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Effective polycrystalline sensor of ultraviolet radiation

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Abstract. Deposition of special thin layers with high and low resistance in space charge region of surface barrier photoconverters based on the *p*-$Cu_{1.8}S$/*n*-CdS structure leads to a sufficient increase in photosensitivity and decrease in dark tunneling-recombination current. Highly efficient and stable polycrystalline photoconverters of ultraviolet radiation based on polycrystalline CdS have been obtained. Electrical and photoelectric properties have been investigated, and the main operational parameters of ultraviolet sensors have been adduced. The reasons for high stability of the parameters inherent to the *p*-$Cu_{1.8}S$/*n*-CdS sensors are as follows: the absence of impurity components additionally doped to the barrier structure and stability of the photocurrent photoemission component.

Keywords: polycrystalline UV sensor, cadmium sulfide, copper chalcogenide, surface-barrier structure, energy band offset diagram.

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Polycrystalline photoconverters (PhC) based on A_2B_6 compounds are among the most sensitive sensors of ultraviolet (UV) radiation. The PhC structure polycrystallinity does not hamper to get not only the maximum photosensitivity but also the electrical characteristics of barrier junction close to optimal and comparable with electrical characteristics of the best monocrystalline sensor analogs. Textured monophase thin-film polycrystalline layers deposited on a conducting substrate represent a system of parallel conjugated single crystals, and the electrical properties of barrier structures created on their basis are not worsie in comparison with single crystal analogs. Realization of direct transition in A_2B_6 bandgap gives the capability to use the thin photoactive layers with the thickness (2…5 μm). Production of thin films for photoconverters simplifies realization of device manufacture planar technology. Planar technology and applying the thin-film polycrystalline structures can significantly reduce the cost of PhC production. Moreover, the technological process of PhC obtaining on the base of A_2B_6 compounds is further simplified by getting the low values of the sensor series resistance R_p without an additional doping procedure. This applies to the compounds CdS and CdSe. It is known [1] that regulating the concentration of point defects by changing the conditions for the crystal growth, the concentration of free carriers can vary in a wide range. The electron concentration of the order of 10^{16} cm^{-3} can be obtained without additional doping with an extraneous impurity. The above concentration of the majority current carriers is sufficient to create an effective ultraviolet sensor with a sufficiently wide dynamic range of detectable powers: no less than 6 orders of magnitude.

The complexity of obtaining the wide-gap A_2B_6 semiconductors with a sufficiently high *p*-type conductivity, as well as the absence of isoperiodic hetero-partner causes the fact that the most effective barrier structure for A_2B_6 compounds is the surface-barrier one. For polycrystalline layers, applying the Schottky diodes is ineffective. Indeed, the metal film should have a thickness of the order of 10 nm, and the deposition of metal film of this thickness, which is continuous on the relief surface of the polycrystalline semiconductor, is problematic.

New perspectives for developing the effective barrier structures are associated with a degenerate semiconductor of *p*-type copper chalcogenide, namely: its stable modification $Cu_{1.8}S$ (digenite) that is an ideal pair for wide-gap A_2B_6 semiconductors of the *n*-type conductivity. The advantage of using p-$Cu_{1.8}S$ in surface-barrier photoconverters instead of metal is associated with the possibility of growing nanometer (~ 10 nm) $Cu_{1.8}S$ film on the surface of polycrystalline layers of A_2B_6 compounds. The developed by us technique for deposition of $Cu_{1.8}S$ on the surface of A_2B_6 compounds polycrystalline layers [2] allows obtaining a continuous transparent film with the thickness d ~10 nm. Applying the degenerate semiconductor instead of metal makes it possible to observe and practically use the photoelectric effect in the UV region of the spectrum, which is associated with the transport of hot electrons (photoemission) into an A_2B_6 semiconductor [3-5]. The transfer of hot carriers is weakly dependent on recombination processes at the interface of the junction, which provides high stability of this component in the photocurrent. It was experimentally ascertained that the largest contribution of hot carriers to the photoeffect in the spectral region of UV radiation is observed at a thickness of $Cu_{1.8}S$ within the range 10 to 15 nm. In the case of p-$Cu_{1.8}S$/n-CdS sensors, emission of hot electrons from $Cu_{1.8}S$ to CdS gives a significant addition, which can reach 50% of the photocurrent generated in the semiconductor structure at UV irradiation.

Possessing high quantum efficiency, p-$Cu_{1.8}S$/n-CdS UV radiation sensors concede to the best surface-barrier structures in terms of electric parameters. The electric parameters worsening are related with the large tunnel-recombination currents flowing through the junction and shunting the minimum above-barrier currents [6, 7]. To reduce the tunnel-recombination currents, it is proposed to insert thin high-resistance low-imperfect interlayers into the space charge region in CdS [8]. This procedure reduces the dark current by 3-4 orders of magnitude. However, a thin high resistive layer adjoining with $Cu_{1.8}S$ reduces the pulling electric field in the photoactive subsurface region, which leads to a decrease in the quantum efficiency of photoconverters. To maintain the high quantum efficiency, we introduce the additional low-resistance region which is formed in the space charge region that facilitates redistribution of the pulling electric field with localization of its maximum values at the p-$Cu_{1.8}S$/n-CdS interface near the illuminated surface of the photosensitive CdS.

The developed method of thermal evaporation with condensation in a quasi-closed volume was used to obtain the base photosensitive layers CdS [9]. Polycrystalline CdS layers with a photosensitive area of 100 mm^2 and 150 mm^2, thickness 5…7 µm and with the concentration of the majority charge carriers $n \approx 10^{15}$ cm^{-3} were grown on metalized dielectric substrates. Then, a high resistive ($n \approx 10^{13}$ cm^{-3}) CdS layer with the thickness close to 100 nm was deposited. A top of the high resistive layer, a low resistive CdS layer was grown with the thickness $d \sim$ 50 nm and electron density $n \approx 10^{16}$ cm^{-3}. The consequent deposition of thin CdS layers with different conductivity in one technological cycle is realized using the special technological procedure developed in this work (know how).

To create the photoconverters a barrier-forming layer of $Cu_{1.8}S$ was deposited on the indicated base layers with low resistive surface regions. The structure has defining features of the surface-barrier one: the electric field is almost completely concentrated in the base layer because of sharp asymmetry in the conductivity of contacting materials (hole concentration in $Cu_{1.8}S$ is $p = 5\cdot10^{21}$ cm^{-3}). The presence of a low-resistivity layer contributes to the optimal space redistribution of the field of the contact potential difference with localization of its maximum values in the near-surface region, where the maximum absorption of UV radiation occurs. This situation is demonstrated by the energy diagram of the p-$Cu_{1.8}S$/n-CdS photoconverter in Fig. 1.

The dashed curve in the diagram indicates the high resistive layer with the concentration N_{d2}, which contacts with the low resistive layer with N_{d1} presented in the CdS base layer before deposition of $Cu_{1.8}S$. Between these layers, there is a space charge region of the n-n junction, in which the value of the potential barrier is:

$$\varphi_1 = eU_{d1} = kT\ln\,(N_{d2} / N_{d1}),$$

where k is the Boltzmann constant, T – current temperature.

After deposition of the $Cu_{1.8}S$ thin layer, the contact potential difference φ_c (between $Cu_{1.8}S$ and CdS) compensates the potential barrier φ_1, and, since $\varphi_c > \varphi_1$, the opposite potential barrier φ is formed. Obviously, the φ value will be equal to the difference in the work functions of $Cu_{1.8}S$ and the CdS high resistive part. In the diagram (Fig. 1) the more abrupt run $\varphi(x)$ corresponds to the low resistive part and, consequently, to the large values of the pulling electric field $E = d\varphi/dx$ in the near surface region CdS.

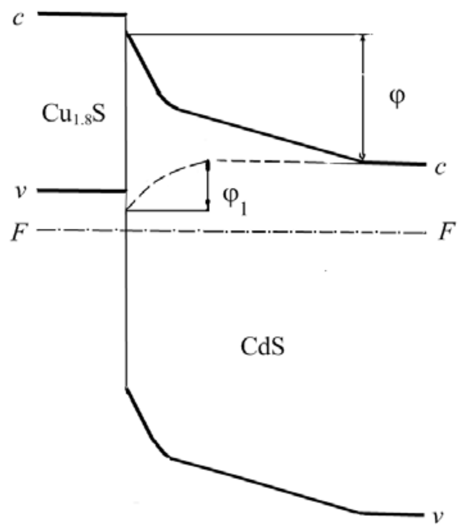

Fig. 1. The energy band diagram of a $Cu_{1.8}S$/CdS heterojunction with a low resistivity surface layer. The dashed line shows the behavior of the CdS conduction band before deposition of $Cu_{1.8}S$; F is the Fermi level; c and v are the conduction and valence bands, respectively.

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Fig. 2 shows the direct branches of the current-voltage (*I-V*) characteristic inherent to the studied PhC with a photoactive area of 100 mm^2. The curve *1* is the typical direct branch of *I-V* characteristic for p-$Cu_{1.8}S$/n-CdS junction with non-optimized space charge area. A significant decrease in dark currents (by 2.5 to 3 orders of magnitude) with introduction of the high-resistance layer is illustrated by the curve *2* in the figure. The dependence of the current on the voltage is always exponential. The differential resistance is $R_d > 10^9$ Ohm (with an external bias voltage of 10 mV). The curve *3* is *I-V* characteristic for p-$Cu_{1.8}S$/n-CdS structure with low resistive layer. It can be seen that at low values of voltage *U*, the parameters of the current-voltage characteristic practically coincide with the curve *2*. However, in contrast to a photoconverter that does not have a low resistive interlayer (Fig. 2, curve *2*), at $U >$ 0.3 V, the exponential part of the current versus the voltage is replaced by the part at which the current tends to saturation with increasing voltage. The current tendency to the saturation with an increase in the positive voltage is illustrated by the *I-V* characteristic that is presented in a natural scale (curve *4* in the figure).

The considered features of the straight branches of the *I-V* characteristics of structures with the low resistive surface layer can be interpreted using the diode model with double saturation [10], the existence of which is possible, for example, in the presence of a back-stop contact. However, as indicated by the capacitance – voltage and load characteristics, the indicated model is not realized. For a diode model with double saturation (or two switched-on connected in series with the opposite polarity of Schottky diodes), capacitance will decrease with increasing voltage applied both in direct, and in the opposite direction.

A different curves behavior is observed for the studied structures. The capacitance decreases for negative bias voltages, and increases at the positive ones. In addition, it is obvious that the diode with double saturation cannot be an effective photoconverter because of the large series resistance of the structure. In our case, we get the effective photoconverter, as it ensues from the high spectral sensitivity of the studied structures. Fig. 3 shows the photocurrent spectra, where curve *2* and *1* are, respectively, with and without the low-resistive layer. A noticeable sensitivity increase is presented in the entire spectrum region when the low-resistive layer is introduced. Observed absolute values of the photocurrent correspond to the best characteristics for known UV sensors [11-15]. Thus, sensitivity in the germicidal region of solar radiation at the wavelength λ = 254 nm reaches values of 120 mA/W.

The fact that the model of a conventional diode with double saturation is not realized in our case is also confirmed by the experimental loading (light) *I-V* characteristics presented in Fig. 4. The series resistance R_s of these structures can be calculated using the load characteristics:

$$R_s = 2(\text{tg}\ \alpha - U_{oc} / I_{sc} + P / I_{sc}^2),$$

where α is the angle indicated in Fig. 4, U_{oc} – open circuit voltage, I_{sc} – short-circuit current, *P* – area under the curve $U = f(I)$. For the sensor, the characteristic of which is shown in Fig. 4, R_s = 7 kOhm. The above-described regularities of dark *I-V* characteristic (Fig. 2) are most likely related to the existence of a hidden *n-n* homojunction, which starts to appear at positive bias

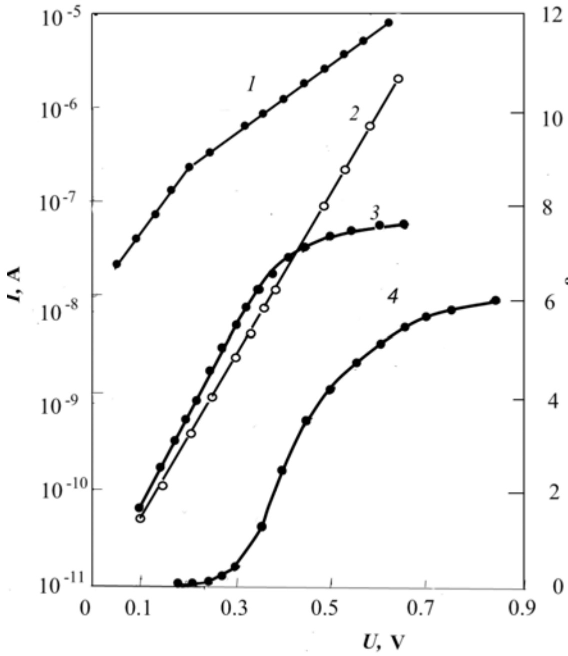

Fig. 2. Direct branches of the current-voltage characteristics for photoconverters of various designs: $Cu_{1.8}S$/CdS structures (*1*) without special surface layers, (*2*) with a high resistive layer, and (*3*) with a low resistive layer on the top of high resistive layer. Curves *1–3* are plotted in the log scale (left vertical axis). *4* – linear scale of currents (right scale).

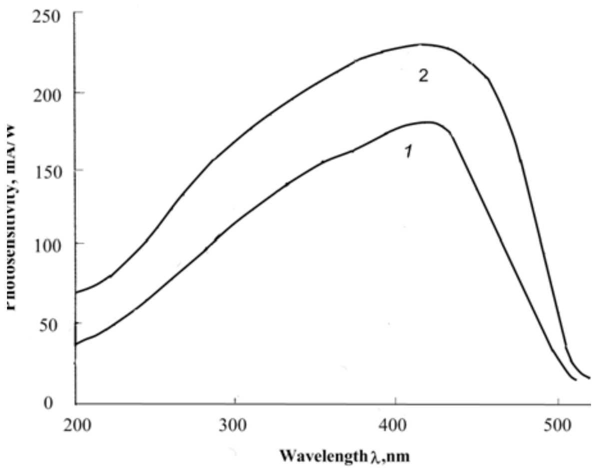

Fig. 3. Spectra of the sensor photocurrent: *1* – $Cu_{1.8}S$/CdS without a low-resistivity layer; *2* – $Cu_{1.8}S$/CdS with a low-resistance layer.

voltages $U > \varphi/e$. In this case, the space charge area which exists between the low-resistance and high-resistance parts of the base layer increases. The fact of space charge increasing leads to dark current limitation (curves *1*, *3* in Fig. 2) and structure capacity diminution under condition of external positive bias increasing.

For UV sensors with large photoactive area, the use of which is effective in the case of detection of low radiation fluxes (metrology of low UV fluxes, control of bio--chemiluminescence, *etc.*), the spatial uniformity of the photoresponse (good zone characteristic of the sensor) becomes critical. The zone characteristic of the sensor with an area of 100 mm^2, obtained in this study, is shown in Fig. 5. The data were obtained under condition of moving the light probe 50 µm wide over the PhC surface along the X and Y axes. As can be seen, deviation from the uniformity of ΔI_{ph} along the axes does not exceed 0.5%, which is at the level of world standards [16, 17].

Thus, the creation of effective and stable polycrystalline UV sensors is possible, due to the original features of the p-$Cu_{1.8}S$/n-CdS surface-barrier structure. Let us point out the main ones: the possibility of creating a thin (<10 nm) continuous $Cu_{1.8}S$ film on the relief surface of a polycrystalline semiconductor. At the indicated thicknesses, the conditions for the maximum absorption of UV radiation in the region of the pulling electric field are realized, and an appreciable contribution to the photocurrent of hot electrons generated by high-energy radiation in the $Cu_{1.8}S$ layer (the transparent component) is observed.

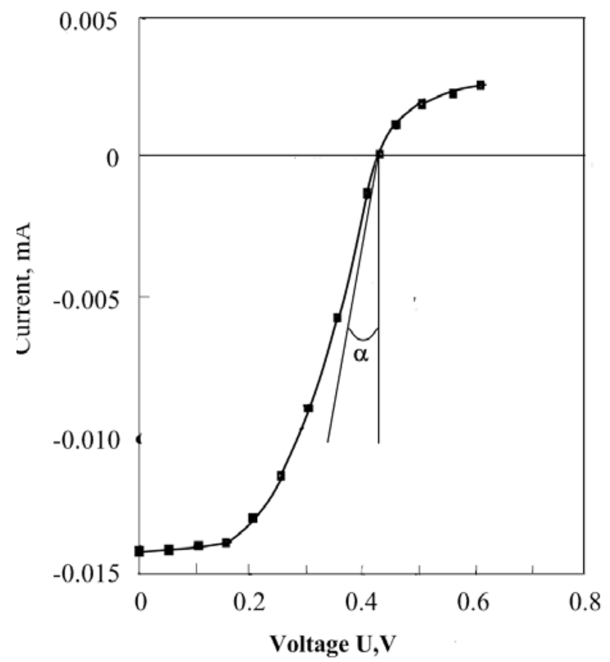

Fig. 4. Load *I-V* characteristics of $Cu_{1.8}S$/CdS sensors with a low-resistance surface layer. Lighting conditions: a mercury lamp with an equivalent power of 1 mW/cm^2. The area of the sensor is 100 mm^2.

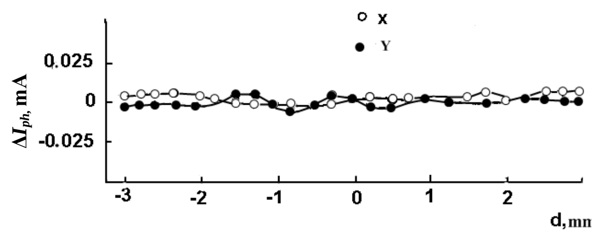

Fig. 5. Deviation of the photocurrent when the light probe moves along the converter surface in the directions X and Y.

We conclude that formation of thin high-resistance and low-resistance layers in the space-charge region leads to a decrease in the dark tunnel-recombination currents and preserves the high quantum efficiency of the UV sensor. The observed regularities of the electrical characteristics at large forward bias voltages are explained by the presence of a hidden *n-n* junction and do not interfere with the achievement of photoconverter high operational parameters. The high stability of the operational parameters of p-$Cu_{1.8}S$/n-CdS sensors is determined by the absence of additional doping with the impurity components of the barrier structure and the stability of the photocurrent photoemission component.

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