Polycrystalline CuIn$_3$Se$_5$ thin film photoabsorber deposited by the pulsed laser deposition technique

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Abstract. Polycrystalline CuIn$_3$Se$_5$ photoabsorber thin films were deposited onto glass/ITO substrates by using the pulsed laser deposition (PLD) technique. Stoichiometric CuIn$_3$Se$_5$ 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$_3$Se$_5$ 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$_3$Se$_5$ layers was investigated.

Key words: CuIn$_3$S$_5$, pulsed laser deposition, photoabsorber, annealing.

INTRODUCTION

CuIn$_3$Se$_5$ 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$_2$Se–In$_2$Se$_3$ [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$_3$Se$_5$ 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 polycrystalline CuIn$_3$Se$_5$ 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$_3$Se$_5$ layers are studied.

EXPERIMENTAL

Polycrystalline bulk CuIn$_3$Se$_5$ 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
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$_3$Se$_5$ 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$_3$Se$_5$ 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] ($T_1 = 320^\circ\text{C},$ $T_2 = 160^\circ\text{C}$). 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$_3$Se$_5$ 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$_3$Se$_5$ films were deposited onto glass substrates; for the investigation of PV properties, the CuIn$_3$Se$_5$ films were deposited onto glass/ITO substrates. The thicknesses of the CuIn$_3$Se$_5$ photoabsorber layers on the glass/ITO substrates were determined by using the scanning electron microscopy (SEM) technique. The average thickness of the deposited CuIn$_3$Se$_5$ films was around 300 nm. The cross-section and surface morphology of the CuIn$_3$Se$_5$ 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$_2$SO$_4$ 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$_3$Se$_5$ for solid-state I–V measurements.

RESULTS AND DISCUSSIONS

In the above-mentioned conditions we obtained well-crystallized CuIn$_3$Se$_5$ 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 CuIn$_3$Se$_5$ and CuInSe$_2$ reference data [7]. The XRD patterns of CuIn$_3$Se$_5$ 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]:

$$D = \frac{0.94\lambda}{\beta\cos\theta},$$

where $\lambda$ is X-ray wavelength, $\beta$ is the full width at half maximum in radian, and $\theta$ is the Bragg angle. The grain-size value calculated from (112) reflex for the deposited CuIn$_3$Se$_5$ 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$_3$Se$_5$ film annealed in the vacuum chamber. The optical band-gap ($E_{\text{opt}}$) of annealed CuIn$_3$Se$_5$ films was determined on the basis of Eq. (2), where optical absorption coefficient ($\alpha$) is related with the energy gap of a semiconductor (for $\alpha > 10^4$ cm$^{-1}$) [13]:

$$\alpha h\nu \equiv A(h\nu - E_{\text{opt}})^n,$$

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. CuIn3Se5 stoichiometry.

<table>
<thead>
<tr>
<th></th>
<th>As-deposited</th>
<th>Annealing in vacuum after contact with air</th>
<th>Annealing in vacuum chamber of deposition setup</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>11.96 (+0.9)</td>
<td>13.31 (+2.2)</td>
<td>15.47 (+4.4)</td>
</tr>
<tr>
<td>In</td>
<td>39.51 (+6.2)</td>
<td>35.41 (+2.1)</td>
<td>34.64 (+1.3)</td>
</tr>
<tr>
<td>Se</td>
<td>48.52 (–7.0)</td>
<td>51.28 (–4.2)</td>
<td>49.90 (–5.6)</td>
</tr>
</tbody>
</table>

Fig. 2. Plot of $(\alpha h \nu)^2$ vs. photon energy for representative CuIn3Se5 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 $E_{\text{opt}}$ (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 CuIn3Se5 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/ CuIn3Se5 structure under chopped white light of 100 mW/cm² 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 additional annealing in vacuum. Figure 4 shows the cross-sectional view of as-deposited and annealed layers of the CuIn3Se5 photoabsorber.

As a result of PLD, well-coherent dense uniform CuIn3Se5 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 CuIn3Se5 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 CuIn3Se5 layer. Figure 4b shows that the size of the CuIn3Se5 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 CuIn3Se5 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-CuIn3Se5 and quasi-metallic ITO layers. The SEM micrograph (Fig. 4c) shows the polycrystalline morphology of dense CuIn3Se5 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 CuIn3Se5 photoabsorber layer resulted in increasing photosensitivity.

The measurements of the photoconductivity of the CuIn3Se5 film under chopped white light in the background electrolyte confirmed high photosensitivity and n-type of the conductivity of the deposited films.
Fig. 4. SEM images of cross-sectional cleavages of prepared glass/ITO/CuIn\textsubscript{3}Se\textsubscript{5} structures: (a) – as-deposited CuIn\textsubscript{3}Se\textsubscript{5} film; (b) – CuIn\textsubscript{3}Se\textsubscript{5} film annealed in vacuum after contact with air; (c) – CuIn\textsubscript{3}Se\textsubscript{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\textsubscript{3}Se\textsubscript{5} photoabsorber film under white light pulses of 100 mW/cm\textsuperscript{2} intensity.

The photoelectrochemical characteristics of the prepared CuIn\textsubscript{3}Se\textsubscript{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\textsubscript{3}Se\textsubscript{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\textsubscript{3}Se\textsubscript{5} electrode electron-hole pairs can be generated by light absorption. Therefore, photo-generated minority carriers (holes) are driven to the CuIn\textsubscript{3}Se\textsubscript{5} surface by the electric field, in which they are consumed in photoelectrochemical processes. As it follows from the dependence, the obtained CuIn\textsubscript{3}Se\textsubscript{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\textsubscript{3}Se\textsubscript{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$_3$Se$_5$ layers can be prepared.

**CONCLUSIONS**

A polycrystalline CuIn$_3$Se$_5$ 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$_3$Se$_5$ photoabsorber layers. The best crystallinity and photosensitivity of the prepared CuIn$_3$Se$_5$ layers was reached at the annealing temperature of 400 °C. The CuIn$_3$Se$_5$ 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$_3$Se$_5$-fotopasakaal**

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On uuritud pulseerival lasersadestamise meetodil valmistatud ohukesekileliste CuIn$_3$Se$_5$-fotopasakaalide termilise käsitsuse mõju kilede fotovoltoomadustele ja morfoloogiale. Ohukesed 300–450 nm paksused polükristallilised CuIn$_3$Se$_5$-kiled on valmistatud klaas/ITO-alustele pulseerival lasersadestamise meetodil stöhhiomeetrilisest polükristallilisest CuIn$_3$Se$_5$-lähtematerjalist, mis on sünteesitud kvartsampullis vaakumsulatuse meetodil 99,999-protsendise puhtuseastega komponentidest. Sünteesitud polükristalliliste lähtematerjalide ja sadestatud kilede koostis on võrreldud XRD-meetodil. On välja tõotatud lasersadestamise protsessi tingimused, tagamaks valmistatud kilede lähtematerjaliga võrreldes sama stöhhiomeetrilise koostis. On näidatud, et lasersadestamise meetodil saab valmistada stöhhiomeetrilise koostisega fototundlikke n-tüüpi juhtivusega CuIn$_3$Se$_5$-kilesid hübriidsete pääkeeselementide jaoks.