

**POLARIZATION  
PHOTOABSORPTION  
SPECTROSCOPY OF  
ZnO/CdS/Cu(In,Ga)Se<sub>2</sub>  
THIN FILM SOLAR CELLS**

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**ABSTRACT**

The photosensitivity of polycrystalline-film Cu(In,Ga)Se<sub>2</sub>/CdS/ZnO solar cells with different thickness of CdS and ZnO films have been studied. These structures exhibit a conversion efficiency 11-12% in the spectral region from 1.2 to 2.4 eV at T= 300 K. Polarization photosensitivity was observed for oblique incidence of linearly polarized light on the ZnO surface of these structures. The induced photopleochroism and an increase of the photocurrents as a result of a decrease of reflection losses were found. The induced photopleochroism coefficient  $P_1$  increases with the angle of incidence  $\Theta$  as  $P_1 \sim \Theta^2$  and its value is found to be 10-17% at  $\Theta = 75^\circ$ . The results of these polarization investigations demonstrate the sensitivity of the photoelectric processes to the optical quality of the ZnO films. Such polycrystalline-film solar cells can be employed as polarization-photosensitive devices.

**KEYWORDS**

Cu(In,Ga)Se<sub>2</sub>, thin film, solar cell, photosensitivity, induced photopleochroism

## Introduction

Chalcopyrite-type semiconductors such as  $\text{CuInSe}_2$  and their quaternary and pentenary solid solutions have been attracted an attention for their large absorption coefficients and the desirable band gaps for photovoltaic energy conversion. Polycrystalline  $\text{Cu(In,Ga)Se}_2$  film has emerged as an important material for high efficiency, stable, and radiation hardness thin film solar cells (Stolt et al., Schmidt et al., Ruckh et al.). Thin film solar cells with active area efficiencies in the range of 15-18% have been fabricated on such absorber films (Stolt et al.). In this paper we report the results by the polarization photoabsorption measurements of  $\text{Cu(In,Ga)Se}_2$  solar cells prepared with various thickness of CdS and ZnO films.

## Experimental methods

In our investigation we used  $\text{Cu(In,Ga)Se}_2$  – based thin film solar cells produced in Germany ( Stuttgart University ). It is based on a  $\text{Cu(In,Ga)Se}_2$  absorber film and ZnO window film ( serving as a transparent top contact ), which are

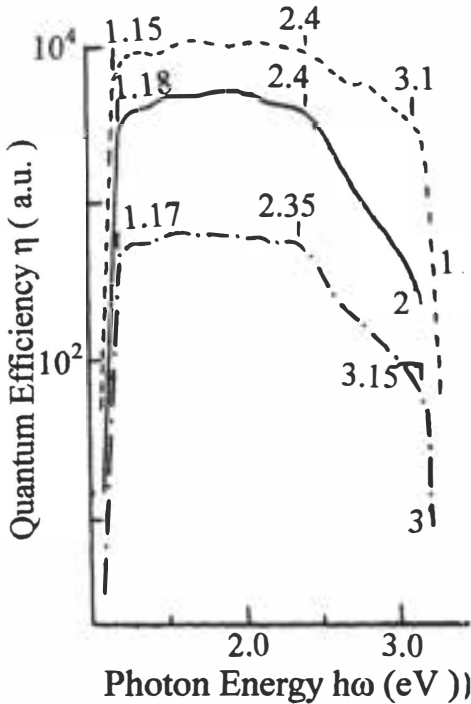
Table 1. Photoelectrical properties of  $\text{Cu(In,Ga)Se}_2/\text{CdS}/\text{ZnO}$  structures at  $T = 300 \text{ K}$ .

No samples	$d_{\text{CdS}}$ , nm	$d_{\text{ZnO}}$ , nm	$U_0$ , mV	$\beta$	$\eta$ , %	$s$ , $\text{eV}^{-1}$	$\delta_{1/2}$ , eV	$h\omega^m$ , eV	$P_1$ , %
1	50	500	595,3	66	11,2	58	1.45	2.03	14
2	100	500	595.6	68	11.4	40	1.36	1.95	17
3	100	1000	619.7	79	12.2	46	1.34	1.64	11

separated by a thin CdS buffer window film. A Mo back electrode is DC-magnetron sputtered on glass plate. The fabrication of  $\text{Cu(In,Ga)Se}_2$  absorber films proceed by multisource sputtering. The composition of the solid solution corresponded to the ratio  $\text{In}/(\text{In}+\text{Ga})=0.25$  and was chosen on the base of the requirements which must be met in order to obtain higher photoconversion efficiency. Next, a CdS buffer film was grown using chemical bath deposition and then a ZnO film was grown using RF-sputtering. The thickness of ZnO and CdS films in thin film solar cells are given in Table 1.

In all experimental results given below, the structures was illuminated through the top film by natural and linearly polarized radiation ( LPR ). To determine the polarization parameters of the solar cells photosensitivity were secured in a STF-1 ( the Fedorov's table in Russian), which made it possible to vary continuously the angle of incidence  $\Theta$  of the radiation on the receiving surface and the azimuthal angle  $\phi$  between the electric vector  $\mathbf{E}$  of the light wave and the plane of incidence of the radiation ( PIR ). The photosensitivity of the solar cells was measured in the regime of a short-circuit photocurrent, which was proportional to the flux density of the incident radiation, making it possible to determine the relative photoconversion quantum efficiency  $\eta$  as the ratio of the photocurrent to the number of incident photons. The spectral resolutions of the setup was no worse than 1 meV.

**Results and discussion**



The photoelectric parameters for thin film devices with different thickness CdS

(  $d_{CdS}$  ) and ZnO (  $d_{ZnO}$  ) films are presented in Table 1. As follows from Table 1, the maximum open-circuit photovoltage  $U_0$ , fill factor  $\beta$ , and photoconversion quantum efficiency  $\eta$  are attained at  $d_{ZnO} = 1000$  nm.

Fig. 1 shows the spectral dependences of the relative quantum efficiency for these structures at  $T = 300$  K. When such structures are illuminated in the direction of the normal to the surface of ZnO film, the window effect, typical for all devices, was observed.

Fig. 1: Room-temperature spectral dependences of the  $\eta$  of  $Cu(In,Ga)Se_2/CdS/ZnO$  structures ( Numbers by curves correspond to Table 1 ).

Here the long-wavelength photosensitivity limit obeys an exponential law and is localized in the region of photon energies corresponding to the band edge absorption in a  $Cu(In,Ga)Se_2$  film. It is characterized by a slope  $s$  from 40 to 58  $eV^{-1}$  for the different photoconverters ( Table 1 ), which is typical for direct interband A-transitions. The short-wavelength limits of the photosensitivity is caused by the appearance of interband absorption in a CdS ( $\hbar\omega > 2.35$  eV) and ZnO ( $\hbar\omega > 3.1$  eV) wide-band films. The full width at half efficiency of the spectral characteristics  $\eta(\hbar\omega)$  is  $\delta_{1/2} = 1.34 - 1.45$  eV for the different solar cells ( see Table 1 ) and it characterizes them as a wide-band photoconverters of natural radiation. The energy position of the photosensitivity maximum  $\hbar\omega_m$  moves to the long-wavelength region and the  $\delta_{1/2}$  have the tendency to fall with the increase of the thickness CdS and ZnO films ( Fig. 1 and Table 1 ).

It should also be noted that the interference features in the  $\eta(h\nu)$  for the investigated solar cells in contrast to (Rud' V. Yu. et al.) are not observed. Probably it is connected with lowering of the quantum efficiency on investigate structures relatively (Rud' V. Yu. et al.).

When the obtained solar cells were illuminated by linearly polarized radiation in a direction normal to the plane of the ZnO film their short-circuit photocurrent  $i$  was independent of the spatial orientation of the electric vector  $E$  of the light wave. Therefore, when  $\Theta = 0^\circ$ , the polarization indicatrix of the photocurrent  $i_\phi$  degenerates into a straight line. This is determined by the isotropic character of the photoactive absorption in the polycrystalline ZnO, CdS, and Cu(In,Ga)Se<sub>2</sub> films. As a result, the induced photopoleochroism coefficient

$$P_i = (i^P - i^S) / (i^P + i^S), \quad (1)$$

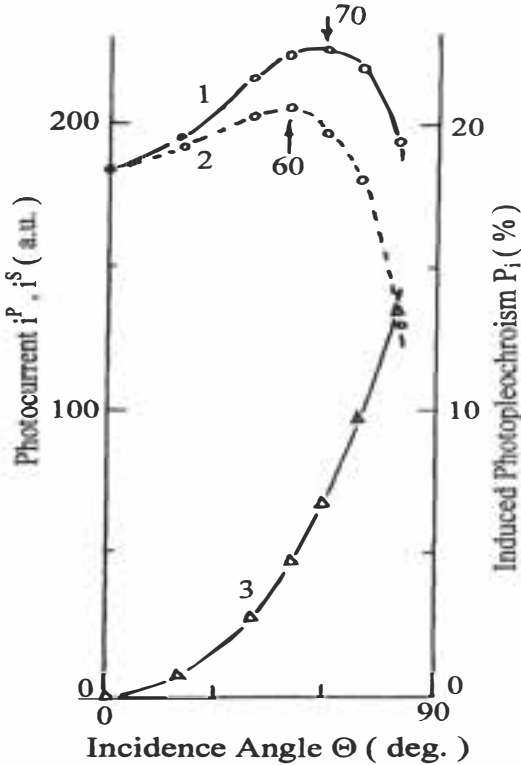


Fig. 2: Angle of incidence dependences of the photocurrents ( $i^P$  - 1,  $i^S$  - 2) and induced photopoleochroism (3) of Cu(In,Ga)Se<sub>2</sub>/CdS/ZnO structures ( Sample No 3,  $\lambda = 0.50 \mu\text{m}$ ).

where  $i^P$  and  $i^S$  are, respectively, the photocurrents with  $E \parallel PIR$

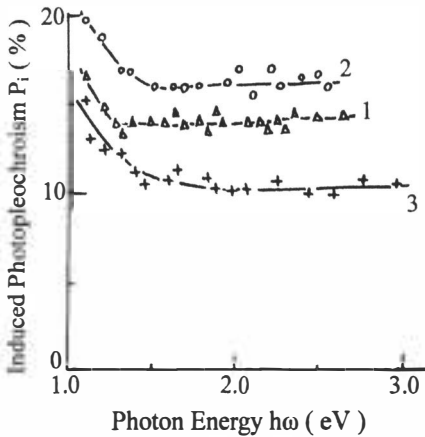


Fig. 3: Spectral dependences of induced photopleochroism of  $Cu(In,Ga)Se_2/CdS/ZnO$  structures (Numbers by curves correspond to Table 1,  $\Theta=75^\circ$ ).

and  $E^\perp PIR$ , is equal to zero in the entire region of the solar cells photosensitivity. For this reason, there are grounds for believing that these solar cells do not possess natural photopleochroism ( Figs. 2 and 3 ) ( Kesamanly et al. ). Switching to measurements of the photosensitivity of solar cells in a geometry with oblique incidence of LPR on the receiving plane of the cells, i.e.,  $\Theta > 0^\circ$ , differences appear in the values of the photocurrents  $i^P$  and  $i^S$ . As a result, the  $P_1$  becomes different from zero and increases continuously with increasing angle of incidence as a square law  $P_1 \sim \Theta^2$ . Indeed, as one can see from Fig. 2, the function  $P_1(\Theta)$  leaves zero at  $\Theta = 0^\circ$ , which shows that there is no natural photopleochroism ( Kesamanly et al. ). In the case  $\Theta > 0^\circ$  the photo-pleochroism which appears is classified, according to ( Kesamanly et al. ), as induced, and in the coordinates  $(P_1)^{1/2} - h\omega$  these curves are straight lines in agreement with the analyses ( Medvedkin et al. ).

The dependences of the photocurrents  $i^P$  and  $i^S$  on the incidence angle of the LPR for the examined thin solar cells exhibit a similar behavior over the entire photosensitivity range. The examples of such dependences are shown in Fig. 2. At first, photocurrents for p- and s-polarization increase with the  $\Theta$ , then reach a maximum values for each polarization,

and only then start to drop rapidly. These features may be connected with the elimination of the reflection losses for the radiation of each polarization. Formerly the similar regularity was found for structures with higher quantum efficiency ( Rud' V. Yu. et al., Rud' V. Yu.).

The induced photopleochroism coefficient on structures with varying thickness of the CdS and ZnO films ( Fig. 3 ) remains virtually constant in the wide energy region from 1.4 to 3 eV in contrast to the solar cells with higher efficiency where the oscillation  $P_1$  was observed (

Rud' V. Yu. et al.). An estimate of the refraction index on the basis of value  $P_1 = 10 - 17\%$  at  $\Theta = 75^\circ$  for the different structures with  $\eta = 11 - 12\%$  gives  $n = 1.2 - 1.4$ . These values differs from known value of  $n$  for ZnO ( Baranskii et al. ). The observed changes of the  $P_1$  at  $\hbar\omega > 1.4$  eV may be cause the modifications of antireflection properties of the examined solar cells. If to take in account the drop  $P_1 \rightarrow 0$  as the antireflection measure ( Botnaryuk et al. ) then the maximum of the enlightenment effect for obtained solar cells was reach at  $d_{\text{ZnO}} = 1000$  nm. Important marked that exactly on this structure obtained the maximum value of the  $\eta$ . The fall of thickness ZnO films caused on the decreasing of enlightenment effect and photoconversion efficiency.

### Summary

Measurements have been made of the photosensitivity of the polycrystalline-film  $\text{Cu}(\text{In,Ga})\text{Se}_2/\text{CdS}/\text{ZnO}$  structures. These structures exhibit a quantum efficiency  $11 - 12\%$  at  $T = 300$  K. Polarization photosensitivity was observed for oblique incidence of linearly polarized light on the ZnO surface of these structures. The photopleochroism was studied as a function of the thickness CdS and ZnO films. The polarization photoabsorption spectroscopy applied to polycrystalline structures showed that they can be used in a new function for this type devices –wide-band photo-analyzers of the LPR. It is shown that the induced photopleochroism is sensitive to the quality of the polycrystalline-film structures.

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