PHOTOVOLTAIC EFFECT IN Cd$_2$SnO$_4$–CdGeP$_2$ HETEROJUNCTIONS

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It is shown experimentally to be possible to form rectifying photosensitive heterojunctions by using the method of reactive cathodic sputtering to deposit layers of Cd$_2$SnO$_4$ on the surface of n- and p-type CdGeP$_2$ single crystals. It is demonstrated that photosensitivity is seen in the range between the widths of the forbidden bands of CdGeP$_2$ and Cd$_2$SnO$_4$; photosensitivity is 3-4 orders of magnitude greater for n-n junctions than for n-p junctions. The parameters of polarizational photosensitivity were established and analyzed, providing evidence that the investigated system, with an n–n contact, can be used to make polarimetric photodetectors.

The straight-band semiconductor CdGeP$_2$ (E$_{IG}$ = 1.72 eV, 300 K [1]) is one of the most promising of the compounds AIIBIVcV$_2$, being of interest in the development of different types of photosensors [1]. The present study examines the feasibility of developing photosensitive heterojunctions (PH) based on n- and p-type CdGeP$_2$ crystals and wide-band layers of the oxide n-Cd$_2$SnO$_4$ (CTO) with E$_{IG}$Cd$_2$SnO$_4$ = 2.8 eV [2]. Our study is part of a series of investigations devoted to finding an effective energy barrier for ternary compounds AIIBIVcV$_2$ [3-5], and it contains results of the first studies of physical processes in the above system.

Thin (nd = 0.3-0.4 μm) polycrystalline layers of CTO with a resistivity $\rho = 0.1-1$ Ω·cm at T = 300 K were deposited by the method of reactive sputtering of a target of pure Cd and Sn (atomic ratio 2:1) in an Ar + O$_2$ atmosphere [6] on the polished surface (100) of monocrystalline plates of n- and p-type CdGeP$_2$ (Table 1) with average dimensions of 3 × 3 × 0.2 mm$^3$. Cadmium oxide and tin oxide have good adhesion relative to CdGeP$_2$ with an optical transparency $T = 80\%$ in the spectral range 0.5-2.5 eV. Heterojunctions of the n-n and n-p type exhibit distinct rectification (~10$^2$, $U = 2$ V, Fig. 1a). The transmission direction corresponds to "+" and "-" polarity of the external bias on the CTO layer in isotypical and anisotypical structures, respectively. The reverse branch is characterized by a smooth current rise. It can be attributed to the effect of leakage current due to defects in the periphery of the structures. The forward branch cannot be described by a constant value of the defectiveness factor, as in the case of the use of oxides of other compositions as the wide-band layer [5]. As our studies showed, illumination of the resulting HS's generates a photoelectric voltage $U_{xx}$. This voltage is significantly greater for isotypical junctions than for anisotypical junctions. The sign of $U_{xx}$ corresponds to "+" for n-n heterojunctions and "-" for n-p heterojunctions (this is the polarity of the photoelectric voltage of the CTO layer). The rectification direction and the sign of the photovoltage – which does not change with a change in the coordinate or the wavelength of the generating beam – are in qualitative agreement with the approximate diagram of the n–n and n–p contacts based on data on electron affinity and other parameters of the materials [2, 7, 8]. According to estimates, the discontinuities in the bands for the heteroboundary are $\Delta E_C = 0.5$ eV and $\Delta E_V = 1$ eV. Table 2 shows some of the experimentally obtained parameters of the resulting structures. The short-circuit photocurrent $i_{sc}$ and the no-load photovoltage $U_{xx}$ depend on incident flux density $L$ in accordance with the usual relations for photosensors [9]. The value obtained for the saturation photovoltage, $U_{xx, sat} = 0.4-0.5$ V, is greater than the value for the total diffusion potential $V_d = 0.2$ eV estimated from the Anderson model. This is probably connected with the fact that the contribution of the boundary states was not considered. The higher photosensitivity of the n-n heterostructures and the well-produced value of maximum voltaic sensitivity $S_{P,m}$ (Table 2) point to the clear superiority of such junctions over n-p heterostructures in the given case. This in turn can probably be attributed to the fact that the photosensitivity of isotypical structures is determined only by the main charge carriers – free electrons.

Figure 1b and Fig. 2 show typical photosensitivity (PS) spectra seen in n-n structures. It follows from these results that the method that was employed [6] for depositing the CTO layers makes it possible to check the character of the spectral dependence of PS in the shortwave region and to influence the range $\Delta\omega_m$ of the maximum PS. The longwave boundary of PS in unpolarized light is described by an exponential law with high values of curvature in all n-n heterostructures. At $\hbar\omega = 1.5$ eV, photosensitivity is due to the activation of deep centers and takes the form of a monotonic reduction to $\hbar\omega = 0.5-0.7$ eV. The curvature of the longwave boundary of PS is generally smaller in n-p heterojunctions and is connected with the large compensation of p-CdGeP$_2$. The shortwave decay of PS in the heterostructures we obtained begins near the energy associated with indirect transitions in CTO $E_{IG}$ (Fig. 2). However, in several cases, we succeeded in obtaining an n-n heterojunction without pronounced shortwave decay of PS until $E_{IG}$ (Fig. 1b). This is direct empirical evidence that the method of CTO deposition can be used to obtain a high-quality heteroboundary. In such structures, the maximum PS is obtained between $E_{IG}$ and $E_{IG}$, i.e., we obtain the well-known "window effect" in the relation of photosensitivity to unpolarized radiation [9]. In the range 125-240 K, the PS of n-n heterojunctions increases by the law $S_u \sim \exp(-E/kT)$, where $E = 0.1$ eV. Above 250 K, the increase is slowed so much that it depends only slightly on temperatures up to 370 K. This pattern of behavior is typical of the heterostructures we obtained and reflects features of the temperature dependence of recombination processes.

When a heterostructure is exposed to linearly-polarized radiation on the CTO side along a normal to the heteroboundary, with the (100) crystallographic orientation for CdGeP$_2$, the photoelectric response in the range of polarizational photosensitivity of the ternary semiconductor obeys the well-known periodic law [1]. For a heterojunction with the boundary in the (001) plane, the photoresponse is independent of the position of the electrical vector of the light wave $E$. Thus, the resulting system makes it possible to create both traditional polarization-insensitive heterostructures and heterostructures exhibiting the polarimetric effect. In polarized light, the PS spectra display the polarizational branching characteristic of photoactive absorption in uniform CdGeP$_2$ crystals (Fig. 1b and Fig. 2). We should point out that a step clearly appears in polarization $E \parallel c$. This step is connected with photoactive absorption involving the participation of In donor centers which form levels with an activation energy $E_D = 40-80$ meV. Meanwhile, in unpolarized light and in