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Fabrication and characterization of $CuInSe_2$ thin films on Mo-coated perlite and polycor ceramic substrates

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Abstract. $CuInSe_2$ (CIS) thin films have been grown on molybdenum (Mo) coated perlite glass-ceramic and polycor substrates by DC magnetron sputtering. The morphology and average grain size of the films were determined by atomic force microscopy. Finally, X-ray photoelectron spectroscopy was used to examine the formation of molybdenum diselenide ($MoSe_2$) layer at Mo/CIS interface for Mo ohmic contact. Obtained data shows that the Na out-diffusion has a noticeable impact on the average grain size. Presence of the diselenide (Se_2) layer suggests that Mo can be used as an ohmic back contact for the development of solar cells based on CIS with a ceramic substrate.

Keywords: CIS thin film, perlite, polycor, DC magnetron sputtering, AFM, XPS.

1. Introduction

Photovoltaic (PV) devices based on polycrystalline chalcopyrite $Cu(In,Ga)Se_2$ absorber layers used for the direct conversion of sunlight into electricity (conversion efficiencies of up to 20.3%) [1], are a viable alternative to single crystal silicon technology, which has attained industrial maturity [2]. The system of copper chalcopyrites includes a wide range of structures with direct band-gaps and band-gap energies varying from 1.04 to $2.4eV$, hence covering most of the visible spectrum and making them suitable for the production of thin film PV devices [3]. Moreover, most of the thin film deposition techniques are available for the mass production of CIS based solar cells. One of the key elements of the present $Cu(In,Ga)Se_2$ technology is the molybdenum coated substrate used for back contact, which became the most frequently used material for that purpose due to its convenient thermal, mechanical and electrical properties [4-6].

The most reported processes of CIS thin film preparation techniques are co-evaporation from elemental sources and the selenization of metallic precursors, which can be performed by a number of deposition techniques [3].

The purpose of our research is to study the CIS material grown on various substrates, thus extending the scope of applicability of CIS based solar cells. In our previous study [7] we established the optimal temperature for the selenization of as prepared Cu-In layers on soda lime glass (SLG). In this study, we had produced CIS thin films by DC magnetron sputtering on Mo-coated perlite glass-ceramic and polycor (corundum) substrates. The advantage of using glass-ceramic substrates is a possibility for the integration of solar cells on the surfaces of various construction elements.

2. Experiment

$CuInSe_2$ thin films were fabricated by the DC magnetron sputtering technique consisting of two steps. Firstly, copper and indium metallic precursors were sputtered on the 1x1 cm^2 square-shaped Mo-coated perlite glass-ceramic (PGC) and polycor (PC) substrates. The distance between the substrate and the target was 10 cm and the base pressure in the chamber was approximately $10^{-5}\,mTorr$, which rose up to $10^{-5}\,mTorr$ after Ar flow into the chamber. The detailed description of the sputtering conditions of the CIS films is presented in our previous paper [7]. The deposition of $0.5\mu m$ Mo film took place under the same pressure and working current of $600mA$. The in-depth investigation of the effect of Mo sputtering pressure on Na out-diffusion shows that for pressures higher than $8mTorr$ Na out-diffusion exceeds the limit that is desirable for improving device performance [8]. However, this result was obtained for Mo layers deposited on SLG, which for more than 13% consists of Na_2O. The substrates used in our experiments contain insignificantly small amount of Na. In particular, PC does not contain any Na and PGC contains only 3-4%.

For the second step, Cu-In deposited samples were selenized using granules of pure selenium. This process itself consists of 3 steps with different temperatures and durations. The first two steps provide stable physical properties and complete saturation of the Cu-In alloy with the Se. The third step, which takes place at 450^0C, causes formation of the CIS layer and its recrystallization. During absorber deposition, a molybdenum diselenide ($MoSe_2$) p-type semiconductor layer can be formed at the molybdenum surface [9], which has $1.3eV$ band gap energy [10, 11]. This layer provides a low-resistance contact for the holes in the CIS thin film [3] and was called quasi-ohmic contact [12].

Atomic force microscope (AFM) measurements were performed to examine the morphology and grain sizes of the obtained layers. Additionally, the samples were scanned by X-ray photoelectron spectroscopy (XPS) to confirm the formation of $MoSe_2$ layer at the Mo/CIS interface. The narrow-scan XPS measurements were performed using non-monochromatized Mg X-rays $(CuK_\alpha = 1253.6eV)$ with a pass energy of $50eV$, applied current of $20mA$ and chamber Ar pressure of $10^{-4}\,mTorr$. The chemical states of Mo/CIS interface were assigned with the help of NIST X-ray photoelectron spectroscopy database.

3. Results and discussion

Figure 1 shows the AFM images of the CIS films grown on PGC and PC substrates. The layers show characteristic rough surface [13] with relatively small round shaped individual grains. As it was reported previously, Mo contact also serves as a transport gate for Na out-diffusion from the substrate into the CIS layer causing an increase of the grain size of $CuInSe_2$ phase [14]. In our case, only PGC substrate contains a small amount of Na_2O, which can be the main reason for obtaining small grain size. Since PC does not contain any Na_2O at all, its grains are smaller. A number of morphological and structural properties such as CIS film thickness, average (R_a) and root mean square (RMS) roughness, average size of the grains, *etc*. derived from AFM analysis are presented in Table 1. The average grain size for the samples grown on PGC substrate was almost $0.6\mu m$. Moreover, the whole range of sizes includes grains with sizes from 0.05 up to $1.6\mu m$ (8% of the grains are larger than $1\mu m$). Contrary to PGC, the grains are relatively small (average size is $0.3\mu m$) and the distribution is more uniform $(0.1-0.65\mu m)$ for the CIS films grown on PC (Fig. 2). It is also noticeable that the roughness of the surface increases with increasing grain sizes.

Smoothed data of the measured XPS spectra for the PGC/Mo/CIS sample is presented in Fig. 3 (identical spectra were obtained also for the PC/Mo/CIS sample). The two direct evidences of the formation of $MoSe_2$ layer at the Mo/CIS interface are Mo $3d_{5/2}$ peak at 227.8eV [15] and Se $3d_{3/2}$ peak at $54.5eV$ [16] which was formed during the third step of the selenization process at $450°C$. The Se 3d line observed at $53.9eV$ also provides an evidence of the formation of $MoSe_2$ phase, which occurs at Mo coverage $> 6Å$ [17].

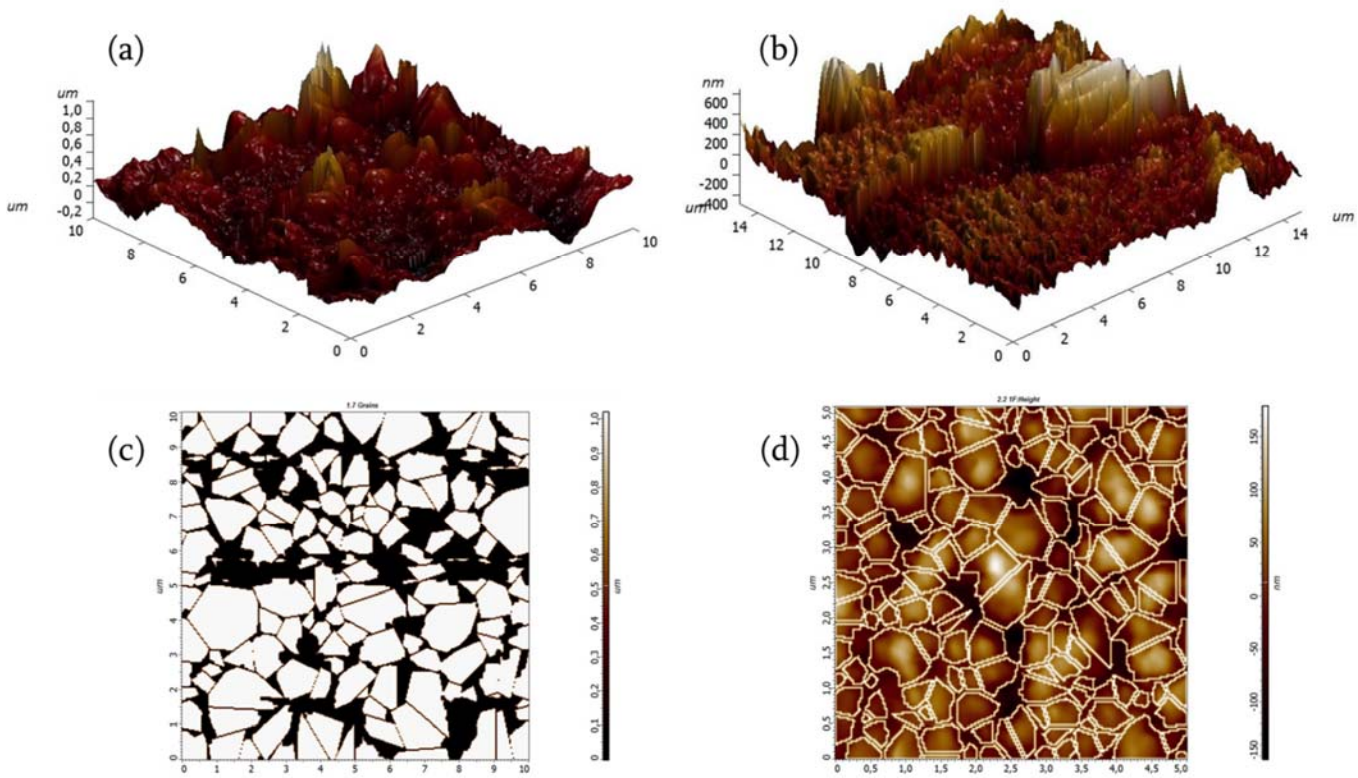

Fig. 1. AFM images of the CIS films grown on PGC (a, c) and PC (b, d) substrates.

Sample by substrate type	CIS film thickness (nm)	Average roughness (R_a, nm)	RMS roughnes s (R_q, nm)	Average grain size (nm)	Binding energy (BE, eV)	
					Mo $3d_{5/2}$, $3d_{3/2}$	Se 3d, $3d_{5/2}$
Perlite	1280	89	127	576	227.8, 231	53.9, 54.5
Polycor	1130	70	90.5	316	227.7, 231.1	53.9, 54.5

Table 1. Morphological and structural properties of CIS thin films.

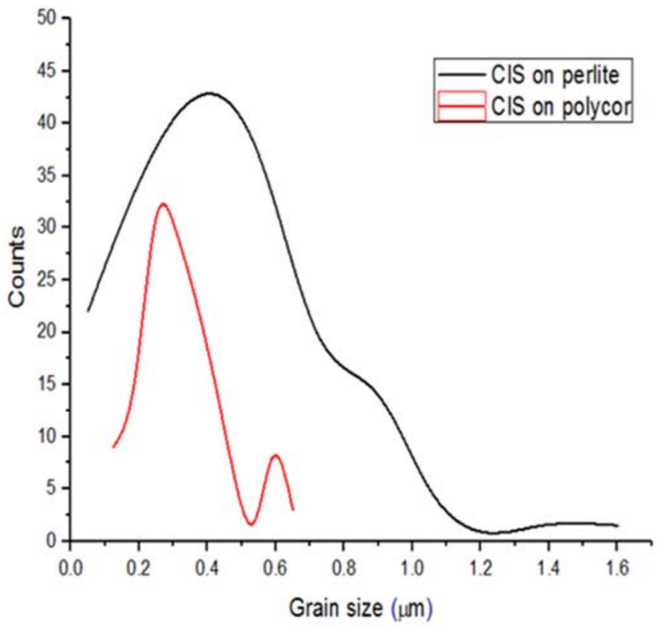

Fig. 2. Grain size for PGC/Mo/CIS and PC/Mo/CIS.

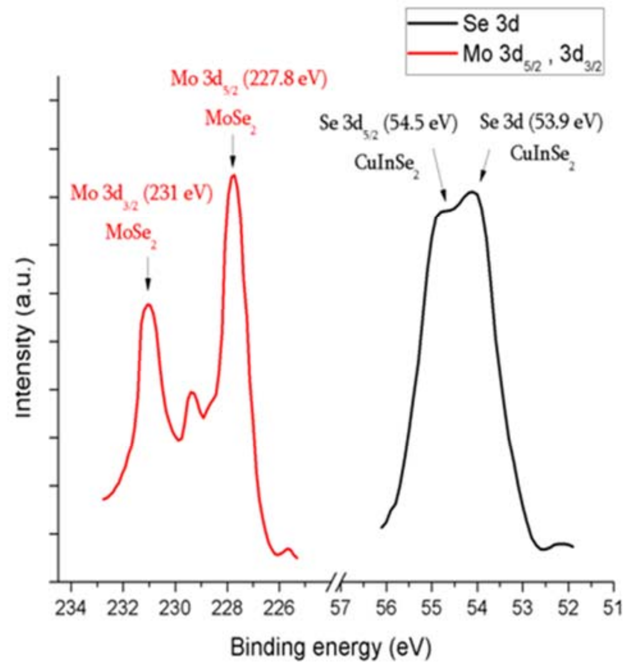

Fig. 3. XPS spectra of the Mo/$CuInSe_2$ interface grown on the PL substrate.

4. Conclusions

Thus, $CuInSe_2$ thin films have been grown on two different substrates by DC magnetron sputtering technique under $10mTorr$ Ar pressure to provide sufficient amount of Na out-diffusion from the Mo-coated perlite substrate. AFM measurements show, that Na out-diffusion has a significant impact on the average size of the grains. Grains of the film grown on PC are smaller from the ones grown on PGC by the amount of $\sim 200nm$, which, presumably, will cause more loss of photogenerated carriers on grain boundaries. Size of the grains in the PGC/Mo/CIS sample varies from $0.05\mu m$ up to $1.6\mu m$, whereas in the PC/Mo/CIS the maximum size is $0.65\mu m\, m$. Finally, XPS measurements prove the formation of $MoSe_2$ layer at the Mo/CIS interface for both samples, which will serve as ohmic back contact in the further developed CIS based solar cell with ceramic substrate.

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