

STUDIES OF CU(IN,Ga)SE₂ THIN FILMS OBTAINED BY CO-EVAPORATION IN A PVD SYSTEM WITH KNUDSEN CELLS MBE TYPE FOR SOLAR CELL APPLICATIONS

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ABSTRACT

Cu(In,Ga)Se₂ (CIGS) is an important semiconductor material for thin film solar cell applications because of its high absorption coefficient ($\sim 10^5 \text{ cm}^{-1}$) thus layers of only $\sim 2 \mu\text{m}$ thickness are required to absorb most of the usable solar radiation. On the other hand, several research groups around the globe have developed CIGS solar cells with efficiencies larger than 15% using evaporation techniques, making it an attractive and reliable technique for thin film deposition. For these reasons, we have carried out the implementation and characterization of a co-evaporation system with Knudsen cells MBE type, to deposit CIGS thin films with physical properties close to those reported by other authors, which make them suitable to be used in high efficiency CIGS/CdS solar cell devices. Characterization of co-evaporated CIGS thin films was performed by XRD, SEM and EDS techniques; preliminary results show that high quality polycrystalline films were obtained, confirmed by the XRD patterns. SEM micrographs show films having a very uniform appearance with large grain sizes ($\sim 1 \mu\text{m}$). EDS analysis allowed us first to verify

that a Cu film could be successfully selenized and converted into Cu_3Se_2 (Cu = 60 at%, Se = 40 at%), a condition necessary to obtain CIGS films from the co-evaporation process of the pure elemental Cu-In-Ga-Se starting materials. EDS studies have shown that our PVD system allows us to vary film composition at will. An important issue is the feasibility to scale up these structures to large area devices with a moderate increase in the cost.

1. Introduction

Development of high efficiency thin film solar cells has become an attractive issue nowadays because of the low cost production of these devices compared to other technologies. Among the materials which have shown promising properties to obtain high efficiency thin film solar cells are CdTe and $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS). Nowadays, the efficiency records for these materials are 16.5% [1] and 19.9% [2] respectively. An important issue is the feasibility to scale up these structures to large area devices with a moderate increase in the cost.

On the other hand, polycrystalline CIGS/CdS solar cells are attractive because low cost techniques can be used to obtain high efficiency thin film photovoltaic devices. Several research groups around the globe have developed CIGS/CdS solar cells with efficiencies larger than 15% using evaporation techniques, making it an attractive and reliable technique for thin film deposition. *Repins et al.* from NREL have achieved the conversion efficiency record of 19.9% for CIGS thin film solar cells by using a three stages co-evaporation process [3].

The aim of this work is to obtain CIGS thin films, deposited in a physical vapor deposition (PVD) system, with characteristics close to ideal for high efficiency solar cell applications. CIGS thin films are obtained by co-evaporation in the PVD system which has four Knudsen cells MBE type for each material, to allow having an optimal control of the deposition speed and the film thickness.

2. Experimental

We have carried out the implementation and characterization of a co-evaporation system with Knudsen cells MBE type, shown in Figure 1, to deposit CIGS thin films with physical properties close to those reported by other authors, suitable to be used in high efficiency CIGS/CdS solar cell devices. High purity (99.999%) Cu, Ga, Se (Alfa Aesar) and In (Kurt Lesker) elements were used to deposit Cu(In,Ga)Se_2 thin films. The use of Knudsen cells MBE type in the PVD system allows us to have an optimal control of the deposition speed ($1\text{--}5 \text{ \AA/s}$) for each elemental material and to modulate the thickness of the deposited film ($0.5\text{--}2 \text{ }\mu\text{m}$). CIGS thin films are deposited on soda-lime glass substrates coated with a $0.7\text{--}1 \text{ }\mu\text{m}$ sputtered Mo layer. A CIGS thin film prepared by the evaporation technique, provided by the Institute of Energy Conversion at the University of Delaware, has been used throughout the complete study as our reference CIGS sample (34133.12).



Figure 1. Physical vapour deposition system for co-evaporation of Cu(In,Ga)Se_2 films. In the left picture it can be seen the vacuum chamber with the four Knudsen-type effusion cells below; the cooling unit is at the left. The right picture shows the control unit.

X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersion spectroscopy (EDS) techniques were used for thin film characterization. XRD patterns of the films were obtained using a Siemens Mod. D-5000 diffractometer with $\text{CuK}\alpha$ 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 20kX with 10 kV applied voltage. Film thicknesses of ~2-3 μm were measured with a profilometer Ambios XP 100 stylus type.

3. Results and discussion

Table 1 shows the deposition conditions used to prepare the CIGS thin films in both cases, for the reference sample (34133.12) and the ones with the best chemical composition prepared in our lab (CIGS-5 y CIGS-8).

Table 1. Deposition conditions for CIGS samples

Sample	Cu T _{sp} / °C	In T _{sp} / °C	Ga T _{sp} / °C	Se T _{sp} / °C	Sub T _{sp} / °C	t / min
34133.12	1340	972	1075	248	500	60
CIGS-5	1230 + 50	925	1015	215	400	30
CIGS-8	1230 + 50	925	1015	230	350	30

Chemical composition results in atomic % for 34133.12, CIGS-5 and CIGS-8 samples obtained by EDS are shown in Table 2. From this table it is observed that there is a good agreement in the *Ga* and *Ga+In* as well as in the *Cu* and *In+Ga* ratios between the CIGS reference and the samples prepared in our lab, although it also shows that the Ga concentration is a little bit off the stoichiometry values of CIGS, which could be easily fixed by lowering the evaporation rate.

Table 2. Chemical composition results for CIGS samples

Sample	chemical composition atomic % (EDS)				$\frac{\text{Ga}}{(\text{Ga}+\text{In})}$	$\frac{\text{Cu}}{(\text{In}+\text{Ga})}$
	Cu	In	Ga	Se		
34133.12	22.22	18.95	7.48	51.35	0.28	0.84
CIGS-5	21.27	16.73	8.88	53.69	0.35	0.83
CIGS-8	23.04	16.20	8.24	53.47	0.34	0.94

Figure 2 shows the SEM micrographs for the CIGS film (34133.12) used as the reference sample (a), and for the CIGS films (CIGS-5 and CIGS-8) deposited by co-evaporation in the PVD system (b) and (c), in order to compare the quality of the film surface morphology of our sample against the reference sample. The measured thickness of the 34133.12 sample was 2 μm while the CIGS-5 and CIGS-8 samples were 3 μm . Deposition time for our samples was 30 min. Thus, if we are looking to obtain a 2 μm thickness for our films, deposition time should be shortened to 20 min.

SEM images show similar characteristics for the three samples: all of them have a uniform surface made of small particles ($\sim 1 \mu\text{m}$ grain size) and regular shape. Thus the morphology of our CIGS films is similar to the reference sample

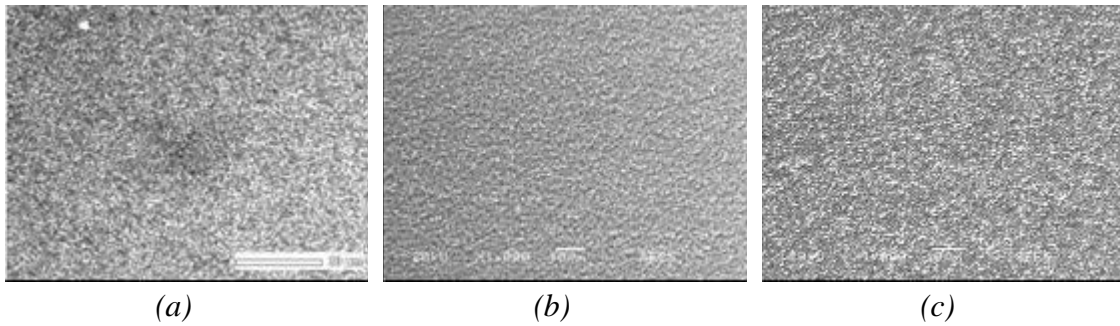


Figure 2. SEM images of a) 34133.12, b) CIGS-5, and c) CIGS-8 samples.

Figure 3 shows the diffraction patterns of the three CIGS samples. The XRD patterns of the films show sharp and well defined peaks located in the same positions for the reference sample and our samples. They also indicate that the 34133.12 and CIGS-8 have a preferential orientation in the (112) direction, while the CIGS-5 sample has an approximately random orientation in the (112), (220) and (312) directions. The expected shift of the (112) reflection is also observed which is consistent with the film stoichiometry of $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ (see, for example, JCPDS 35-1102). The peak located at 40.321 deg (110) corresponds to the Mo substrate, used to deposit the CIGS samples.

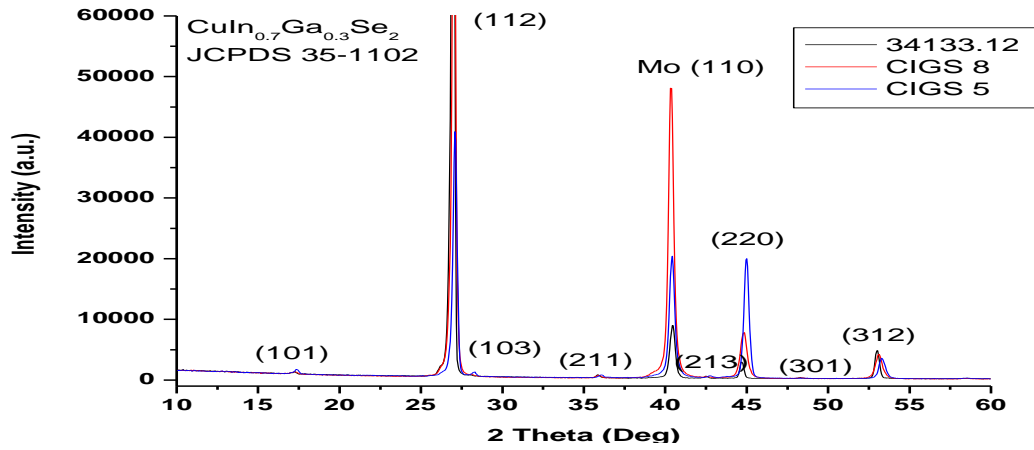


Figure 3. XRD patterns for 34133.12, CIGS_5 and CIGS_8 samples prepared by co-evaporation.

Table 3 shows all the indexed diffraction peaks appearing in Figure 3. In order to complement the characterization of the CIGS films, photoluminescence (PL) and Raman spectroscopy (RMN) measurements are in process in order to obtain the optical properties of the films. PL preliminary results [4] indicate that CIGS films obtained in our PVD system have good crystalline quality. On the other hand, peaks appearing in Raman spectra confirm the chalcopyrite phase of our samples [5]. Further PL and Raman measurements are in process in order to resolve the results interpretation for both spectra.

Table 3. Indexed peaks for CIGS samples from figure 3.

Peak No.	2-Theta / deg	CuIn _{0.7} Ga _{0.3} Se ₂ / 35-1102	
1	17.236	17.272	5.13 (101)
2	27.034	26.898	3.312 (112)
3	28.068	28.037	3.180 (103)
4	35.897	35.862	2.502 (211)
5	40.321		2.225 (110) Mo
6	42.495	42.423	2.129 (213)
7	44.859	44.647	2.028 (220)
8	48.404	48.213	1.886 (301)
9	53.131	52.946	1.728 (312)

4. Conclusions

It has been shown that the preparation of CIGS thin films by co-evaporation (CIGS-5 and CIGS-8) using a PVD system with Knudsen cells MBE type, allows us to grow films with a chemical composition very close to that used as our reference. XRD studies have confirmed the growth of a single phase corresponding to the $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ (JCPDS 35 1102). Films with this quality are believed to have a good performance when used in the preparation of CIGS solar cells. Additional work, consisting in CdS deposition by chemical bath deposition (CBD) and on the CdS film ohmic electrical contacts made out of ZnO, ZnO:Al and Ni-Al, is being performed in order to complete these CIGS films into high efficiency CIGS/CdS solar cells.

5. Acknowledgements

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6. References

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