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MATERIALS SCIENCE

Polycrystalline $CuIn_3Se_5$ thin film photoabsorber deposited by the pulsed laser deposition technique

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Abstract. Polycrystalline $CuIn_3Se_5$ photoabsorber thin films were deposited onto glass/ITO substrates by using the pulsed laser deposition (PLD) technique. Stoichiometric $CuIn_3Se_5$ samples for PLD targets were synthesized in evacuated quartz ampoules by the vacuum melting of pure elements. The synthesized samples and deposited films were tested by using XRD analysis. The conditions of the PLD process were developed for the preparation of polycrystalline $CuIn_3Se_5$ thin films of the same composition as a source target and with the thickness in the range 300–450 nm. The influence of thermal annealing on photovoltaic properties and morphology of as-deposited $CuIn_3Se_5$ layers was investigated.

Key words: $CuIn_3S_5$, pulsed laser deposition, photoabsorber, annealing.

INTRODUCTION

$CuIn_3Se_5$ is a promising photoabsorber of n-type conductivity [1,2] for solar cells due to the band gap value of about 1.3 eV [3], which is close to the optimal value of 1.4 eV, 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 has been mainly investigated in a bulk state and only a few papers describe the preparation of and characterize the thin films fabricated by flash evaporation and laser ablation techniques [1,3,5].

The main purpose of the present work was preparation and investigation of a polycrystalline $CuIn_3Se_5$ thin film photoabsorber and optimization of the deposition technique for its solar cell application. It should be noted that this study was connected with our current aim to prepare a number of n-photoabsorbers for new organic–inorganic hybrid photovoltaic (PV) structures where an inorganic photoabsorber layer of n-type forms an n–p PV junction with an organic layer of p-type (conductive polymers, phthalocyanines, etc.) [6,7]. We demonstrate formation of high-quality polynanocrystalline $CuIn_3Se_5$ photoabsorber layers grown on glass/indium tin oxide (ITO) substrates by using the pulsed laser deposition (PLD) technique. PV properties with both as-deposited and annealed $CuIn_3Se_5$ layers are studied.

EXPERIMENTAL

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

The films were deposited by using the PLD technique in accordance with the method developed by

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us for the $CuInSe_2$ based films [8]. Ablation of the targets was carried out with a XeCl excimer laser. For preventing a decrease of the Se content in the film during the deposition on the heated substrate we used an advanced 3-stage temperature–time regime of deposition: at the first stage the initial $CuIn_3Se_5$ film was deposited at room temperature of the substrate, then deposition was stopped and the deposited glassy film was heated up to temperature T_1 for crystallization, and finally deposition was continued at a relatively lower temperature of the substrate T_2. The value of T_2 can be lower than of T_1 because the initial layer of the polycrystalline $CuIn_3Se_5$ is already formed and therefore nucleation is not a limiting stage for the process of crystallization. The appropriate values of T_1 and T_2 were chosen in accordance with our previous results [8] ($T_1 = 320\,°C$, $T_2 = 160\,°C$). Both additional annealing processes – in situ (immediately after the film deposition, without opening the vacuum chamber) and after contact with air – were performed in vacuum at 400 °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 the excimer laser.

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

Optical transmission spectra of the films were measured with a spectrophotometer SF-8 (USSR) in the spectral range 350–2050 nm.

All the electrochemical PV measurements were performed in a standard three-electrode cell in 0.1 M H_2SO_4 background solution using an AUTOLAB PGSTAT 30 potentiostat/galvanostat. White light with an intensity of 100 mW/cm^2 from a halogen lamp was used for irradiation. Aqueous based graphite suspension (Alfa Aesar) was used for the preparation of contacts on the surface of $CuIn_3Se_5$ for solid-state I–V measurements.

RESULTS AND DISCUSSIONS

In the above-mentioned conditions we obtained well-crystallized $CuIn_3Se_5$ films, as it was confirmed by the XRD spectroscopy (Fig. 1). The position of the main peak at the interplanar distance of 3.33 Å coincides with

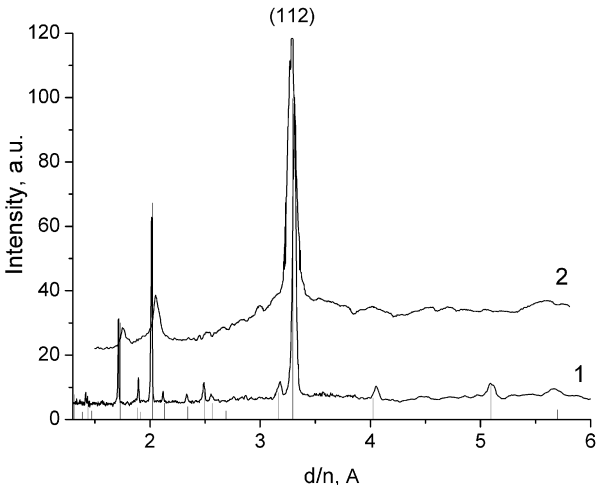


Fig. 1. X-ray diffractograms of $CuIn_3Se_5$ PLD target (curve 1), deposited film (curve 2), and reference data for bulk $CuIn_3Se_5$ [9] (vertical lines).

$CuIn_3Se_5$ and $CuInSe_2$ reference data [7]. The XRD patterns of $CuIn_3Se_5$ and $CuInSe_2$ are very similar except for a few additional reflections of low intensity [10].

Intensive reflection from (112) plane (Fig. 1) means columnar growth of the film crystals with preferred orientation along (112) direction. The columnar structure may be due to the direction of the stream of plasma from the target nonperpendicular to the substrate [11]. It was done in order to increase the thickness uniformity of the films (the appropriate angle was about 45 degrees).

The grain size of film crystals (D) was calculated using Scherrer's equation [12]:

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

where λ is X-ray wavelength, β is the full width at half maximum in radian, and θ is the Bragg angle. The grain-size value calculated from (112) reflex for the deposited $CuIn_3Se_5$ thin films was about 20 nm.

Analysis of the composition of the as-deposited polynanocrystalline film by using the EDS technique showed a small excess of In and a small deficiency of Se against stoichiometry (see Table 1).

Figure 2 shows the optical absorption spectra of representative $CuIn_3Se_5$ film annealed in the vacuum chamber. The optical band-gap (E_{opt}) of annealed $CuIn_3Se_5$ films was determined on the basis of Eq. (2), where optical absorption coefficient (α) is related with the energy gap of a semiconductor (for $\alpha > 10^4\,cm^{-1}$) [13]:

$$\alpha h\nu \cong A(h\nu - E_{opt})^n, \qquad (2)$$

where A is a constant (which equals about $10^5\,cm^{-1}eV^{-1}$ at $n = 2$), $h\nu$ is energy of the incident photon, n is a

Table 1. Results of EDS analysis of representative as-deposited film and after thermal annealings. The values in the brackets show the deviations in the composition of samples vs. $CuIn_3Se_5$ stoichiometry

	Content, at.%		
	As-deposited	Annealing in vacuum after contact with air	Annealing in vacuum chamber of deposition setup
Cu	11.96 (+0.9)	13.31 (+2.2)	15.47 (+4.4)
In	39.51 (+6.2)	35.41 (+2.1)	34.64 (+1.3)
Se	48.52 (–7.0)	51.28 (–4.2)	49.90 (–5.6)

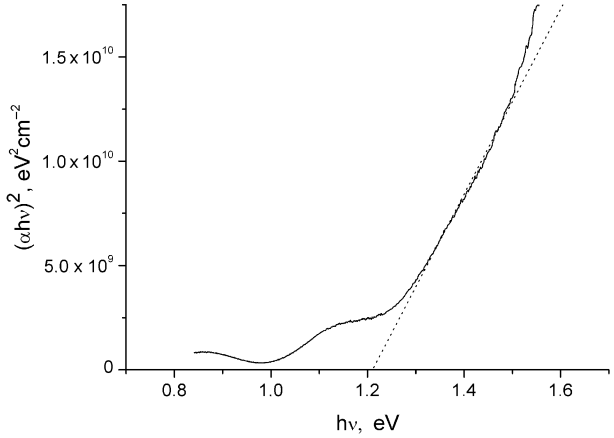


Fig. 2. Plot of $(\alpha h\nu)^2$ vs. photon energy for representative $CuIn_3Se_5$ film annealed in the vacuum chamber. Dashed straight line is approximation.

parameter that characterizes the process of electronic transition between the valence and conduction bands. For the Cu–In–Se compounds, direct allowed transitions $(n = 1/2)$ are proposed. Therefore the optical band gap for film can be defined as the intersection of the line approximating the experimental curve in the coordinates $(\alpha h\nu)^2 - h\nu$ with abscissa. The determined value of E_{opt} (1.21 eV) is in a good agreement with the reference data 1.23 eV [1] and 1.26 eV [3] and looks like typical for such photoabsorbers.

Photosensitivity of the deposited $CuIn_3Se_5$ photoabsorber films was estimated as the difference between the values of 'dark' and 'light' currents in I–V curves. Figure 3 shows that the I–V curve of the glass/ITO/$CuIn_3Se_5$ structure under chopped white light of 100 mW/cm^2 intensity has a non-linear character and demonstrates a relatively high photosensitivity of the film with increasing photoconductivity under white light illumination pulses.

In addition, we tried to enhance the morphology and PV parameters of prepared photoabsorber films by

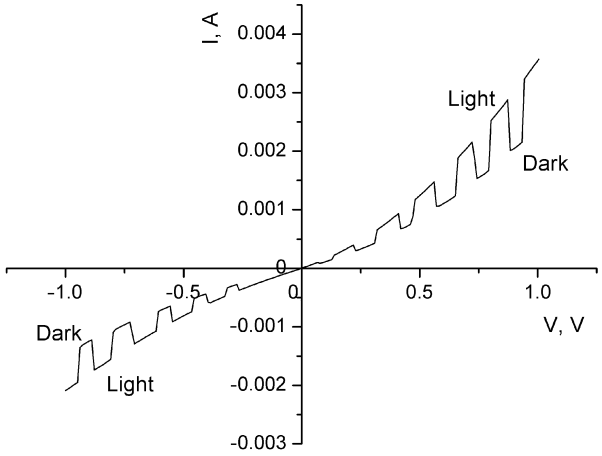


Fig. 3. I–V measurements of representative as-deposited $CuIn_3Se_5$ film under white light pulses of 100 mW/cm^2 intensity.

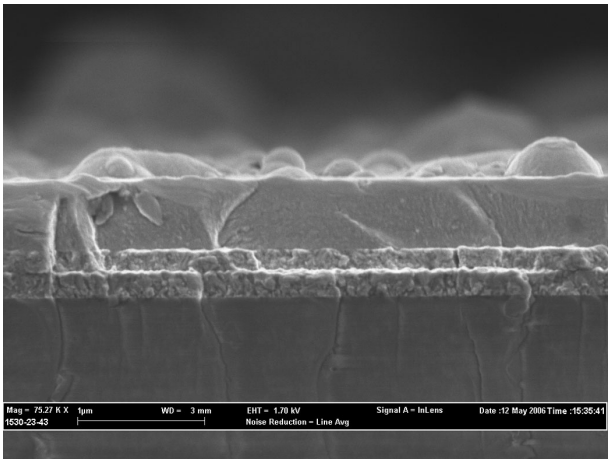
additional annealing in vacuum. Figure 4 shows the cross-sectional view of as-deposited and annealed layers of the $CuIn_3Se_5$ photoabsorber.

As a result of PLD, well-coherent dense uniform $CuIn_3Se_5$ film was prepared (Fig. 4a). It was found that additional annealing in vacuum (after intermediate contact with air) led to a decrease of the photoconductivity of the deposited $CuIn_3Se_5$ film. At the same time, the composition of the annealed film became closer to the stoichiometric composition and the crystalline structure became more pronounced (Fig. 4b). According to our assumption, oxygen and moisture from air affect dramatically the active 'just-deposited' semi-amorphous $CuIn_3Se_5$ layer. Figure 4b shows that the size of the $CuIn_3Se_5$ crystallites after annealing in vacuum was in the range 50–200 nm.

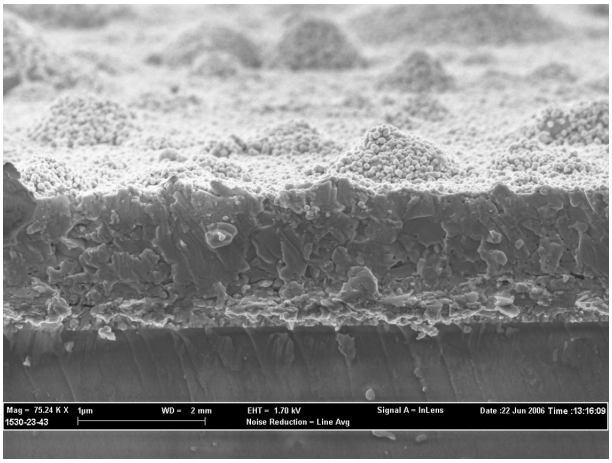
On the other hand, additional annealing in vacuum in situ (immediately after the film deposition, without opening the vacuum chamber) at 400 °C for 20 min led to increasing photoconductivity of the annealed $CuIn_3Se_5$ layer in comparison with the as-deposited layer (Figs 3, 5), the shape of the I–V curve became typical of a diode junction (Fig. 5). The shape of the I–V curve confirmed the existence of the Schottky junction between n-$CuIn_3Se_5$ and quasi-metallic ITO layers. The SEM micrograph (Fig. 4c) shows the polycrystalline morphology of dense $CuIn_3Se_5$ films prepared in this way. The films include interconnected grains with an average grain size of 50–200 nm. It should be noted that the formation of a more crystalline structure of the $CuIn_3Se_5$ photoabsorber layer resulted in increasing photosensitivity.

The measurements of the photoconductivity of the $CuIn_3Se_5$ film under chopped white light in the background electrolyte confirmed high photosensitivity and n-type of the conductivity of the deposited films.

(a)



(b)



(c)

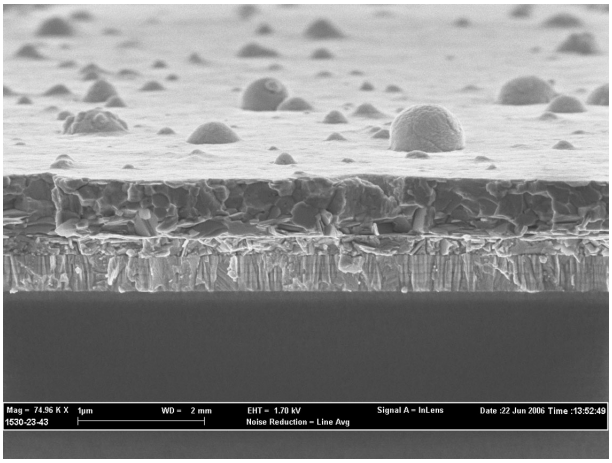


Fig. 4. SEM images of cross-sectional cleavages of prepared glass/ITO/$CuIn_3Se_5$ structures: (a) – as-deposited $CuIn_3Se_5$ film; (b) – $CuIn_3Se_5$ film annealed in vacuum after contact with air; (c) – $CuIn_3Se_5$ film annealed in situ in the vacuum chamber of the deposition setup.

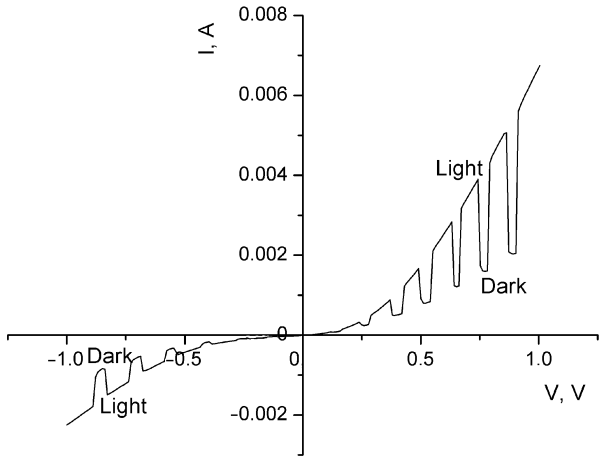


Fig. 5. I–V measurements of the annealed in vacuum chamber $CuIn_3Se_5$ photoabsorber film under white light pulses of 100 mW/cm^2 intensity.

The photoelectrochemical characteristics of the prepared $CuIn_3Se_5$ films were determined in 0.1 M sulphuric acid background solution under chopped white light according to the technique described in our previous paper [6]. Figure 6 shows that annealed in situ $CuIn_3Se_5$ film is a photosensitive material and produces a positive photocurrent under white light pulses in the positive range of the applied potential values. In the glass/ITO/$CuIn_3Se_5$ electrode electron-hole pairs can be generated by light absorption. Therefore, photogenerated minority carriers (holes) are driven to the $CuIn_3Se_5$ surface by the electric field, in which they are consumed in photoelectrochemical processes. As it follows from the dependence, the obtained $CuIn_3Se_5$ photoabsorber film has n-type conductivity and could be applied as an n-photoabsorber in complete cell

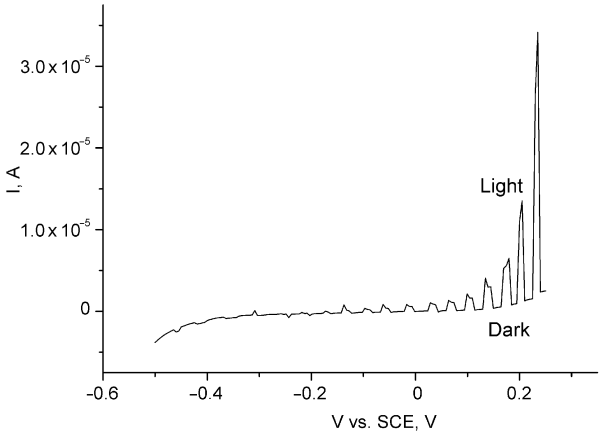


Fig. 6. Typical dependence of photocurrent vs. electrode potential for representative $CuIn_3Se_5$ film under chopped light in three-electrode cell.

structures; for example, in combination with organic semiconductors of p-type. Thus, by adjusting the deposition temperature and post-deposition annealing in situ, polycrystalline photosensitive $CuIn_3Se_5$ layers can be prepared.

CONCLUSIONS

A polycrystalline $CuIn_3Se_5$ thin film photoabsorber of n-type was prepared by using the pulsed laser deposition technique. It was found that additional annealing in situ in a vacuum chamber improved the polycrystalline structure and PV properties of deposited $CuIn_3Se_5$ photoabsorber layers. The best crystallinity and photosensitivity of the prepared $CuIn_3Se_5$ layers was reached at the annealing temperature of 400 °C. The $CuIn_3Se_5$ layers prepared in this way can be potentially applied as n-photoabsorber layers for example in heterojunction hybrid organic–inorganic solar cells as well as for the preparation of devices with controlled donor–acceptor interfaces.

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Pulseerival lasersadestamise meetodil valmistatud polükristalliline $CuIn_3Se_5$-fotoabsorberkile

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On uuritud pulseerival lasersadestamise meetodil valmistatud õhukesekileliste $CuIn_3Se_5$-fotoabsorberkilede termilise käsitsuse mõju kilede fotovoltomadustele ja morfoloogiale. Õhukesed 300–450 nm paksused polükristallilised $CuIn_3Se_5$-kiled on valmistatud klaas/ITO-alustele pulseerival lasersadestamise meetodil stöhhiomeetrilisest polükristallilisest $CuIn_3Se_5$-lähtematerjalist, mis on sünteesitud kvartsampullis vaakumsulatuse meetodil 99,999-protsendise puhtuseastmega komponentidest. Sünteesitud polükristallilise lähtematerjali ja sadestatud kilede koostist on võrreldud XRD-meetodil. On välja töötatud lasersadestamise protsessi tingimused, tagamaks valmistatud kiledele lähtematerjaliga võrreldes sama stöhhiomeetriline koostis. On näidatud, et lasersadestamise meetodil saab valmistada stöhhiomeetrilise koostisega fototundlikke n-tüüpi juhtivusega $CuIn_3Se_5$-kilesid hübriidsete päikeseelementide jaoks.