

Photoconversion in heterocontacts of CdTe and its analogs with protein

Yu. V. Rud'

A. F. Ioffe Physicotechnical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia

V. Yu. Rud'

St. Petersburg State Technical University, 195251 St. Petersburg, Russia

I. V. Bodnar' and V. V. Shatalova

Belarus State University of Information Science and Radio Engineering, 220027 Minsk, Belarus

G. A. Il'chuk

State University "L'vov Politechnika," 293000 L'vov, Ukraine

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Semiconductor/natural-protein photosensitive structures based on CdTe crystals and its ternary analogs have been created. The photoelectric properties of these structures in natural and linearly polarized light are examined. The wideband character of the photosensitivity of these semiconductor/protein structures is established in the range between the width of the semiconductor band gap and the energy ≈ 3.5 eV, where the latter is assumed to be the pseudogap in the band spectrum of the protein. It is shown that the natural photopleochroism of the semiconductor is reproduced in its contact with the protein. Potential applications of a new class of photosensors are discussed. © 1999 American Institute of Physics. [S1063-7826(99)01110-2]

1. INTRODUCTION

The properties of various classes of heterocontacts (HC) are now being studied extensively, opening up entirely new and, in the initial stages of study, unexpected possibilities of these unique objects.¹ However, along with solid-state structures of the kind semiconductor/semiconductor and semiconductor/metal, an increasing amount of attention is being given to semiconductor contacts with electrolytes and substances of biological origin.^{2–4} In this paper we report the results of the creation of a new class of converters consisting of contacts of cadmium telluride and its ternary analogs with natural protein.

As the semiconductor materials for creation of the heterocontacts we used crystals of CdTe and its ternary analogs from the group I–III–VI₂, which can be formally represented as the result of substitution of two atoms from the second group by atoms from the first and third groups of the periodic table (see Table I).

TABLE I. Photoelectric properties of the contacts of CdTe and its ternary analogs I–III–VI₂ with protein ($T = 300$ K).

Compound	Type of conductivity	$1/R \cdot e$, cm ⁻³	$\hbar\omega_1$, eV	S , eV ⁻¹	S_u , V/W	S_f , mA/W	$\delta_{1/2}$, eV
CdTe	n	10^{16}	1.51	38	10^3	45	1.82
		10^8	1.48	90	10^4	...	
CuInSe ₂	p	3×10^{17}	1.02	50	570	18	2.00
CuInS ₂	p	2×10^{16}	1.53	60	1×10^4	7	2.02
CuGaS ₂	p	10^7	2.48	40	3×10^3	...	1.84

2. EXPERIMENTAL PART

CdTe crystals were grown by two methods. One was zonal recrystallization of a melt with composition similar in stoichiometry to CdTe in the controlled vapor phase. This method made it possible to obtain electrically uniform crystals with n -type conductivity in which the Hall mobility grew as the temperature was lowered below 300 K, which is characteristic of lattice scattering. Wafers were obtained from slabs of these newly grown crystals by cleavage and therefore had specular (001) planes, which did not require further processing. The second type of sample was grown by the gas-phase method, which led to doping of the resulting CdTe crystals with iodine. The crystals obtained in this way were semi-insulating and also did not require further processing.

Crystals of the ternary compounds I–III–VI₂ were grown from melt (CuInSe₂, CuInS₂, and AgInS₂) or from the gas phase (CuInS₂ and CuGaS₂). The surfaces of the latter did not require processing and had orientation (112), whereas the samples obtained from melt, after being cut, were mechanically processed and then chemically polished.

As a result of a multipart study, we developed the following technique for creating a new class of photoconverters. On a glass substrate with a semitransparent metal layer (Mo, Ni, $d \approx 0.5 \mu$), we placed a drop of natural protein. The semiconductor wafer was placed into contact with the surface of the protein in such a way that the liquid protein was "compressed" between the metallized surface of the glass and the semiconductor wafer, filling the gap between them.

After completing the procedure of putting the semiconductor in contact with the substrate through the layer of pro-

tein, the position of the wafer was fixed relative to the glass with the help of a dielectric lacquer. The system semiconductor/protein/metal (Fig. 1) was outfitted with electrical contacts making it possible to study photoelectric phenomena in two different geometries of illumination.

3. DISCUSSION OF THE RESULTS

The steady-state current–voltage characteristic of one of the structures is shown in Fig. 2. For all of the investigated heterocontacts in which we used crystals of *n*- and *p*-type conductivity for thicknesses of the protein layer $\cong 10$ – $50 \mu\text{m}$ the current–voltage characteristics manifest a distinct rectification effect, which for different semiconductors varied in the limit 1.8–4.5 for voltages up to 5 V. The reverse characteristic, as a rule, obeys a power law with exponent close to one. The residual resistance of the structures depends strongly on the properties of the semiconductors and varies in the limits 10^3 – $10^{10} \Omega$ at 300 K. In the course of our studies the characteristics of the structures were essentially constant and showed good reproducibility.

When heterocontacts with different semiconductors (see Table I) were illuminated, a photovoltaic effect was reproducibly observed; its sign remained unchanged for both geometries of illumination, for different positions of the light probe on the surface of the structures (diameter $\cong 0.2 \text{ mm}$), and variation of the energy of the incident radiation over the entire range of photosensitivity of each of the investigated heteropairs. It is important to emphasize that the photosensitivity always predominates when the heterocontacts are illuminated from the protein-layer side. The table shows the maximum values of the voltage S_u and current S_i photosensitivity. Comparison of these data with the data known for other classes of photoconverters on crystals of similar quality^{2,5–7} gives reason to believe that the new heterocontacts while still in the first stage of their development are at least as good as photoconverters presently available.

Typical curves of the spectral dependence of the relative quantum efficiency of photoconversion η for the obtained heterocontacts are shown in Fig. 3. It can be seen from the figure that the photosensitivity of the heterocontacts based on CdTe and its ternary analogs with illumination from the protein side has a wideband character, revealing a maximum

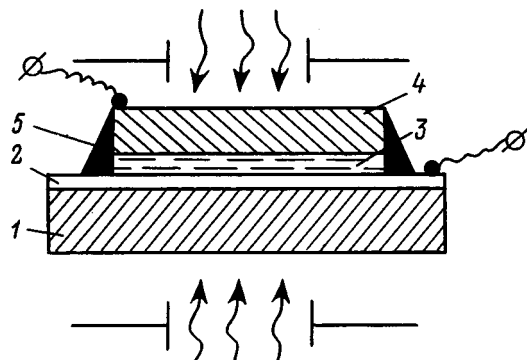


FIG. 1. Design and illumination scheme of a semiconductor/protein heterocontact (1 — glass plate, 2 — semitransparent metal layer, 3 — layer of natural protein, 4 — semiconductor, 5 — insulating lacquer).

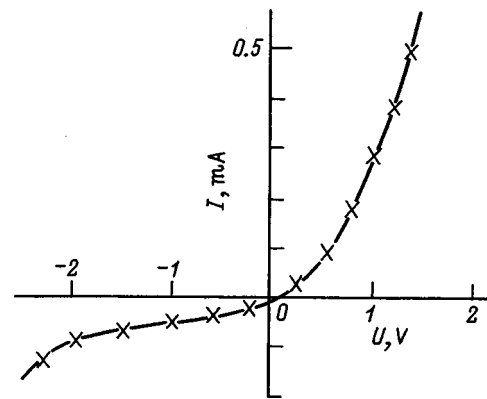


FIG. 2. Steady-state current–voltage characteristic of an *n*-CdTe/protein heterocontact at $T=300 \text{ K}$. (The transmitting direction corresponds to positive polarity of the external bias on the protein.)

value of η in the interval between the width of the band gap of the semiconductor E_G (Ref. 8) and the short-wavelength falloff of the photosensitivity near 3.5 eV. This is the “window effect,” typical for ideal solid-state heterojunctions,⁹ which in the given case does not require a careful choice of the semiconductor with definite lattice parameters, type of structure, etc. The appearance in all the heterocontacts of a short-wavelength boundary near 3.5 eV allows us to take this energy as the pseudogap in the energy spectrum of the protein. The long-wavelength boundary of photosensitivity of the investigated heterocontacts is movable and depends on the value of E_G in the semiconductor used in the heterocontact. The long-wavelength edge of η is exponential and its

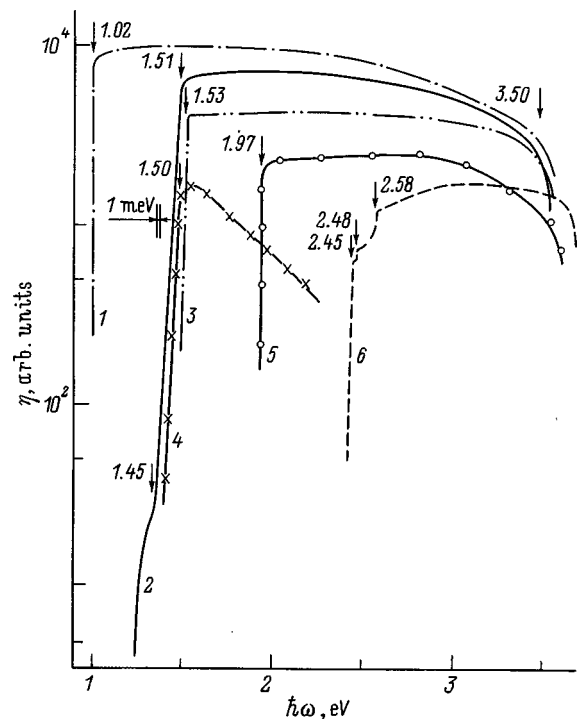


FIG. 3. Spectral dependence of the relative quantum efficiency of photoconversion of semiconductor/protein heterocontacts in natural light at $T=300 \text{ K}$. (1 — CuInSe₂, 2 — CdTe, 3, 4 — CuInS₂, 5 — AgInS₂, 6 — CuGaS₂. Illumination from the protein side).

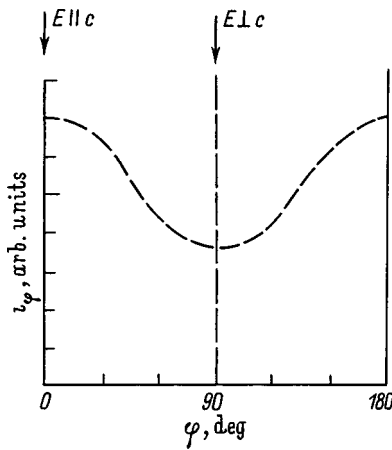


FIG. 4. Polarization indicatrix of the short-circuit photocurrent i_φ of a CuGaS₂/protein heterocontact at $T=300$ K. (Illumination along the normal to the (112) plane of CuGaS₂, $\hbar\omega=2.48$ eV).

logarithmic slope $S = \delta(\ln\hbar\omega)/\delta\hbar\omega$ is high, which corresponds to direct interband transitions in these semiconductors. The exponential growth of η comes to an end at $\hbar\omega_1$, which is close to the band gap E_g of the semiconductor.⁸ Note that the energy $\hbar\omega_1$ also depends on the doping of the semiconductor. In the case of CdTe crystals, where growth from the gas phase is accompanied by the incorporation of an iodine impurity, for example, $\hbar\omega_1$ is shifted to 1.47–1.49 eV due to the participation in the photoconductivity of shallow-center levels. In the case of heterocontacts based on CuGaS₂ with orientation of the contacting plane (112), several steps show up in the long-wavelength edge of η upon illumination by natural light, which are due to splitting of the levels in the tetragonal field.⁶ In the case of heterocontacts based on CuInS₂ (Fig. 3), we also see a pronounced short-wavelength falloff of η (curve 3), which is characteristic of surface recombination of charge carriers. This falloff shows up in heterocontacts which are obtained using mechanically processed semiconductor surfaces, whereas when using the post-growth natural plane (112), the short-wavelength falloff disappears (Fig. 3, curve 4). This feature was also confirmed when using heterocontacts made from CdTe and CuInSe₂.

As a result of changes in E_G and the state of the semiconductor surface, the FWHM (full-width at half-maximum) of the η spectra, $\delta_{1/2}$, changes. As follows from the table, the largest values of $\delta_{1/2}$ are obtained for heterocontacts made from CuInSe₂ and CuInS₂.

If the heterocontact is now illuminated on the semiconductor side, the η spectra become narrowly selective with a maximum near E_G , which is a natural consequence of the influence of strong absorption of radiation in direct-band crystals for $\hbar\omega \geq E_G$.

For the new class of heterocontacts based on oriented anisotropic semiconductors, one can also expect the appearance of natural photopleochroism,¹⁰ which was obtained for the CuGaS₂/protein structures.

As can be seen from Fig. 4, when these structures are illuminated with linearly polarized light (LPL) along the normal to the (112) plane, the polarization indicatrix of the short-circuit photocurrent i_φ exhibits a periodic dependence,

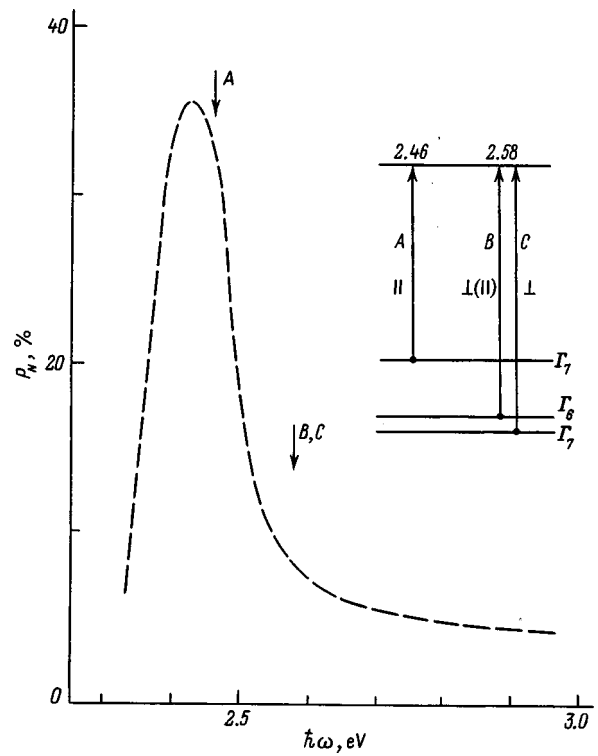


FIG. 5. Spectral dependence of the natural photopleochroism coefficient P_N of a CuGaS₂/protein heterostructure at $T=300$ K. The inset shows band structure and selection rules for interband transitions at the center of the Brillouin zone.

characteristic of uniaxial semiconductors, on the azimuthal angle φ between the electric field vector of the light wave \mathbf{E} and the tetragonal axis \mathbf{c} of the crystal

$$i_\varphi = i^\parallel \cos^2 \varphi + i^\perp \sin^2 \varphi, \tag{1}$$

where i^\parallel is measured in the polarization $\mathbf{E} \parallel \mathbf{c}$, and i^\perp is measured in the polarization $\mathbf{E} \perp \mathbf{c}$. Since the (112) plane is not coplanar with \mathbf{c} , the polarization $\mathbf{E} \parallel \mathbf{c}$ in these experiments is realized only nominally. Therefore, the experimentally obtained ratio $i^\parallel/i^\perp \approx 2$ is actually even larger.

The main conclusion that should be drawn from the polarization indicatrices i_φ is that as in the case of solid-state structures,⁶ the maximum photocurrent corresponds to the polarization $\mathbf{E} \parallel \mathbf{c}$ and, consequently, penetration of the linearly polarized light into the active region of the heterocontact takes place without distortions of the parameters of the incident light.

The spectral contour of the natural photopleochroism P_N of the heterocontact CuGaS₂/protein (Fig. 5) is also similar to that established for In/CuGaS₂ Schottky barriers.⁶ According to the selection rules for interband A transitions, the natural photopleochroism in CuGaS₂/protein structures exhibits a positive sign and reaches a maximum near the energy of the A transition. Transition to the short-wavelength range initiates principally the optical B and C transitions, allowed in the $\mathbf{E} \perp \mathbf{c}$ polarization, from the detached valence subbands of the valence band, which governs the decay of P_N (Fig. 5).

It follows from Fig. 5 that the maximum of P_N is shifted somewhat toward longer wavelengths relative to the energy of the A transitions. Taking the results of Ref. 11 into ac-

count, this fact points to the presence in the investigated CuGaS₂ crystals of shallow centers which give rise to an anisotropy of the photoconductivity comparable with the interband *A* transitions. The positive sign of P_N for $\hbar\omega < E_G$ suggests that the levels responsible for this absorption are formed from wave functions of the nearest free bands.

4. CONCLUSION

To summarize, heterocontacts of binary II–VI semiconductors (in the case of CdTe) and their ternary analogs of the type I–III–VI₂ with natural protein possess a photovoltaic effect and can be used as wideband photosensors of optical light. They also make it possible to observe variations in the optical properties of proteins. A systematic feature is strikingly manifested in this new class of photoconverters which was established in the investigated crystals of various other groups. This feature can be described as follows: an increased level of complexity of the atomic composition in combination with diamond-like phases is the source of new functional dependences which lead to the creation of new devices. In the context of the above remarks, our study shows that the transition from the binary phase (CdTe) to ternary compounds endows such heterocontacts with a new

functional capability, consisting in the appearance of polarization photosensitivity.

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