Polarimetric sensors on the basis of CdS/CuInSe₂ heterocontact: Influence of the heat treatment on photosensitivity spectrum

V. Yu. Rud'

*Peter the Great St. Petersburg Polytechnic University,
St. Petersburg, 195251, Russia
rudvas.spb@gmail.com*

Yu. V. Rud'

*Ioffe Physico-Technical Institute of RAS,
St. Petersburg, 194021, Russia*

E. I. Terukov

*Ioffe Physico-Technical Institute of RAS,
St. Petersburg, 194021, Russia*

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CuInSe₂ thin films were grown by vacuum evaporation of presynthesized material from a single source. The room-temperature photoconductivity spectra of the film show a strongly dependence on the evaporation conditions and, especially, on the evaporation temperature. A shift of the long-wavelength photoactive absorption edge and the evolution of the photoconductivity spectra of the films were observed. The influence can be explained by allowing for deviations of the compositions of the condensed phase from CuInSe₂ stoichiometry.

Keywords: Heterostructures; photoconductivity; stoichiometry; evaporation; thin film; photopleochroism.

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1. General Appearance

Copper and indium diselenides CuInSe₂ (CIS) are direct-band semiconductors with chalcopyrite structure; they attract interest owing to their use in solar power engineering, since they have in deal band gap ($E_g = 1.03\text{eV}$ at $T = 300\text{K}$) and high absorption coefficient over the entire spectral range of solar radiation. The use of

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CIS in thin film solar cells is especially promising. Thin film solar cell technology offers the best hope for obtaining photovoltaic devices with low cost and reasonable efficiency.

Photosensitive structures, consisting of a heterostructures of p-CuInSe₂ (CIS) film (magnetron sputtering) with a n-CdS<In> film (vacuum thermal evaporation), have been fabricated and then studied. These heterocontact have a current photosensitivity of 5 mA/W in the spectral region between the band gaps of CIS and CdS.

Heat treatment of the film heterocontact in vacuum at 200-400° C influence on transformation of the spectral dependence of the photosensitivity contour. Photosensitive structures, consisting of heterocontact of p-CuInSe₂ film ($d \leq 5 \mu\text{m}$, magnetron sputtering of synthesized bulk material) with a n-CdS<In> film ($d \leq 5 \mu\text{m}$, vacuum thermal evaporation), have been fabricated and then studied. These heterostructures have a current photosensitivity of 5 mA/W in the spectral region between the band gaps of CuInSe₂ and CdS. Heat-treatment of the film heterostructure in vacuum at 200–400° C transforms the spectral dependence of the photosensitivity contour. This transformation is attributable to the compensation of CdS by diffusion of copper out of the narrow-band component in the heterostructure.

One of the most promising thin film materials in the respect is CIS. Thin film structures of solar cells based on CIS and related materials (CuInGaSe₂ for example) have been previously reported to show an efficiency of 19–20%.

The possibility to improve the photoelectric parameters of the film heterocontacts based on CIS by heat — treatment is well known. The spectral reconstructions of the photosensitivity has, however, not been discussed. But it is very important to create new structures based on this material, such as structures with nanostructured layers, for example with a conductive layer of carbon nanotubes.

2. Experimental Results and Discussion

CIS films were synthesized by magnetron sputtering of a polycrystalline target of undoped n- or p-CIS. We obtained reproducible CIS films with p-type conduction, thickness up to $d \approx 5 \mu\text{m}$, and resistivity in the range $0,5 \div 10^3 \text{ Ohm}\cdot\text{cm}$ at 300 K. X-ray data showed that this films had a polycrystalline structure and the lattice constants agreed with known values for bulk CIS crystals.^{1,2} Microprobe x-ray spectral analysis confirmed the correspondence between the atomic compositions of the films and the target. To obtain photosensitive structures on the specular surface of the electrically homogeneously p-CIS films, without preliminary heat treatment, they were deposited by vacuum thermal evaporation at temperatures of 150 to 200° C, through a masking layer of n-CdS<In>. The thickness of the CdS<In> layers reached $1\text{--}2 \mu\text{m}$ ($p \approx 0.3 \div 0.5 \text{ Ohm}\cdot\text{cm}$, $n \approx (1 \div 5) \times 10^{18} \text{ cm}^{-3}$ at 300 K), and the layer itself had high adhesion to the CIS surface. As ohmic contacts we used In for the CdS and Au for the p-CIS.

The film heterostructures which we studied were contacts of p-CIS and n-CdS<In> films, deposited by magnetron sputtering on optical glass with a pre-deposited layer of molybdenum. Studies of the steady-state voltage-current characteristics showed that the film n-p heterostructures were rectifying ≤ 5 at $U \approx 1$ V, with the direction always corresponding to the external negative bias on CdS. Illumination of the film heterostructures revealed a photovoltaic effect. The films of CdS were always negatively charged, in accordance with the energy diagram of the contact between these materials. The current sensitivity of the wide-band component of the heterostructures reached 5 mA/W and was maximal upon illumination from the side of the wide-band component of this heterocontact.²

Figure 1 shows a typical spectrum of the short-circuit photocurrent i_{SC} , immediately after fabricating the film heterostructure. The short-wave edge is caused by the outset of direct interband transitions in the material with a wide-band window, while the long wave edge is due to direct transitions in CIS.

Also we studied the effect of successive heat treatments on the photoelectric properties of these film structures. Fig. 2 shows typical photosensitivity spectra of the heterostructures for various heat-treatment temperatures t_T . We see that with increasing of t_T , there occurs a reconstruction of the photosensitivity spectra, that consists in a reduction in the contribution of the photoactive absorption by the narrow-band material. Upon reaching $t_T = 400^\circ \text{C}$, for example, the heterocontacts were predominantly sensitive in the absorption region of the wide-band CdS film. It can be seen from Fig. 3 (curves 1 and 2) that the photosensitivity in the region of interband absorption of CIS decreases by four orders of magnitude, as compared

Fig. 1. Photosensitivity spectral function of CdS/CIS heterocontact at $T=300$ K. Illumination from the CdS side.

Fig. 2. The effect of the temperature of isochronous heat-treatment on $t_T = 10$ min and $T = 300$ K. t_T in $^{\circ}\text{C}$: curve 1 — initial structure; curve 2–250; curve 3 – 350 and curve 4–400.

Fig. 3. The dependence of the i_{SC} on the temperature isochronous heat-treatment at $t_T = 10$ min and $T = 300$ K. $\hbar\omega$ in eV: curve 1–1 and curve 2–2.1.

with the initial value, upon reaching $t_T = 400^{\circ}\text{C}$. In the interband absorption region of CdS, the photosensitivity of the heterocontacts, plotted as a function of heat treatment temperature t_T , goes through a maximum in the region $t_T \approx 200^{\circ}\text{C}$, which may indicate that the crystal structure of the heteroboundaries and the bulk of the CdS<In> films are of a higher quality.

Fig. 4. The effect of isothermal heat-treatment time of the i_{SC} ($\hbar\omega$) in min: curve 1 — initial structure; curve 2–10; curve 3–30 and curve 4–140.

Isothermal heat treatment of such heterocontacts in the temperature region in which the photosensitivity is raised is also accompanied by spectra reconstruction of i_{SC} (Fig. 4, curves 1–4). This reconstruction consists in an increase in photosensitivity with increasing of heat treatment time τ .

The increase in the photosensitivity occurs since radiation is also absorbed in the wide-band film, with a corresponding decrease in the photoactive absorption in the narrow-band film. It can be seen in Fig. 5 (curves 1 and 2) that a decrease in photosensitivity in the region $\hbar\omega = 1$ eV accompanies the increase in the photosensitivity at $\hbar\omega = 2.1$ eV.

The i_{SC} kinetics have a shape of curves with saturation. The time it takes to reach the equilibrium state increases significantly with decreasing heat-treatment temperature. If at $t_T = 250^\circ\text{C}$ the rapid increase in i_{SC} at $\hbar\omega = 2.1$ eV lasts for example, 30–40 min, then at $t_T = 200^\circ\text{C}$ the duration of this process increases to 2–3 hours.

Such heterocontacts used as a based thin film solar cells. They based on CIS absorber film and a ZnO window film (which serving as a transparent top contact, which are separated by thin CdS buffer window film. When such obtained heterostructures 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 of the light wave. Therefore, when the angle of incidence equal 0° , the polarization indicatrix of the photocurrent i_ϕ degenerates into a straight line. This experimental finding is a result of the isotropic character of the photoactive absorption in the polycrystalline ZnO, CdS and CIS

Fig. 5. The dependence of the $i_{SC}(\hbar\omega)$ on the isothermal treatment time at $t_T = 250^\circ\text{C}$ and $T = 300\text{ K}$. $\hbar\omega$ in eV: curve 1–1 and curve 2–2.1.

films. As a consequence, the induced photopoleochroism is equal to zero in the entire region of the heterostructures photosensitivity.⁴ Switching to measurements of the photosensitivity of such heterostructures in a geometry with oblique incidence of linearly polarized light on the receiving plane of such structure, i.e., when incidence angle start to be more the 0° , difference appear of in the values of the photocurrents i^P and i^S (Fig. 6).

Fig. 6. Angle of incidence dependencies of the photocurrent of different polarization (i^P – 1, i^S – 2) and induced photopoleochroism (P_I – 3) for thin film heterocontact based on CdS/CIS ($\hbar\omega = 2.0\text{ eV}$).

As a result, the photopleochroism becomes different from zero and increases continuously with increasing angle of incidence for square law.⁵ Indeed, as we can see from Fig. 6, the photopleochroism as a function from the incident angle, leaves zero at the incident angle equal zero, which shows that there is no natural photopleochroism. Then the photopleochroism starting rise with rising of the incidence angle we can classify this photopleochroism as induced.⁵ This result can be interesting to use such structures as polarimetric sensors.

3. Conclusion

The possibility to improve the photoelectric parameters of the film heterostructures based on CIS by heat treatment well known.³ The spectral reconstruction of the photosensitivity has, however, not been discussed. The results presented above seem to point to the fact that heat-treatment of the heterostructures causes copper to diffuse into the CdS film. As a result, the resistance of the p-CIS can be reduced and the resistance of n-CdS increased, which, as a final analysis shows, is accompanied by a shift of the active region of the heterocontact into CdS and the correspondingly increase in the short -wave photosensitivity. Polarization photosensitivity was observed for oblique incidence of linearly polarized radiation on the ZnO frontal surface of heterostructures based on CdS/CIS. The polarization photoabsorption spectroscopy applied to polycrystalline structures showed that these structures can be used in new function as polarimetric sensor wide band photoanalyzers of the linear polarized radiation. The results of the presented work is also important for further development of the applications of structures based on this material, as of thin-film CIS solar panels can be integrated on CMOS chips.

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