GROWTH AND PROPERTIES OF $CuIn_5Se_8$ TERNARY COMPOUND THIN FILMS

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(Received 6 October 2006)

Method of pulsed laser deposition (PLD) is widely used for preparation of films of various semiconductor compounds. The indicated technology has a number of preferences as compared with traditional methods of deposition and makes it possible to deposit complex semiconductor compounds of stoichiometric composition, this being important for practical use.

Data on preparation of $CuIn_5Se_8$ ternary compound thin films by PLD and investigation of their optical properties have been presented in the work. $CuIn_5Se_8$ single crystals grown by a directional crystallization of the melt in evacuated quartz ampoules from elemental components have been used as targets.

The PLD system consisted of a free–running commercial Nd:YAG laser working in a regime of a free generation (λ = 1.06 μm, $\tau_p = 10^{-3}$ s). Laser beam was focused on a surface of $CuIn_3Se_5$ target using a glass lens with a focus distance 550 mm. The pulse frequency was $3\cdot10^{-2}$ Hz, the pulse energy was equal to 150-180 J. The film deposition was carried out in a vacuum chamber at residual pressure $2\cdot10^{-3}$ Pa, the deposition rate was equal to $(2\text{-}4)\cdot10^5$ Å/s. A chemically cleaned glass was used as substrates. The temperature of the substrates during the deposition process was equal to ~570 K.

Composition of crystals and films was established by means of X-ray microprobe spectral analysis using “Cameca – SX100” analyzer. It was established, that composition of the films corresponds to formulae of $CuIn_5Se_8$ compound and it is reproducible for different parts both for crystals and films. Structure and cell parameters of the crystals and films were established by X-ray method. Diffractograms were recorded on the X-ray diffractometer DRON-3M automatically controlled by computer in CuKα – radiation using a graphite monochromator. Taken from different parts of single crystals (Fig. 1, top) and films (Fig. 1, bottom) the diffractograms corresponded to hexagonal structure (Fig. 1). The cell parameters calculated by the method of least squares on lines $2\theta > 50°$ are proved to be equal to: a=4.038± 0.002 Å, c = 32.782 ± 0.005 Å.

Transmission spectra of the films in the band gap edge region have been detected by “Perkin – Elmer – Lambda – 19” spectrophotometer at T = 300 K in the region of 0.5-2.5 μm. Germanium detector was used as a sensor. The obtained spectra are presented in Fig. 2.

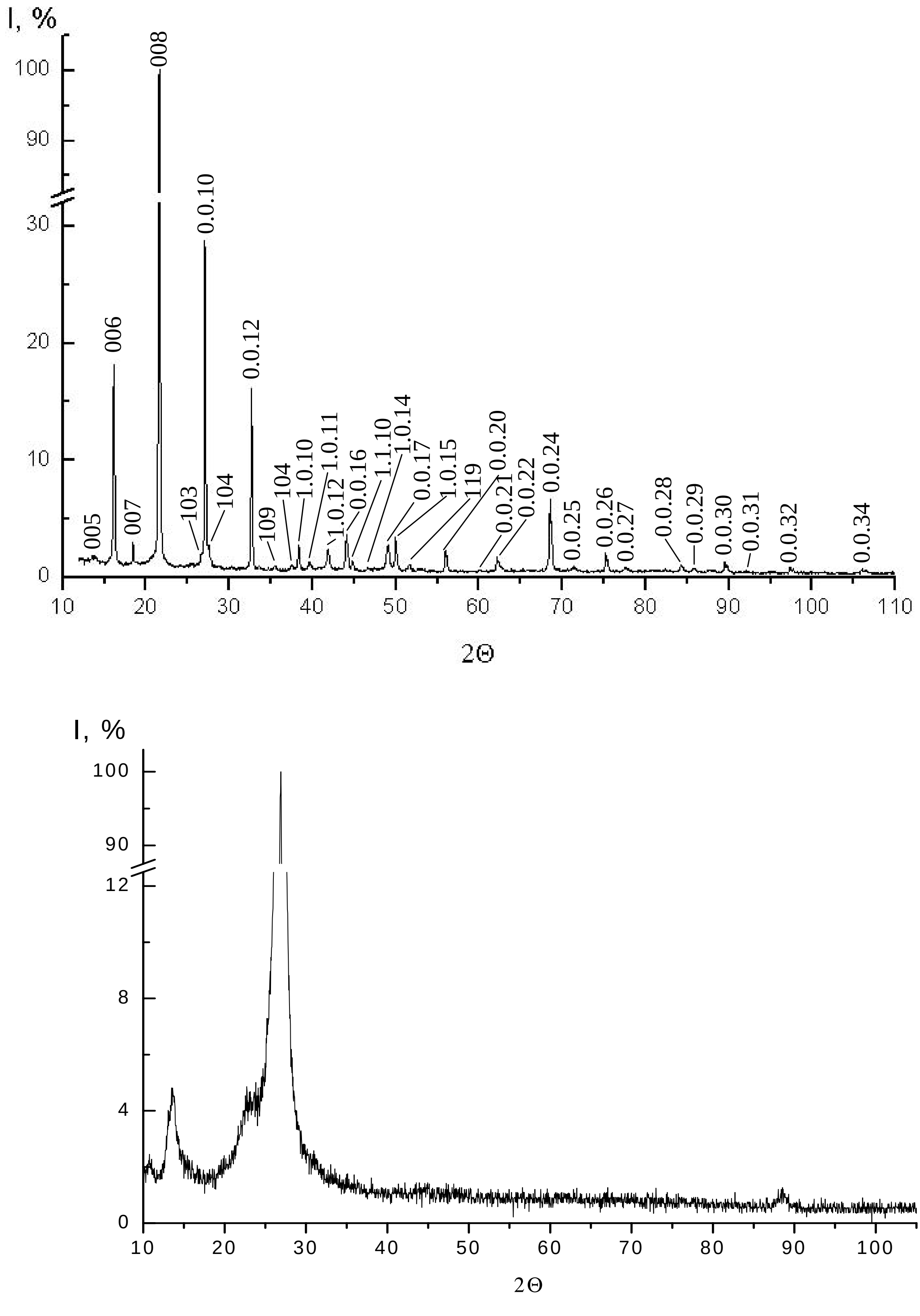

Fig.1. Diffractograms of $CuIn_5Se_8$ single crystal (top) and film (bottom)

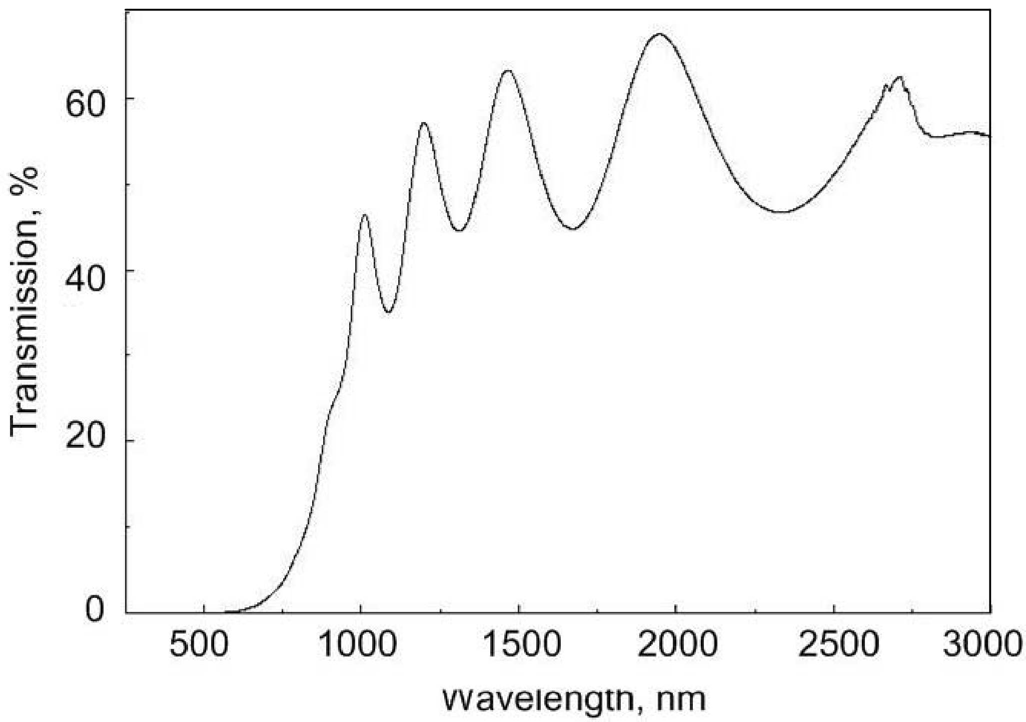

Fig. 2. Transmission spectra of $CuIn_5Se_8$ film.

Absorption coefficient (α) was calculated on transmission (T) spectra by the formula, which takes into account many repeated time reflections inside a plane-parallel sample [1]:

$$\alpha = \frac{1}{d}\ln\left\{\frac{(1-R)^2}{2T} + \sqrt{\left[\frac{(1-R)^2}{2T}\right]^2 + R^2}\right\}, \tag{1}$$

where d is the film thickness, $R = 0.25$ is the reflection coefficient.

Analysis of the spectral dependence of the optical absorption coefficient (α) on photon energy has shown that the obtained $CuIn_5Se_8$ films display high absorption coefficient in the region of investigation (> 10^4 cm^{-1}) and reveal a complex structure of the band absorption edge, what has been caused by p-d-hybridization of valence band in this type of compounds.

Similar to other compounds of this class the band gap value (Eg) was determined by extrapolation of the linear section of the $(\alpha \cdot h\nu)^2$ dependence versus photon energy ($h\nu$) to its intersection with the abscissa axis. The values of optical transitions obtained by us for $CuIn_5Se_8$ compound are equal to: $Eg_1 = 1.32 \pm 0.01$ eV, $Eg_2 = 1.43 \pm 0.01$ eV and $Eg_3 = 1.52 \pm 0.01$ eV.

Proceeding from the results obtained by us one can suppose that the transition with energy $Eg_1 = 1.32$ eV corresponds to $\Gamma_7^V - \Gamma_6^C$ transition (valence band – conduction band transition). Transition $Eg_2 = 1.43$ eV is connected with the splitting of the valence band under crystal cell field action (Δ_{cr}) $\Gamma_6^V - \Gamma_6^C$ and $Eg_3 = 1.52$ eV transition is caused by spin-orbital (Δ_{so}) splitting of the valence band $\Gamma_7^V - \Gamma_6^C$.

According to the Hopfield quasi-cubic model, values of energies of crystal (Δ_{cr}) and spin-orbit (Δ_{so}) splitting of the valence band have been calculated using the relationships [2]:

$$\Delta_{cf} = \frac{E_2 + E_1}{2} - \frac{1}{2}\left[(E_2 + E_1)^2 - 6E_1E_2\right]^{1/2}, \quad (2)$$

$$\Delta_{so} = \frac{E_2 + E_1}{2} + \frac{1}{2}\left[\left(E_2 + E_1\right)^2 - 6E_1E_2\right]^{1/2}, \quad (3)$$

where $E_1 = Eg_1 - Eg_2$; $E_2 = Eg_3 - Eg_2$.

The indicated values for $CuIn_5Se_8$ films are equal to: $\Delta_{cr} = -0.132$ eV, $\Delta_{so} = 0.112$ eV.

Acknowledgement

The work has been financed by the INTAS, grant 03-6314.

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