen cells to deposit CIGS thin films on glass/Molibdenum (Mo) substrates. The deposition conditions for each metal source have been established by doing a deposition profile of temperature data vs. growth rate by co-evaporation to obtain CIGS thin film for solar cells. Characterization of the co-evaporated CIGS thin films was performed by X-ray diffraction (X-RD), scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) techniques. Good quality polycrystalline films were obtained as shown by X-RD patterns. SEM micrographs show films having a very uniform appearance with large grain sizes ($\sim$1 μm). Photoluminescence (PL) studies on CIGS samples with different Ga and Cu concentrations (Ga/Ga+In) = 0.25 and 0.34 and (Cu/In+Ga) = 0.83, 0.88 and 0.94) have been performed. The EDS results have shown that is possible to control very precisely the CIGS thin film composition using these Knudsen cells. Film thicknesses of $\sim$3-4 μm, were measured with an Ambios profilemeter XP 100 stylus type. A conversion efficiency of 10.9 % has been achieved for solar cells made from the co-evaporated absorbers.

Keywords: Cu(In; Ga)Se$_2$; Co-evaporation; thin films; solar cells.

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1. Introduction

The CuInSe$_2$ has a band gap of $\sim$1.02 eV, but it can be varied from 1 to 1.68 eV, through the addition or partial substitution of Ga in the In atomic sites. It has a direct band gap, requiring only a few microns of material to absorb almost 90% of sunlight and also it has an absorption coefficient of $\sim 1\times10^5$ cm^{-1} at energies higher than 1.4 eV (requiring thicknesses < 2 μm). In our case, as several research groups around the globe have also developed CIGS/CdS solar cells with efficiencies larger than 15% using evaporation techniques, making it an attractive and reliable technique for thin film deposition, our research group decided to work on the implementation and characterization of a co-evaporation system with Knudsen cells MBE type, to grow CIGS thin films for high efficiency solar cell devices. The highest conversion efficiency for CIGS thin film solar cells of 19.9% has been achieved by Repins *et al*. [2] using a three stages co-evaporation process. For this substrate configuration the CdS film is at best deposited by CBD.

The objective of this work is to develop photovoltaic devices with high conversion efficiencies of solar to electric energy. For this purpose quaternary semiconductor thin film compounds are deposited on soda-lime glass substrates coated with a Mo conducting layer to obtain polycrystalline thin film devices. An important issue is the feasibility to scale up these structures to large area devices with a moderate increase in the cost.

2. Experimental

Figure 1 shows the physical vapor deposition (PVD) system that we are using for processing CIGS solar cells by the co-evaporation of the film elements. This system has four Knudsen type MBE cells that allows an optimal control of the deposition speed (1-5 Å/s) for every material and on the thickness for the deposited film (0.5 - 4 μm). The base pressure in the vacuum chamber at which the deposition process is carried out reaches a value of 10^{-6} Torr. High purity Cu (Kurt Lesker, 99.999 %), Ga (Alfa Aesar, 99.9999 %). Se (Kurt

FIGURE 1. PVD deposition system: a) Deposition chamber, b) Knudsen-type effusion cells, c) General control panel, d) chiller system and e) High purity N_2 for venting the chamber.

Lesker, 99.999%) and In (Kurt Lesker, 99.999%) starting materials were put into the MBE type effusion cells in order to deposit CIGS thin films by co-evaporating all materials on soda lime glass substrates with a Mo sputtered layer ($\sim$0.7 μm). Source temperatures of every material were: T_{so}(Cu)=1300°C, T_{so}(In) = 930°C, T_{so}(Ga) = 1100°C and T_{so}(Se) = 215°C, to ensure a growth rate of 1.4, 2.2, 0.9 and 20.0 Å/s respectively for the metals and selenium during film growth. In all cases, the substrate temperature was above 400°C and the deposition time was 30 min.

X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersion spectroscopy (EDS) techniques were used for CIGS thin film characterization. X-RD patterns of the films were obtained using a Siemens Mod. D-5000

diffractometer with CuKα radiation. SEM and EDS measurements on CIGS films were carried out with a JEOL 6360 LV scanning electron microscope; micrographs were obtained with a magnification of 5 K with 20 kV applied voltage. Optical properties of CIGS films were studied through photoluminescence (PL) measurements carried out in the temperature range of 6.5 – 120 K with a system that used a He-Ne laser, as the excitation source, emitting at 632.8 nm and an In-Ga photodiode as detector. Raman studies were also performed using a Horiba Jobin Yvon (HR) LabRaman Spectrometer equipped with a microscope and a 17 mW He-Ne laser. The system had a spectral resolution value of 1 cm^{-1} and a spatial resolution of 12 μm (100X objective). Film thicknesses were measured with an Ambios XP 100 profilemeter.

3. Results

The chemical composition results for the CIGS-8C, CIGS-12 and CIGS-13 samples obtained by EDS are shown in Table I. From this table it is observed that there is a good agreement in the Ga/In+Ga as well as in the Cu/In+Ga ratios with those of the CIGS reference [3]. It also shows that the Ga concentration is slightly off stoichiometry, which can be easily fixed by lowering the Ga evaporation rate. CIGS thin film solar cells with a high conversion efficiency are those with a relatively low content of Ga, Ga/(In+Ga) $\sim$25-30% [4]. In more stoichiometry absorber CIGS solar cells have been reported a decreasing conversion efficiency primarily caused by a voltage-dependent current collection and also at greater Ga content it was showed that the open circuit voltage did not increase proportionally to the band gap and the efficiency decreased [5] .
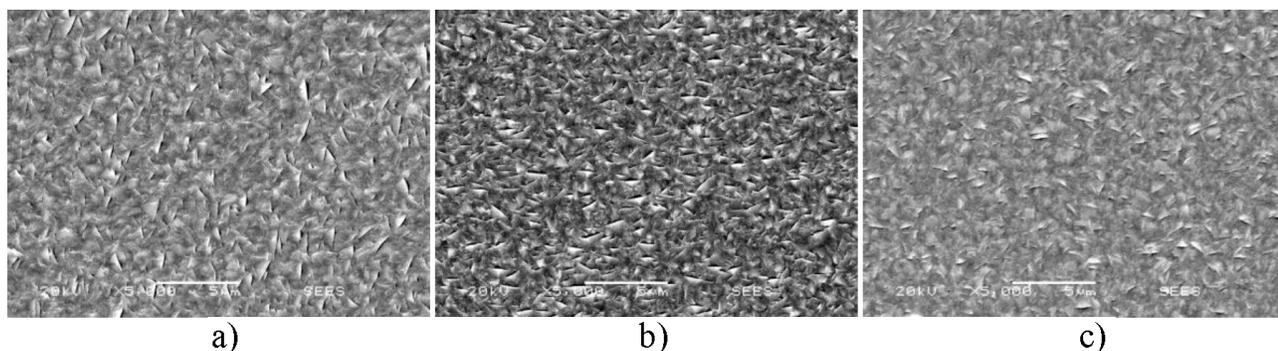
FIGURE 2. Surface SEM images of a) CIGS-8C, b) CIGS-12, and c) CIGS-13 samples.

TABLE I. Chemical composition results for CIGS samples

Sample	Cu[%At]	In[%At]	Ga[%At]	Se[%At]	Ga/(In+Ga)	Cu/(In+Ga)
CIGS-8C	23.04	16.20	8.24	53.47	0.34	0.94
CIGS-12	22.92	19.43	6.55	51.10	0.25	0.88
CIGS-13	21.53	19.39	6.46	52.34	0.25	0.83

TABLE II. Solar cells parameters for CIGS thin films by co-evaporation at 25°C

Sample	Area (cm^2)	R_S (Ω-cm^2)	G (mS/cm^2)	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	η (%)
CIGS17-1	0.470	3.9	1.0	532	31.1	64.2	10.6
CIGS17-2	0.470	3.8	1.3	536	31.7	64.0	10.9
CIGS18-4	0.470	3.8	2.2	558	29.9	63.1	10.5
CIGS18-5	0.470	2.9	3.9	540	30.6	61.5	10.2
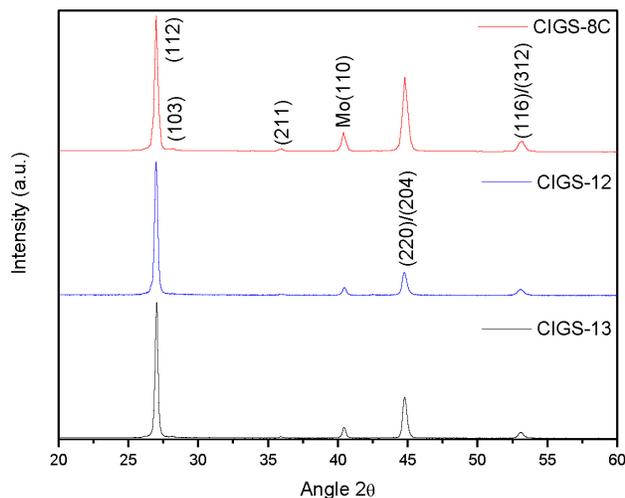
FIGURE 3. XRD patterns for CIGS-8C, CIGS-12 and CIGS-13 samples prepared by co-evaporation.

FIGURE 4. PL spectra as a function of temperature for co-evaporated CIGS-8C thin film.

Figure 2 shows the SEM images of the CIGS films deposited by the co-evaporation technique. In the three samples a uniform surface made of small grains ($\sim$1 μm) and spike-like features are observed. The measured thicknesses of the CIGS-12 and CIGS-13 samples were around 4 and $\sim$3 μm for the CIGS-8C.

From the XDR measurements a value of 30 nm for the crystal size was calculated using the Scherrer equation, the Fig. 3 shows the diffraction patterns of the three CIGS samples. The XRD patterns of the films show that the samples are polycrystalline without a preferential orientation. The reflections (112), (220)/(204), (211), (116)/(312), (103) related to chalcopyrite structure have been observed. A shift of the (112) reflection is also observed which is consistent with the CuIn$_{0.7}$Ga$_{0.3}$Se$_2$ film stoichiometry (JCPDS 35-1102). The peak located at 2θg 40.32 deg corresponds to the (110) Mo substrate used to deposit the CIGS thin films.

Also the structural parameters a and c have been calculated from the XDR patterns of coevaporated polycrystalline films resulting in the averages values of a = 5.73 Å and c=11.38 Å, with a positive value of tetragonal distortion (Δ=2-c/a) that indicates compression rather than dilation. The temperature dependence of the PL spectra shows two main emission peaks at approximately at 1.18 eV and 1.12 eV for CIGS-8C, respectively, in the temperature range of 6.5 to 77 K, whereas above 77 K less intense emission peaks are observed (see Fig. 4). In all samples, widening of the emission peaks is observed with the decrease in the emis-

sion intensity, which can be attributed to the effect of super-position of other peaks due to thermalization effects. This type of emission is associated to a donor-acceptor pair transition (DAP), between shallow donor and acceptor energy levels close to the band gap edge, where assuming band gap bowing, a value of 1.25 eV was calculated for the CIGS-8C sample [6]. The near band edge luminescence is caused by exciton recombination. The excitonic emissions occur in samples with small Ga/(Ga+In) deviations from the pure CuInSe$_2$ ternary compound [7].

Figure 5 shows the Raman spectra which reveal three peaks related to Cu(In$_{1-X}$Ga$_X$)Se$_2$. These peaks are located at 184, 212 and 226 cm^{-1} [8]. The peak observed at 184 cm^{-1} corresponds to the A1 mode resulting from the vibrations of the Se atoms with Cu, In and Ga atoms remaining at rest and the peaks at 212 and 226 cm^{-1} are due to the B2 and E modes, which correspond to the combined motion of all the atoms [9]. These frequencies modes are shifted from the Raman CuInSe$_2$ modes due to the low Ga incorporation. The full width at half maximum of the A1 mode decrease in the Raman spectra with decreasing the Ga content of the films due to better crystallinity and reduced disorder in the films.

The solar cells were fabricated using co-evaporated CIGS films similar to the CIGS-13 described lines above, because its compositional rate [Ga]/([Ga]+[In]) value is in the typical range of 0.1 - 0.3 for high efficiency CIGS devices and then
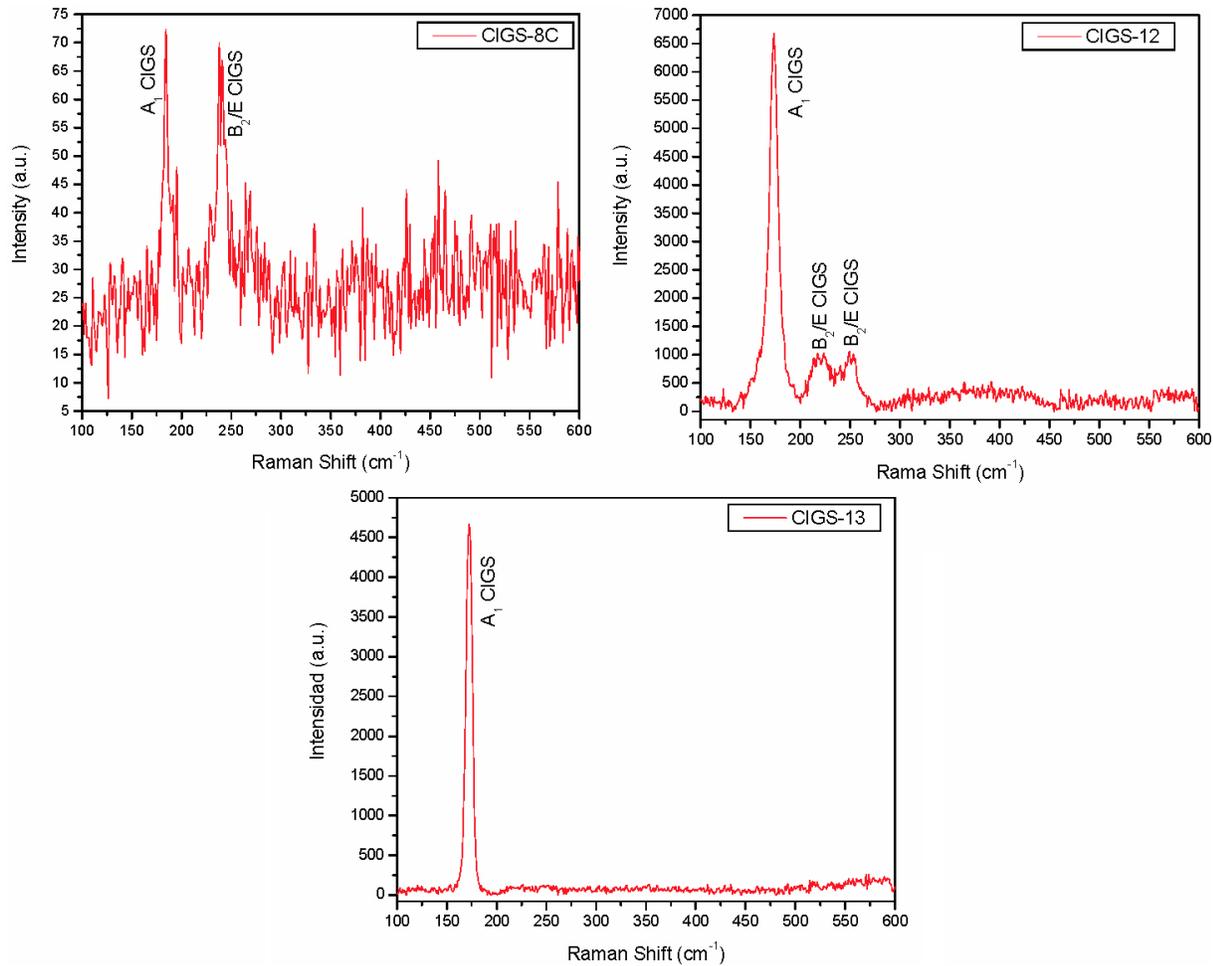
FIGURE 5. Raman spectra of CIGS thin films grown on glass/Mo substrate by co-evaporation.
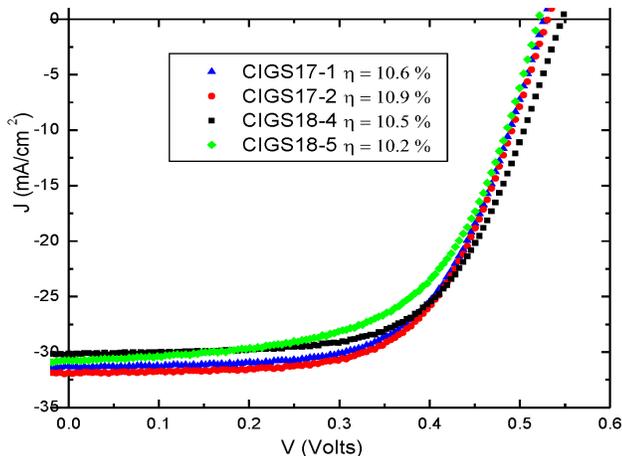
FIGURE 6. J-V characteristics of CIGS thin film solar cells under AM1.5 illumination. They were measured at 25°C on an effective area of 0.47 cm^2.

a sequential deposition of CdS thin films were deposited on CIGS films by Chemical Bath Deposition technique (CBD), we used as precursor solution $CdCl_2$ (0.1 M), NH_4Cl (0.2 M),

NH_3 (2 M) and tiourea (0.3 M). The substrates were cleaned using distilled water. We obtained layers of CdS of 30 nm with deposited time of 10 min. at 75°C, ZnO and ITO layer were deposited by rf sputtering and Ni/Al grids. The device characterization was determined from the J-V measurements at 25°C, and the results are listed in Table II, with the corresponding J-V curves as shown in Fig. 6. It will be possible to produce higher efficiency solar cells by further optimization of J_{sc}, V_{oc} and FF, in addition to improving the ohmic contacts. We are in this process.

4. Conclusions

Our results show that we have a good control and thus an efficient CIGS thin film deposition process with the use of MBE type effusion cells. This allows us to vary the deposition parameters in our PVD system to grow films with a chemical composition close to that of CIGS films used to obtain solar cells with high conversion efficiencies. X-RD studies have confirmed the growth of a single phase corresponding to the $CuIn_{0.7}Ga_{0.3}Se_2$ (JCPDS 35-1102). SEM micrographs show

that we have obtained films with the quality to have good performance when used in CIGS solar cells. The observed PL emission peaks can be ascribed to donor-acceptor transitions, between shallow donor and acceptor energy levels close to the band edge. Further work on PL as a function of excitation intensity is in progress to extend our knowledge about the origin of the defects in this material. Raman analyses showed that CIGS thin films were polycrystalline and do not form mixed phases like ordered defect or Cu-Se compounds. Solar cells fabricated from these films have efficiencies close to 11%, although V$_{oc}$ is not highs (558 mV). However, these are our first devices and therefore the work for improving them is in progress.

Acknowledgements

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