

## **ELECTRICAL AND PHOTOELECTRICAL PROPERTIES OF HETEROJUNCTIONS ON THE BASE OF $\text{Cu(InGa)Se}_2$**

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CdS films deposited by hot wall technique on mica were used as substrates for  $\text{Cu(InGa)Se}_2$  deposition. Two methods were used for the deposition of  $\text{Cu(InGa)Se}_2$  films: a) vacuum thermal evaporation from a single source and b) "flash" evaporation. The obtained films were of p-type conductivity with hole concentration varied from  $2 \times 10^{18} \text{ cm}^{-3}$  to  $6 \times 10^{20} \text{ cm}^{-3}$  depending on the fabrication method. The structures  $\text{Cu(InGa)Se}_2\text{-CdS}$  were divided into two groups: the structures of type I having the CdS film thickness from 1.6  $\mu\text{m}$  to 2.8  $\mu\text{m}$  and the structures of type II having the CdS film thickness from 0.6  $\mu\text{m}$  to 0.8  $\mu\text{m}$ . It was established that the direct/reverse current ratio is 8-16. For the first type heterostructures the diffusion potential is 1.2-1.8 V and for the second type is 0.2-0.34 V. The  $\text{Cu(InGa)Se}_2\text{-CdS}$  photosensitivity is situated in the wavelength region from 0.51  $\mu\text{m}$  to 1.1  $\mu\text{m}$  and is determined by the electron-hole pair generation in both materials.

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### **1. Introduction**

The interest in new materials of photovoltaic conversion increases continuously [1]. The chalcopyrite semiconductors of the class I – III – IV are intensely studied due to their applications in thin film solar cells [2,3]. The quaternary compound semiconductors  $\text{CuI}_{1-x}\text{Ga}_x\text{Se}_2$  are promising materials for multijunction photovoltaic devices.

This paper is related to the investigation of  $\text{Cu(InGa)Se}_2\text{ - CdS}$  heterojunctions, as perspective solar cells.

### **2. Experimental**

#### **2.1 CdS layers fabrication and their properties**

CdS layers deposited by hot wall technique (HWT) method on to mica and glass substrates were used as a component of  $\text{Cu(InGa)Se}_2\text{ - CdS}$  heterojunctions [4,5]. The CdS layers deposition was carried out in the reactors the design of which takes into consideration the method features and doping conditions.

CdS powder of "semiconductor" purity, annealed for the evaporation of Cd and S excess components which did not interact was used as a source deposition. The dielectric substrate was covered by  $\text{SnO}_2$  thin layer ( $d \sim 0.2 \dots 0.3 \mu\text{m}$ ) with the resistivity of  $\sim 10^{-3} \Omega\text{-cm}$ , charge carrier mobility  $\sim 30 \text{ cm}^2/\text{V}\cdot\text{s}$  and transparency of  $\sim 80\%$  in the wavelength region of 0.4 - 75  $\mu\text{m}$ . The influence of the source and substrate temperature on the crystalline structure, electrical and optical properties of the obtained films are studied for the determination of the optimal technological

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conditions. The source temperature  $T_{\text{sour}}$  was varied in the range of 620-680 °C and the temperature of the substrate,  $T_{\text{sub}}$ , in the range 350 °C - 500 °C.

The fabrication conditions and electrophysical parameters of CdS layers are brought in the Table 1, where  $\nu$  – growth rate,  $d$  – layer thickness,  $\rho$  – resistivity.

Table 1.

Material	$T_{\text{sour}}$ , °C	$T_{\text{sub}}$ , °C	$T_{\text{In}}$ , °C	$\nu$ , $\mu\text{m}/\text{min}$	$d$ , $\mu\text{m}$	$\rho$ , Ohm·cm
CdS	640	350	-	0.04	0.2	$2.4 \times 10^5$
	650	380	-	0.08	0.5	$4.4 \times 10^3$
	650	390	-	0.23	0.7	$1.2 \times 10^3$
	660	420	-	0.25	2.5	$4.9 \times 10^3$
CdS:In	660	400	650	0.20	1.5	$1.2 \times 10^{-1}$

A group of samples was obtained after the additional annealing before deposition of the source material in the quasi-closed volume during one hour. The obtained layers resistivity is  $(1-5) \times 10^3$  Ohm·cm. The size of the crystallites increases from 0.5 to 3  $\mu\text{m}$  when the substrate temperature is raised. The layers with the thickness less than 0.2  $\mu\text{m}$  have high resistance (up to  $2.4 \times 10^5$  Ohm·cm). The addition in the reactor during the technological process of indium doping impurity decreases the film resistivity down to  $1.2 \times 10^{-1}$  Ohm·cm.

The absorption spectrum of CdS layers show that their structure is a mixture of amorphous and crystalline states. This is confirmed also by the excessive X-ray diffraction maxima. At the photons energy decrease from 3.0 eV to 2.5 eV the absorption coefficient slowly decreases from  $5000 \text{ cm}^{-1}$  to  $800 \text{ cm}^{-1}$ . In the range from 2.36 eV to 2.60 eV a linear dependence of  $\alpha^2 = f(h\nu)$  is observed, which is characteristic for the amorphous state of the substance. The band gap value of 2.47 eV and impurity level of 1.62 eV, formed at the layer annealing were estimated from the extrapolation of  $(\alpha h\nu)^2 = f(h\nu)$  to the fundamental absorption.

## 2.2 Cu(InGa)Se<sub>2</sub> film fabrication and their properties

The  $A^1B^3C^4$  chalcopyrite compound thin films can be deposited by a large variety of methods including three source evaporation, molecular beam epitaxy, metalloorganic chemical vapor deposition, pulverization, selenization of  $A^1B^3$  e.t.c. In our studies the polycrystalline CuGaSe<sub>2</sub> (CGS) and CuGa<sub>1-x</sub>In<sub>x</sub> Se<sub>2</sub> (CGIS) films were fabricated by three methods: a) vacuum thermal evaporation from a single source (TE); b) “flash evaporation” (FE); c) chemical transportation from gaseous phase (CT).

During the “flash” evaporation the evaporated semiconductor was injected on the evaporator in the form of a very small granules and the evaporator temperature was maintained high enough for the evaporation of the less volatile component. Due to the continuous injection of the granules and their low thermal capacity the vapour flow has a composition close to the evaporated material. The evaporator temperature was of 1140 °C and the substrate temperature was varied from 200°C to 350°C. The distance from the evaporator to substrate was 5 cm so that at the maximum evaporator temperature its influence on the substrate is minimum.

The film growth rate depending on the evaporated material and substrate temperature was of 0.1-0.4  $\mu\text{m}/\text{min}$ . The obtained layers had the thickness of 1-5  $\mu\text{m}$  and contained grains of 0.2-0.5  $\mu\text{m}$  in diameter.

The film conductivity was of p-type. The vacuum evaporated silver or copper, followed by sample annealing at 200 °C during 20 minutes in the hydrogen atmosphere, were used as electrical contacts. After the annealing, the resistance of the silver contacts do not change, but that of the copper ones decreases by 2 orders of magnitude. The contacts were deposited symmetrically at the disc form layer edges and Van-der-Pau method [3] was used for the investigation of the galvanomagnetic properties of the films. By taking into consideration the shape of the samples, the Hall coefficient and conductivity were determined by the following expressions:

$$R_H = \frac{U_{24}d}{I_{13}B}, \quad (1)$$

$$\sigma^{-1} = \frac{\pi d}{2 \ln 2} \left( \frac{U_{34}}{I_{12}} + \frac{U_{41}}{I_{23}} \right) f(R), \quad (2)$$

where

$$f(R) = 1 - \frac{\ln 2}{2} \left( \frac{(U_{34}/I_{12}) - (U_{41}/I_{23})}{(U_{34}/I_{12}) + (U_{41}/I_{23})} \right)^2 \quad (3)$$

The Hall effect and conductivity were studied in the temperature range 100-440 K. Depending on CGS and CGIS film composition and fabrication method their parameters are given in Table 2.

It was established, that for the films with charge carrier concentration  $p \approx 10^{21} \text{ cm}^{-3}$  the Hall coefficient and conductivity are constant in the whole temperature range. This is caused by the electronic gas degeneration (at 300 K Fermi level enters the conduction band at the hole concentration of  $\approx 3 \times 10^{19} \text{ cm}^{-3}$ ).

Table 2. Transport properties of the Cu(InGa)Se<sub>2</sub> and related films.

Composition	Method	$p, \text{ cm}^{-3}$	$\sigma, (\text{Ohm}\cdot\text{cm})^{-1}$	$\mu, \text{ cm}^2/\text{V}\cdot\text{s}$
CGS	ET	$1 \times 10^{21}$	90	0.4
CGS	ED	$2 \times 10^{18}$	2.5	4.0
CGIS	TC	$6 \times 10^{20}$	9.0	0.1

In the samples with the hole concentration of  $\sim 10^{18} \text{ cm}^{-3}$  the Hall coefficient does not change when the temperature increases to 200 K and then decreases, which indicates the presence of an impurity level with the activation energy of 0.13 eV. The experimental results analysis have shown that the impurity compensation with the compensation coefficient of 0.9-0.95 occurs in the films.

### 3. Results

The current-voltage (I-V) dependencies of CdS–CuInGaSe<sub>2</sub> heterojunctions with the different CdS layer thickness are given in Fig. 1. As one can see the dependencies are asymmetrical, the direct current surpasses the invers one by 6...8 times. For the heterojunctions with the CdS film thickness of 1.6...2.8  $\mu\text{m}$  (structures of type I) the diffusion potential  $U_d$  determined by the extrapolation of linear segment of I-V direct dependence to  $I=0$  was 1.2..18V (Fig. 1a), and for the structures with CdS layer thickness of 0.6...0.6  $\mu\text{m}$  (structures of type II)  $U_d=0.2...0.34\text{V}$  (Fig. 1b)

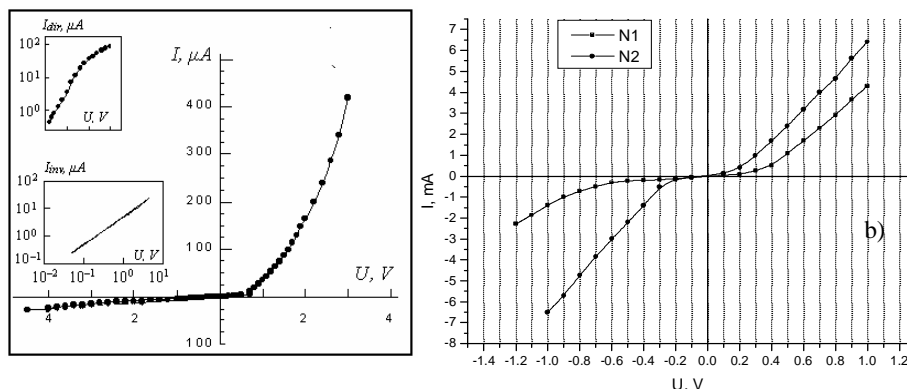


Fig. 1. CdS–CuInGaSe<sub>2</sub> heterojunctions current-voltage (I-V) dependencies: the structures of type I; b) the structures of type II.

The series resistance of the studied heterojunctions was of  $3.3 \times 10^3$  Ohm for the structures of type I and  $1.4 \times 10^2$  Ohm for the structures of type II. The  $\ln I_{dir} = f(U)$  dependence contains linear segments both for the I<sup>st</sup> type heterojunctions, as well as for the II<sup>nd</sup> one. This indicates an exponential dependence of current on voltage, which is described by the expression:

$$I_{dir} = I_S \left( e^{\frac{eU}{AkT}} - 1 \right), \quad (4)$$

where  $I_S$  is the saturation current and has a value of  $3 \times 10^{-7}$  A for the heterojunctions of type I and of  $7 \times 10^{-7}$  A for the heterojunctions of type II,  $A$  - is a quality factor. At 300 K the factor  $A$  has the value of 7.4 for the heterojunctions of type I and of 1.26 for the heterojunctions of type II up to the voltages of 0.15 V and of 4.77 for higher voltages.

At the reverse voltages the current-voltage dependence is given by the power dependence:

$$I_{inv} \sim U_{inv}^m \quad (5)$$

and a mild threshold is observed. For CdS–CuInGaSe<sub>2</sub> heterojunctions of type I at 300 K the power factor  $m = 1.03$ . For the heterojunctions of the type II the power factor  $m = 1.08$  up to the voltages  $U = 1.15$  V and  $m = 3.88$  at higher voltages. The power factor  $m \approx 1$  is specific for the leakage currents and  $m \approx 4$  is specific for the tunneling currents.

The exponential dependencies of the current on the applied voltage is specific for the studied heterojunctions in the whole temperature range studied. The quality factor  $A$  increases with the temperature increase: at low voltages ( $< 0.15$  V) from 1.26 at 292 K to 1.6-1.82 at higher temperatures; at the voltages higher than 0.15 V from 4.77 at 292 K to 6.77 at 376 K. The activation energy determined from these experiments was  $\Delta E = 0.31$  eV at  $U = 0.14$  V and  $\Delta E = 0.46$  eV at  $U = 0.10$  V.

The studies of the photoelectrical properties of heterojunctions allow to determine the generation-recombination processes in the heterojunctions components as well as the heterojunction interface. The analysis of the obtained results is necessary for the determination of the data needed in heterojunction band diagram and to elucidate the current flow mechanism through heterojunctions.

The study of the CdS–CuInGaSe<sub>2</sub> heterojunctions open circuit voltage  $U_{oc}$  and of short circuit current  $I_{sc}$  on the illumination has shown that when the illumination increases  $U_{oc}$  tends to saturation and  $I_{sc}$  linearly depends on the illumination (Fig. 2). Such  $U_{oc}$  and  $I_{sc}$  dependencies on light intensity agree with the theory of an abrupt junction.

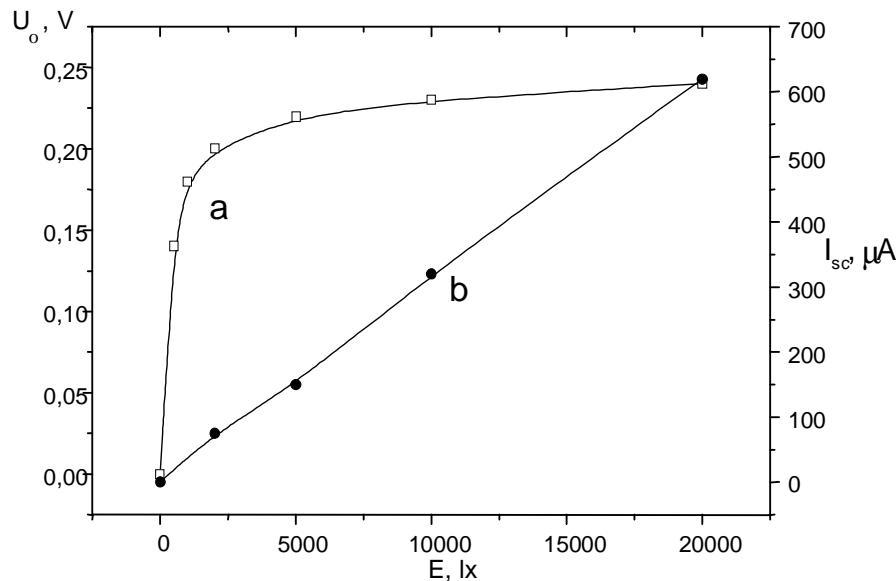


Fig. 2. CdS–CuInGaSe<sub>2</sub> heterojunctions open circuit voltage  $U_{oc}$  (a) and short circuit current  $I_{sc}$  (b) dependence on illumination.

The open circuit voltage is given by the relation:

$$U_{cd} = \frac{akT}{e} \ln\left(\frac{I_{sc}}{I_s} + 1\right), \quad (6)$$

where  $I_s$  is a saturation current (equal to  $(3-7) \times 10^{-7}$  A).

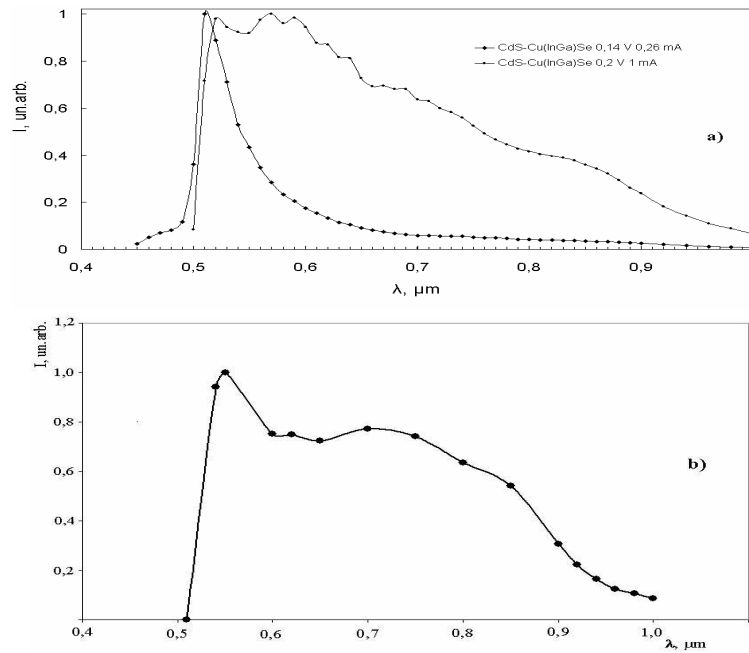


Fig. 3. CdS–CuInGaSe<sub>2</sub> heterojunctions photosensitivity spectrum dependence: a) the structures of type I; b) the structures of type II.

The open circuit voltage  $U_{oc}$  tends to saturation with the light intensity increase and the short circuit current  $I_{sc}$  increases proportional to the light intensity. For the structures with CdS layers with higher thickness at 300 K and light intensity of  $80 \text{ mW/cm}^2$   $I_{sc} = 0.26 \text{ mA/cm}^2$  and  $U_{cd} = 0.14 \text{ V}$  and for the structures with lower thickness  $1.6 \text{ mA/cm}^2$  and  $0.22 \text{ V}$  correspondingly. The fill factor  $FF = 0.26$ . The load characteristics form of CdS–CuInGaSe<sub>2</sub> heterojunctions measured at 300 K points out to the presence in the studied structure of a high value resistance.

The photosensitivity of CdS–CuInGaSe<sub>2</sub> heterojunctions covers the wavelength region from  $0.5 \mu\text{m}$  to  $1.1 \mu\text{m}$  (Fig. 3) and is determined by the electron-hole generation in both component materials. In the structures with the thicker CdS layer the absorption in cadmium sulphide predominates and in those with thinner CdS layer a wide region ( $0.51-0.86 \mu\text{m}$ ) of constant photosensitivity was revealed, which is determined by a weak influence of the recombination process on the charge photocarrier accumulation.

#### 4. Conclusions

CdS–CuInGaSe<sub>2</sub> heterojunctions fabrication technology was elaborated as the successive deposition of the thin films: CdS and CuInGaSe<sub>2</sub> on the glass substrates covered by a thin ( $d \approx 0.1 \div 0.3 \mu\text{m}$ ) SnO<sub>2</sub> film with the resistivity of ( $\rho \approx 10^{-3} \Omega\text{cm}$ ) and transparency of ( $T \approx 80\%$ ).

$I - V$  characteristics of Cu(InGa)Se<sub>2</sub>–CdS heterojunction for different CdS film thickness were studied. The studied structures were divided into two groups: first type structures having the CdS layer thickness from  $1.6 \mu\text{m}$  to  $2.8 \mu\text{m}$  and second type structures having the CdS layer thickness

from 0.6  $\mu\text{m}$  to 0.8  $\mu\text{m}$ . It was established that the direct/reverse current ratio is of 8-16. For the 1<sup>st</sup> type heterostructures the diffusion potential is 1.2–1.8 V and for the 2<sup>nd</sup> type is 0.2–0.34 V.

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