Polynanocrystalline $CuIn_3Se_5$ Thin Film Photoabsorber Layer Produced by Pulsed-Laser Deposition

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Polycrystalline bulk $CuIn_3Se_5$ samples for pulsed laser deposition (PLD) targets were synthesized in evacuated quartz ampoules by vacuum melting of 99.999% pure elements. All the polynanocrystalline $CuIn_3Se_5$ thin films were deposited onto the glass and glass/ITO substrates by using the PLD technique. The synthesized bulk samples and deposited films were tested by using the XRD analysis. The time–temperature regime of PLD process was developed for preparation of polynanocrystalline $CuIn_3Se_5$ thin films with the same composition as the source target. We have used advanced 3-stages temperature-time regime. The thickness of prepared $CuIn_3Se_5$ layers was in the range from 300nm till 450nm. The influence of the thermal annealing on the photovoltaic properties and morphology of the as-deposited $CuIn_3Se_5$ layers was investigated. The technique of preparation of high photosensitive polynanocrystalline thin $CuIn_3Se_5$ films of n-type conductivity was elaborated.

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1. Introduction

$CuIn_3Se_5$ is a promising photoabsorber of n-type of conductivity [1,2] for solar cells due to band gap value about 1.3eV [3] that is close to the optimal value of 1.4eV and high photoconductivity over a broad wavelength range [2]. On the other hand, this compound is less studied in comparison with $CuInSe_2$ in the pseudo-binary system Cu_2Se-In_2Se_3 [4]. Moreover, this compound was mainly investigated in a bulk state and only few papers described preparation and characterization the thin films fabricated by flash evaporation technique [1,3].

The main purpose of present work was preparation and investigation of polynanocrystalline $CuIn_3Se_5$ thin films and optimization of the deposition technique for solar cell application. We demonstrate formation of high-quality polynanocrystalline $CuIn_3Se_5$ photoabsorber layers grown on glass/ITO substrates by using the pulsed laser deposition (PLD) technique. Photovoltaic (PV) properties with both as-deposited and annealed $CuIn_3Se_5$ layers are studied.

2. Experiment

Polycrystalline bulk $CuIn_3Se_5$ samples for the PLD targets were synthesized from 99.999% pure elements in evacuated quartz ampoules. Ampoules were inserted in a pipe furnace, heated up to 1100°C, kept at this temperature for 5 hours and then very slowly cooled down. The synthesized samples were tested using the XRD analysis carried out on DRON-3.0 diffractometer equipped with monochromatic FeK_α source.

The films were deposited by using the PLD technique in accordance with the method developed by us for the $CuInSe_2$ based films [5]. Ablation of the targets was carried out by using XeCl excimer laser. For preventing of decrease of the Se content in the film during the deposition on the heated substrate we have used advanced 3-stages temperature-time regime of deposition: at the first stage initial $CuIn_3Se_5$ film was deposited at room temperature of substrate, then deposition was stopped and deposited glassy film was heated up to temperature T_1 for crystallization, and finally deposition was continued at relatively lower temperature of

substrate T_2. The value of T_2 could be lower then T_1 because in this case vapor condensed on already formed polynanocrystalline $CuIn_3Se_5$ film and therefore nucleation was not limitative stage for crystallization. The appropriate values of T_1 and T_2 were chosen in accordance with our previous results [5] (T_1=320°C, T_2=160°C).

It should be noted, that the ablation rate for $CuIn_3Se_5$ target was much higher in comparison with the $CuInSe_2$ target at the same power of excimer laser.

For the XRD measurement the $CuIn_3Se_5$ films were deposited onto glass substrates; for investigation of PV properties, the $CuIn_3Se_5$ films were deposited on the glass/ITO substrates. The layers thicknesses on glass/ITO wafers were determined by using optical measurements and microscopy observations. The average thickness of the deposited $CuIn_3Se_5$ films was about 300nm. The cross-section and surface morphology of the $CuIn_3Se_5$ layers were investigated by scanning electron microscopy (SEM), using a commercial high-resolution LEO SUPRA 35 microscope equipped with energy dispersive spectroscopy (EDS) analyzer.

All the electrochemical PV measurements were performed in standard three-electrode cell in 0.1M H_2SO_4 background solution using AUTOLAB PGSTAT 30 potentiostat/galvanostat. The aqueous based graphite suspension (Alfa Aesar) was used for the contacts preparation on the surface of $CuIn_3Se_5$ for the I-V measurements.

3. Results and discussion

At the above mentioned regime we obtained well crystallized $CuIn_3Se_5$ films, as it was confirmed by XRD (Fig. 1). Position of the main peak at interplanar distance of 3.33Å coincides with $CuIn_3Se_5$ and $CuInSe_2$ reference data [6]. XRD patterns of $CuIn_3Se_5$ and $CuInSe_2$ are very similar except for a few additional reflections of a small intensity [6].

Reflection from (112) plane was very intensive (Fig.1). It means that film had columnar growth with preferred orientation along (112) direction. Columnar structure could be arisen because the stream of plasma from the target was directed non perpendicular to the substrate [8]. It was done in order to increase thickness uniformity of the films (the angle was about 45 degrees).

The grain size of film crystals (D) was calculated using Scherrer's equation [9]:

$$D = \frac{0.94\lambda}{\beta \cos\theta} \qquad (1)$$

where λ is X-ray wavelength, β is the full width at half maximum (FWHM) in radian, θ is the Bragg angle

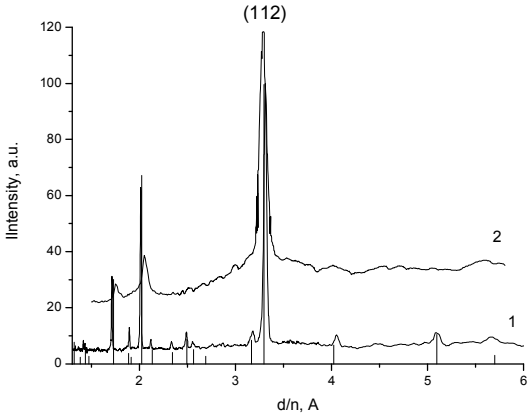


Fig. (1) X-ray diffractograms of $CuIn_3Se_5$ target (curve 1), deposited film (curve 2) and reference data for bulk $CuIn_3Se_5$ [7] (vertical lines)

The grain size value calculated from (112) reflex for the above mentioned sample was about 20nm. Analysis of composition of the as-deposited polycrystalline film with EDS showed small excess of In and small deficiency of Se against the stoichiometry (see Table 1, the second column). The similar composition was found for the films deposited at room temperature (in this case the films were glassy).

Table (1) Results of EDS analysis of as-deposited films and after various thermal treatments. The values in the brackets show the deviations in composition of samples vs. $CuIn_3Se_5$ stoichiometry

at.%	As-deposited	Annealing in air	Annealing in vacuum after contact with air	Annealing in vacuum chamber of the deposition setup
Cu	11,96 (+0,9)	13,82 (+2,7)	13,31 (+2,2)	15,47 (+4,4)
In	39,51 (+6,2)	35,89 (+2,6)	35,41 (+2,1)	34,64 (+1,3)
Se	48,52 (-7,0)	50,29 (-5,2)	51,28 (-4,2)	49,90 (-5,6)

Figure (2) shows that I-V curve of glass/ITO/$CuIn_3Se_5$ structure under chopped white light of 100mW/cm^2 intensity has non-linear character and demonstrates relatively high photosensitivity of the film

We had tried to enhance photovoltaic (PV) parameters of prepared photoabsorber films by additional thermal treatment under various conditions. Additional annealing in air at 450–500°C for 15–20min leaded to complete disappearing of the photoconductivity. Structure of the film became crumbly (Fig. 3b). For comparison, the structure of as-deposited film is represented in the Fig. (3a). Additional annealing in air leaded to oxidation of the film by the oxygen of air.

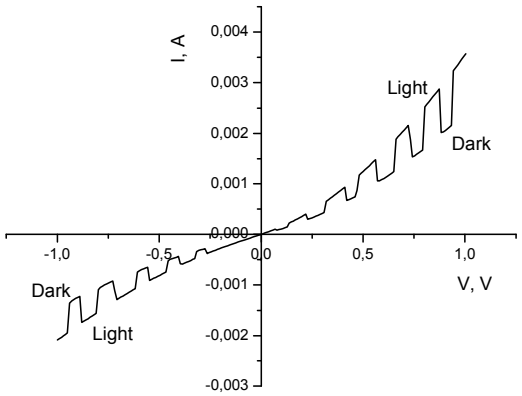


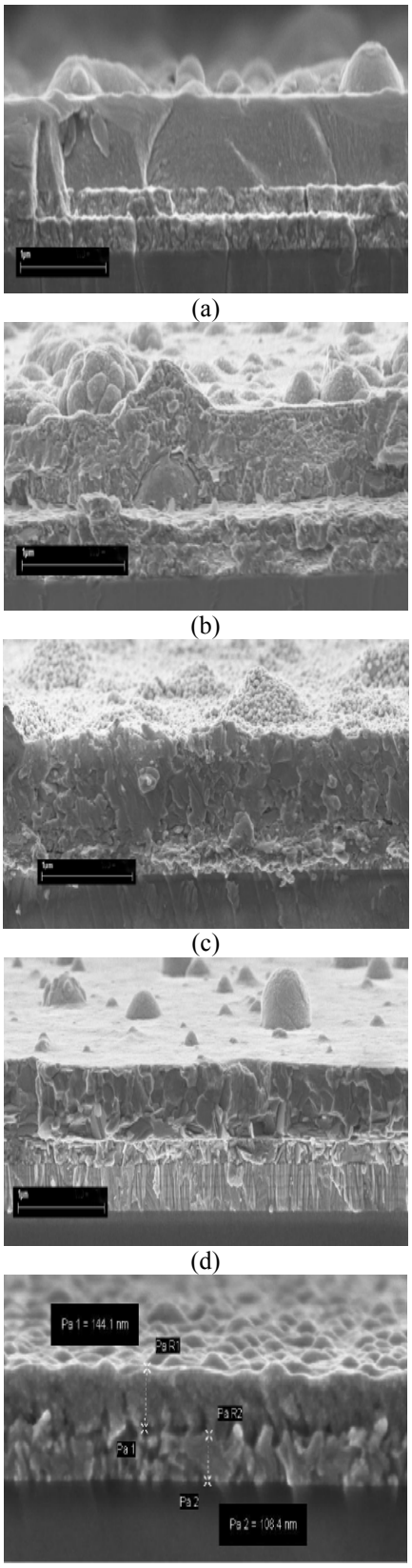
Fig. (2) I-V measurements of representative as-deposited $CuIn_3Se_5$ film under white light pulses of 100mW/cm^2 intensity

It was found, that additional annealing in vacuum (after intermediate contact with air during the time of opening of the vacuum chamber) at 500°C for 30min leaded to decreasing of photoconductivity and linearity of I-V curve with a little higher current in direct region. Composition of the film became more similar to the stoichiometric composition, crystalline structure became more pronounced (Fig. 3c). According to our assumption, oxygen absorbed by the film surface partially oxidized the surface layer. At the same time the ordering of the crystal structure was improved. It has to be mentioned that the width of the $CuIn_3Se_5$ crystallites in Fig. (3c) is of about 50 to 200nm.

On the other hand, additional annealing in vacuum "in chamber" (immediately after the film deposition, without opening of the vacuum chamber) at 400°C for 20min leaded to increasing of photoconductivity, the shape of I-V curve became "like diode" (Fig. 4).

The shape of I-V curve confirmed the existence of Schottky junction between n-$CuIn_3Se_5$ and "like metallic" ITO layers. The SEM micrograph (Fig. 3d) shows the polynanocrystalline morphology of such prepared dense $CuIn_3Se_5$ films which include the interconnected grains with an average grain size of 50-100nm. It should be noted, that the formation of more equilibrium crystal structure of $CuIn_3Se_5$ photoabsorber layer resulted in increasing of photosensitivity.

The measurements of photoconductivity of the $CuIn_3Se_5$ film under chopped white light in background electrolyte confirmed high photosensitivity and n-type of conductivity of the deposited films. The photoelectrochemical characterizations for prepared CISe films were determined in 0.1M sulfuric acid background solution under chopped white light.



(a) (b) (c) (d) (e)

Fig. (3) SEM images of cross-sections of the $CuIn_3Se_5$ films: (a) as-deposited film; (b) film after annealing in air; (c) film after annealing in vacuum after contact with air; (d) film after annealing in vacuum chamber of the deposition setup; (e) image of $CuIn_3Se_5/CuInSe_2$ thin film sandwich structure

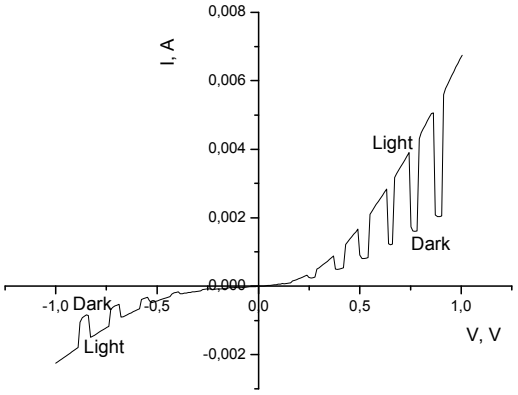


Fig. (4) I-V measurements of the deposited $CuIn_3Se_5$ film under white light pulses of 100mW/cm^2 intensity after additional annealing in vacuum chamber of the deposition setup

Figure (5) shows that obtained $CuIn_3Se_5$ films are photosensitive material and have the positive photocurrent in positive range of applied potential values. In the $CuIn_3Se_5$ electrode electron-hole pairs can be generated by light absorption. Therefore, photogenerated minority carriers are driven to the $CuIn_3Se_5$ surface by the electric field, at which they are consumed in photoelectrochemical processes. As it follows from the dependence, obtained films had the n-type of conductivity and could be applied as n-photoabsorber in complete cell structures. Thus, by adjusting the deposition temperature and post-deposition annealing "in chamber", nanostructured photosensitive $CuIn_3Se_5$ layers can be achieved.

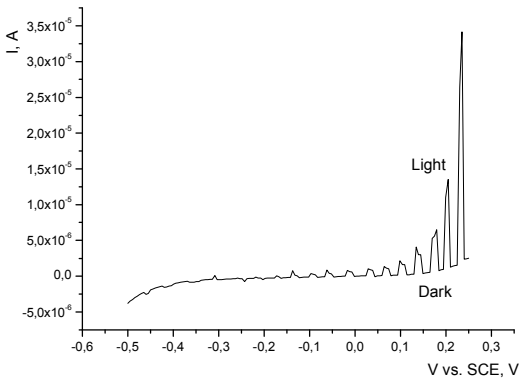


Fig. (5) I-V measurements in the electrochemical cell of the deposited $CuIn_3Se_5$ film after additional annealing in vacuum chamber of the deposition setup. Measurements were performed in 0.1M H_2SO_4 background solution vs. saturated calomel electrode (SCE) under white light pulses of 100mW/cm^2 intensity

One of the possibilities to increase the conversion efficiency of photovoltaic solar cells is creation of hybrid photovoltaic/thermal solar panels. A priory the optical properties of $CuIn_3Se_5/CuInSe_2$ thin film sandwich structure are optimal for such type devices. We prepared the $CuIn_3Se_5/CuInSe_2$ bi-layer structure by using developed PLD technique. The SEM cross section image of the structure is shown in Fig. (3e). Thickness of each layer was about 100nm. It is clearly seen polynanocrystalline structure of the deposited films. It should be noted, that mentioned structure is not yet optimized from the point of view of PV properties.

4. Conclusions

The technique of pulsed laser deposition of $CuIn_3Se_5$ films was developed and following thermal treatment allowed preparing of the high-photosensitive polynanocrystalline thin films of n-type conductivity. It was found, that additional annealing in vacuum (after the PLD process, without opening the vacuum chamber) leads to increasing of the photosensitivity and improving of polynanocrystalline structure of prepared $CuIn_3Se_5$ films. The best crystallinity of the $CuIn_3Se_5$ layers is attained at substrate temperatures ranging between 320°C and 400°C. With these characteristics $CuIn_3Se_5$ layers can be successfully applied for the preparation of heterojunction hybrid solar cells with controlled properties, as well as for the preparation of devices with controlled nanostructured donor-acceptor interfaces.

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