

DEPOSITION OF HETEROSTRUCTURES BASED ON CIGSE AND CdS BY ELECTRON-BEAM ABLATION

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A two step deposition technology of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGSE) polycrystalline films was developed: deposition with the help of a "e-beam ablation" process at 250°C followed by selenization at 500°C . The X-ray diffraction analysis of films reveals the chalcopyrite phase with orientation preferential $\langle 112 \rangle$. Thin films have optical absorption coefficients in the 10^4 cm^{-1} range and the band gaps are 1.0, 1.4 and 1.65 eV for $x = 0, 0.25, 1.0$. The obtained heterostructures $\text{CdS}/\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ display good photovoltaic properties. The method of admittance spectroscopy for determination of density of deep states ($N(E)$) was applied for optimization of the deposition process and photovoltaic properties. The continuous distribution of electronic states and new type of metastable centers have been found.

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1. Introduction

The chalcopyrite semiconductors of the class I-III-IV are intensely studied due to their applications in thin film solar cells [1,2].

The quaternary compound semiconductors $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ are promising materials for the multijunction photovoltaic devices. Compounds with $x = 0.2 - 0.3$ are optimum for absorption of sunlight [1]. The photovoltaic cells on the basis of quaternary chalcopyrite structure compounds have reached high efficiency of solar energy conversion in electricity. However, further increase of conversion effectiveness is connected with searching of new methods of controlled deposition of films and possible monitoring of deep trap centers. Preliminary researches of CuInSe_2 films obtained by e-beam ablation method [2] have shown good reproducibility of the target composition and structure of the films.

2. Experimental details

Thin $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGSE) ($x = 0.25$) films have been obtained by e-beam ablation technology. In this method, the deposition of films is implemented by pulses of electrons of large density, which are self-focused (see more details in [3]). The target consists of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ bulk crystal. The substrate temperature has been measured by a thermocouple fixed on the surface of a control glass and covered by the In-Ga alloy for better thermal contact. The deposition of the CIGSE films on silica glass substrates has been performed under following technological conditions: voltage 10-20 kV, pulse duration 50 ns, pulse repetition frequency 1-5 Hz, power density $5 \times 10^8 \text{ W/cm}^2$, beam diameter 1.5 mm, with argon gas pressure in the range 1-3 Pa, while the temperature of the substrate varied in the range $250\text{-}550^\circ\text{C}$. During deposition of films the electron beam was scanned

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on the surface of the target to eliminate a local overheating and formation of holes on the surface. The system allowed to get nanolayers of about 10 Å thickness.

The procedures of selenization or sulfurization the thin films were subsequently conducted at 500 °C for CIGSE and CdS. Selenization allows for the conversion from poor packed microstructure of precursor into densely packed one for selenized films. After selenization a well defined absorption edge and increase of surface resistivity by more than three orders higher than the value suitable for the heterojunction fabrication have been observed.

Microscopy studies, X-Ray Diffraction (XRD), optical, electrical and photoelectrical measurements were performed.

3. Results and discussion

The XRD diagrams of the CIGSE target and thin films deposited at 250°C substrate temperature and selenized after deposition are shown in Fig. 1 and 2. We can reliably identify the diffraction peaks associated with (112), (220)/(204), (116)/(312), (316)/(332) and (424) reflections. These peaks are related to the randomly oriented sphalerite of the CIGSE structure [4]. The XRD patterns of the films (Fig. 2) clearly demonstrate the presence of the diffraction reflections typical to the chalcopyrite structure represented by odd l hkl-index. The observed (112) preferential crystalline texture is assumed to correspond to a lateral growth mechanism of the films. It is considered that the (112) plane is the desirable plane in the CIGSE thin film for use in heterojunction with CdS and there is a correlation between strong (112) texture, columnar microstructure, and good photovoltaic properties. The films CIGSE show $\langle 112 \rangle$ orientation, have chalcopyrite structure, columnar and granular microstructure, and a surface morphology consisting of a smooth background of closely packed grains. Precipitates and spherical particles disposed on the film surface have been observed. The structure of the films corresponds to the original composition of the target.

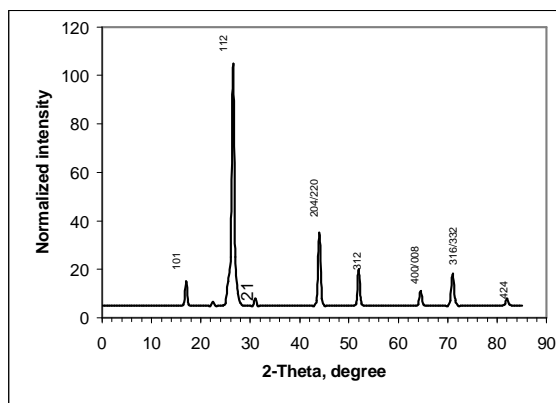


Fig. 1. XRD spectra of CuInSe_2 layers after selenization step.

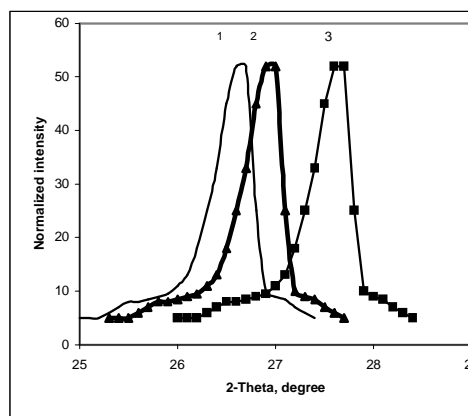


Fig. 2. XRD spectra of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) ($1-x = 0; 2 - 0.25; 3 - 1.0$) layers after selenization step (in the range of (112) diffraction peak).

When the substrate temperature is raised one observes the increase of the $\text{Cu}/(\text{In}_{1-x}\text{Ga}_x)$ ratio and the decrease of Se content. This behavior seems to be conditioned by the process of re-evaporation of volatile $(\text{In}_{1-x}\text{Ga}_x)_2\text{Se}_3$ phase and Se at temperatures above 400 °C leading to the increase of relative content of Cu. However, it is known that high performance CuInSe_2 based solar cells are fabricated from the In-rich material because in this case stable buried heterojunction is formed [5,6]. To increase the $\text{In}_{1-x}\text{Ga}_x$ content in films deposited at high temperatures $\text{In}_{1-x}\text{Ga}_x$ -rich CIGSE targets have been also used. However, even application of the $(\text{In}_{1-x}\text{Ga}_x)$ -rich target led to the deposition of stoichiometric and Se-deficient CIGSE thin films at the substrate temperature of 500 °C. At the same time these results also demonstrate that the evaporation of this compound from target is

congruent and this method makes possible to prepare semiconductor CIGSE films with a given homogeneous reproducible composition. This property can be also useful for the preparation of the precursor in the so-called two-step technological approach. Therefore we subjected the $\text{In}_{1-x}\text{Ga}_x$ -rich films deposited at $T_{\text{sub}} = 250\text{ }^\circ\text{C}$ to selenization procedure at $T_{\text{sub}} = 500\text{ }^\circ\text{C}$ during 15 min. The SEM patterns of two films deposited at $T_{\text{sub}} = 250\text{ }^\circ\text{C}$ and $T_{\text{sub}} = 420\text{ }^\circ\text{C}$ cross section show a columnar grain microstructure, though in the former case the film microstructure is characterized by a poorly packed structure with empty spaces between grains at the bottom of the film, while in the latter case a densely packed microstructure is observed. Very important information on the quality of the films can be obtained from the optical measurements. A significant subband gap absorption is revealed in the film with $T_{\text{sub}} = 250\text{ }^\circ\text{C}$ without steep absorption edge. As the substrate temperature increases the texture of the films improves and the films ($T_{\text{sub}} = 400\text{ }^\circ\text{C}$) are characterized by a little subband absorption and a well-defined absorption edge (Fig. 3).

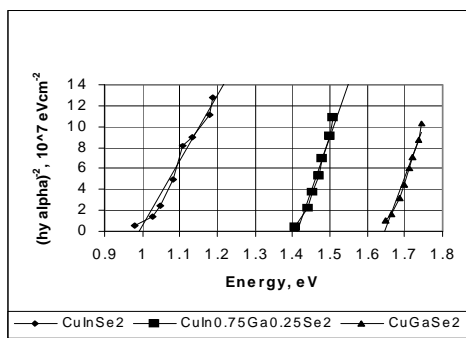


Fig. 3. Optical absorption in CIGSE.

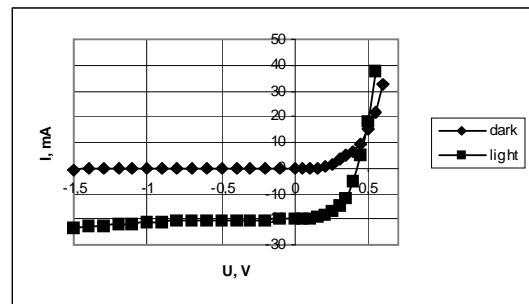


Fig. 4. Volt-Ampere characteristic of $\text{Mo-CuIn}_{1-x}\text{Ga}_x\text{Se}_2\text{-Al}$ structures in dark and under illumination.

By selenization at low temperature the $\text{In}_{1-x}\text{Ga}_x$ -rich CIGSE films improve both their optical and electrical properties. In particular, after selenization, well-defined absorption edge and the increase of surface resistance by more than two orders were observed (Fig. 4). Moreover, values suitable for heterojunction fabrication have been observed. In the two step technology method the absorption coefficient (α) calculated from the interception of a straight line in the coordinates of α^2 versus $h\nu$ yielded for $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ the band gap energy value $E_g = 0.99, 1.41$ and 1.64 eV for direct allowed transitions of $\text{CuInSe}_2, \text{CuIn}_{0.75}\text{Ga}_{0.25}\text{Se}_2$ and CuGaSe_2 , respectively. Films with excess of $\text{In}_{1-x}\text{Ga}_x$ or Cu have significant sensitivity in subband range.

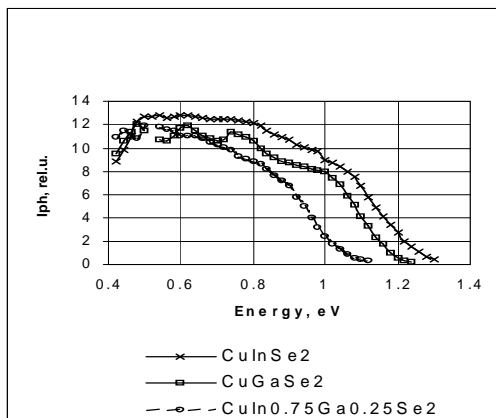


Fig. 5. The spectral dependence of the photo current in CIGSE.

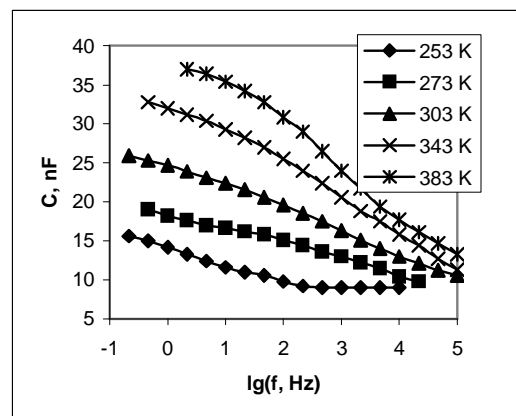


Fig. 6. Capacity-frequency dependence of the structure $\text{Mo-CuInSe}_2\text{-Al}$ before selenization.

The space charge spectroscopy of defects in chalcopyrite semiconductors is a sensitive tool to monitor the properties that affect the performance of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ solar cells. This study combines the electrical defect spectroscopy and XRD investigations. When correlated with preparation parameters the observed differences give an indication of the nature of certain defects and their role in device performance. Charging of defects at the buffer/ $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ interface reveals an inversion of the carrier type. A deep defect distribution at ~ 260 meV above the valence band is related to the bulk part of the $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ grains, while a broad distribution of states is probably due to grain boundaries. The inversion at the surface and the low density of defects in the absorber seem to be the key requirements for efficient devices.

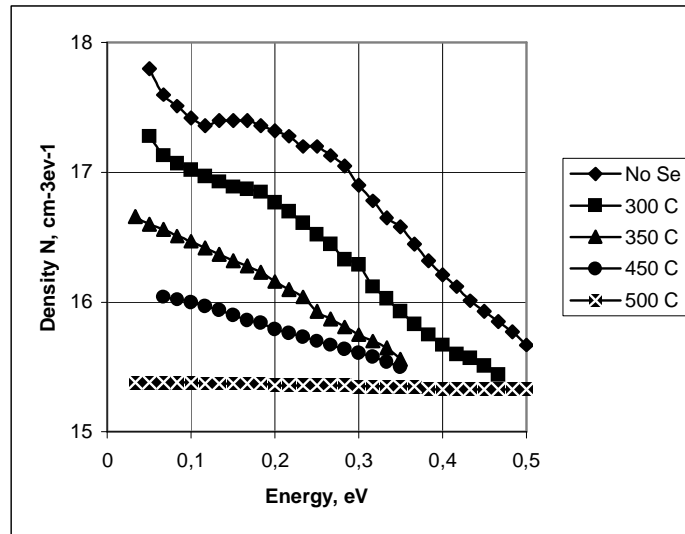


Fig. 7. Density of states of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ at different selenization temperatures.

Fig. 5 shows the spectral dependency of the photocurrent $I_{ph}(h\nu)$ for three types of CIGSE. The photosensitivity threshold is at ~ 1.4 eV. $I_{ph}(h\nu)$ is determined from film absorption and in its form is involved in the multiple light reflection.

The optimization of the deposition process for chalcopyrite-based thin film compound of solar cells is an empirical process. For this purpose, the admittance spectroscopy measurements have been used in order to provide information related to the interface states and to deep states in the bulk of the absorber. The technique involves the measurement of the device capacitance as a function of frequency, voltage and temperature, and can be performed easily on specialized devices [3,7]. To find the properties that are favorable for efficient devices we correlated the results of admittance measurements for the barrier structure $\text{Mo-CuIn}_{1-x}\text{Ga}_x\text{Se}_2\text{-Al}$, to investigations by *in situ* photoconductivity spectroscopy. We introduced some controlled variations of depositing process by varying the profile of the elemental fluxes during the evaporation and the substrate temperature. In such a way we have controlled the deposition process of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ thin films on Mo-coated soda lime glass substrates.

The inflection point of the $C(f)$ curve is related to the emission time constant τ_e of defects according to

$$2\pi\nu = 2/\tau_e = 2\sigma v_{th} N_{eff} \exp(-E_\omega/kT), \quad (1)$$

where σ is the capture cross section of the defect, v_{th} – the thermal velocity of free electrons, N_{eff} – the effective density of states in the band and E_ω is the binding energy of trapped carriers. We considered the parabolic potential approximation in the space charge region and calculated the N_{eff} from the relationship [6]

$$N_{eff}(E_\omega) = 2 U_d^{1/2} / (w \sqrt{q(E_\omega - E_F(\infty))} \omega / (kT)) dC/d\omega \quad (2)$$

where U_d is the diffusion potential, w – the space charge width, and $E_F(\infty)$ denotes the position of the Fermi-level at the edge of the space charge region. The capacitance data allow for the estimation of these parameters. In Fig. 6 are shown the typical results of capacity-frequency measurements for the structure Mo-CuInSe₂-Al before selenization at various substrate temperatures.

Fig. 7 shows the density of states in CuIn_{0.75}Ga_{0.25}Se₂ films prepared at substrate temperature of 250 °C. The data are remarkable in demonstrating the ability of the method to tailor high performance photo-voltaic cells.

4. Conclusions

A new and rather cheap technological process of deposition of polycrystalline films of a quaternary structure CuIn_{1-x}Ga_xSe₂ and CdS was developed on the basis of two steps method comprising deposition of films by e-beam ablation at 250 °C and subsequent selenization and sulfurization at 500 °C. The optical properties of the bulk and film materials are practically identical.

There was developed the capacity spectroscopy method for monitoring the density of deep trap centers. With this method it is possible to optimize the preparation process of films deposition.

The localized states and the quasi-continuous distribution of states in the forbidden band of amorphous CuIn_{1-x}Ga_xSe₂ films down to 0.5 eV have been found and characterized.

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