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SEMICONDUCTOR STRUCTURES, INTERFACES, AND SURFACES

Photosensitive Structures Based on $CdGa_2Se_4$ Single Crystals

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Abstract—Photosensitive structures based on $CdGa_2Se_4$ single crystals have been fabricated for the first time: In/$CdGa_2Se_4$ surface-barrier structures and InSe/$CdGa_2Se_4$ heterostructures. The current–voltage characteristics and the quantum efficiency spectra of these structures were studied. The polarization photosensitivity of In/$CdGa_2Se_4$ structures were found. The photosensitivity is discussed taking into account the photoactive absorption in $CdGa_2Se_4$ crystals in the impurity-related and intrinsic spectral ranges. A conclusion has been made that $CdGa_2Se_4$ single crystals are promising for commercial applications in photoelectric converters of unpolarized and linearly polarized light. *© 2003 MAIK "Nauka/Interperiodica".*

Anisotropic semiconductors $A^{II}B_2^{III}C_4^{VI}$ (where II stands for Cd or Zn; III, for Ga, In; IV, for Se, S) with a wide (up to ~4 eV) band gap can significantly extend the capabilities of modern semiconductor electronics for the short-wavelength spectral range [1, 2]. However, the issues of single-crystal growth, fabrication of semiconductor structures, and the study of their physical properties remain virtually unexplored. The current study, which deals with a promising new branch of semiconductor electronics, presents results obtained in the design of the first photosensitive structures based on single crystals of cadmium selenogallate $CdGa_2Se_4$, a representative of a new class of ternary compounds. These data open up new opportunities for investigations of the photoelectric properties of these compounds in natural and linearly polarized radiation (LPR).

1. $CdGa_2Se_4$ single crystals were grown by directed crystallization from a nearly stoichiometric melt of this compound in evacuated quartz crucibles coated with a film of pyrolytic carbon to suppress the interaction between the melt and the quartz surface. The crystallization was performed with the temperature gradient $\Delta T \cong 10°C\ cm^{-1}$ at a velocity of the crystallization front motion ~0.5 mm h^{-1}. According to X-ray diffraction data, the single crystals obtained belong to the space group S_4^2 with lattice constants $a = 5.740 \pm 0.003$ and $c = 10.739 \pm 0.006$ Å, which is in satisfactory agreement with the data [1, 3]. The grown crystals are easily cleaved along {112} facets, forming mirror planes. In transmitted white light, ~1-mm-thick $CdGa_2Se_4$ wafers have a uniform light-orange color. The average size of the obtained $CdGa_2Se_4$ single crystals was $\sim 10 \times 5 \times mm^3$. Without intentional doping, all of the grown single-crystals had *n*-type conduction with a dark resistivity $\rho \approx 10^7–10^9\ \Omega$ cm at $T = 300$ K.

The first studies of the electrical properties of contacts between $CdGa_2Se_4$ and metals have shown that the deposition of thin layers of ($d \approx 0.1$ mm) pure indium metal onto the cleaved surface of this compound enables the fabrication of In/$CdGa_2Se_4$ structures with pronounced electrical rectification. Figure 1 shows typical current–voltage (*I*–*V*) characteristics of such a structure in the dark (curve *1*) and under illumination from the side of the thin layer of barrier metal (curve *2*). The forward bias in In/$CdGa_2Se_4$ structures, in the dark and under illumination, always corresponds to the positive voltage applied to $CdGa_2Se_4$ crystal. The rectification factor, defined as the ratio of the forward to reverse current at fixed bias, can be as high as $K \approx 400–500$ (at $U \approx 2$ V) under illumination. This value greatly exceeds the rectification factor in the dark, which can be attributed to a decrease in the resistivity of the semiconductor when the surface-barrier structure is illuminated. Under external bias, $U > U_0$, the forward *I*–*V* characteristics are well described, both in the dark and under illumination from the side of the barrier contacts, by

$$I = (U - U_0)/R_0, \qquad (1)$$

where U_0 is the cutoff voltage, and R_0 is the residual resistance (see table) decreasing under illumination (Fig. 1, curves *1* and *2*). The dark cutoff voltage of the

Photoelectric properties of structures based on n-$CdGa_2Se_4$ single crystals (T = 300 K)

Structure type	R_0, Ω	U_0, V	S_U^m, V W^{-1}	$\hbar\omega$, eV	δ, eV
In/$CdGa_2Se_4^*$	2×10^8	0.8	500	2.7–3.7	>1
InSe/$CdGa_2Se_4$	4×10^7	0.9	80	1.95	0.3

* Structure illuminated from the side of the barrier contact.

I–V characteristics of In/$CdGa_2Se_4$ structures remains virtually unchanged under illumination and can be correlated with the potential barrier in the contact between In and the semiconductor. The forward *I–V* characteristics of surface-barrier structures at $U < 0.5$ V follow the standard photodiode equation [4]. The diode coefficient of the obtained structures $n \approx 12$–14 in the dark and decreases to 6–7 under illumination. This reflects the influence of high structure resistance on the forward *I–V* characteristics, which still hinders the discussion on the mechanism of current transport in these structures. The reverse current in In/$CdGa_2Se_4$ structures follows the power law $i \propto U^\gamma$, and in the range $U \le 5$ V the value of γ increases from 1.1 to 1.4 under illumination (Fig. 2, curves *1*' and *2*'), with no evidence of breakdown observed. Usually, the dark reverse currents in the best In/$CdGa_2Se_4$ structures are not higher than 10^{-7}–10^{-8} A under an external bias of ~5 V and T = 300 K.

Under illumination of the In/$CdGa_2Se_4$ structures, the photovoltaic effect appears with a positive voltage to which $CdGa_2Se_4$ corresponds and which is independent of the photon energy and light beam position on the structure surface. Generally, the photovoltaic effect dominates when the structures are illuminated from the side of the barrier contact. For example, under illumination by integral unfocused light of an incandescent lamp ($P \approx 80$ W), the open-circuit voltage is ~20 mV and the short-circuit photocurrent is ~2×10^{-8} A at T = 300 K. The highest voltage responsivity of the best surface-barrier structures was $S_U^m \approx 500$ V W^{-1}.

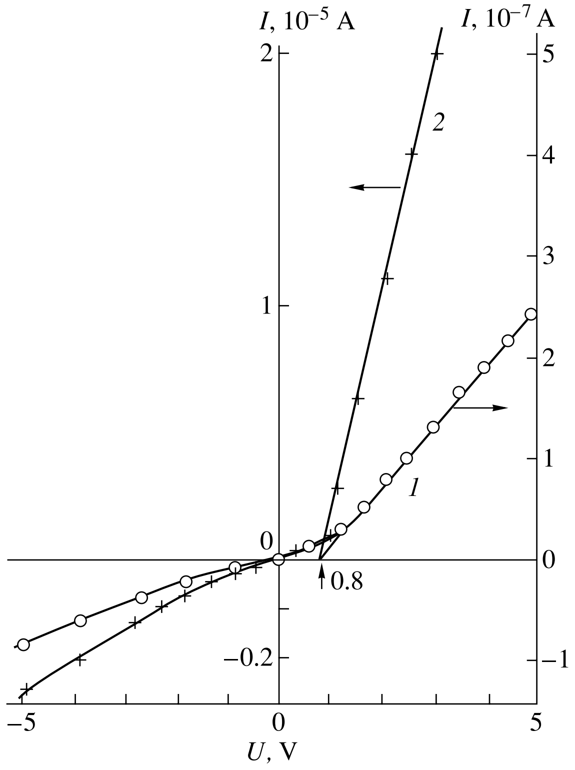

Fig. 1. *I–V* characteristics of a surface-barrier In/$CdGa_2Se_4$ structure at T = 300 K: (*1*) in the dark, (*2*) under exposure to integral light. Sample no. 6. The forward bias corresponds to a positive voltage applied to the $CdGa_2Se_4$ crystal.

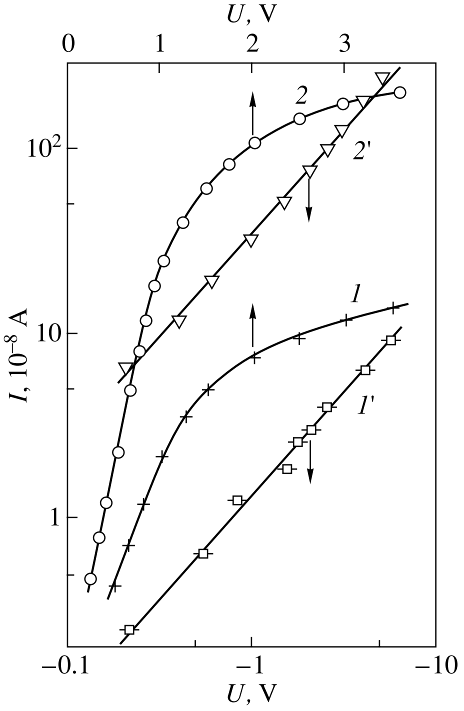

Fig. 2. (*1*, *2*) Forward and (*1*', *2*') reverse *I–V* characteristics of the In/$CdGa_2Se_4$ structure measured (*1*, *1*') in the dark and (*2*, *2*') under exposure to integral light at T = 300 K. Sample no 6.

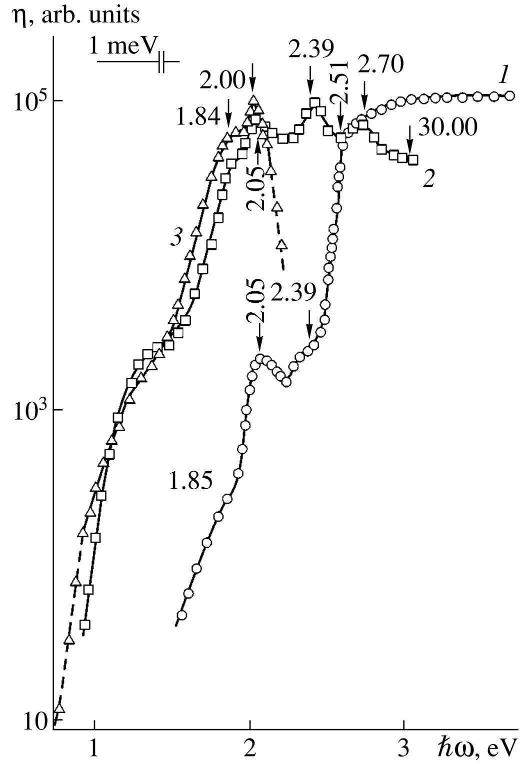

Fig. 3. Spectra of the relative quantum efficiency of photoconversion η of the $In/CdGa_2Se_4$ structure exposed to unpolarized light at $T = 300$ K. The structure is illuminated (*1*, *2*) from the side of In and (*3*) from the $CdGa_2Se_4$ side. Samples: (*1* and *3*) no. 6, (*2*) no. 3.

Figure 3 shows typical spectra of the relative quantum efficiency of photoelectric conversion $\eta(\hbar\omega)$, calculated as the ratio of the short-circuit photocurrent to the number of incident photons, for two $In/CdGa_2Se_4$ structures exposed to unpolarized light. As follows from the figure, the surface-barrier $In/CdGa_2Se_4$ structures enable, in principle, photoelectric conversion in the rather wide spectral range from 0.6 to 3.6 eV. Under illumination from the barrier-contact side (Fig. 3, curves *1* and *2*), photosensitivity is mainly observed in the short-wavelength spectral range; by contrast, a sharp short-wavelength threshold at $\hbar\omega > 2$ eV always exists under illumination from the $CdGa_2Se_4$ substrate side (Fig. 3, curve *3*). This indicates that, in the case of high optical absorption, η decreases as the region of photogeneration of nonequilibrium carriers moves away from the active region of a structure. The long-wavelength part of the spectrum is nearly independent of the geometric characteristics of structure illumination, which is due to bulk photoexcitation at low optical absorption in $CdGa_2Se_4$ crystals. The photosensitivity spectrum of the Schottky barriers at $\hbar\omega < 1.4$ eV is well described by the Fowler law (Fig. 4, curve *1*) and, thus, can be attributed to the photoemission of nonequilibrium carriers. It is noteworthy that the extrapolation of the long-wavelength photosensitivity edge $\sqrt{\eta} \longrightarrow 0$ yields an energy barrier height $\xi_B \cong 0.75$ eV, which is in satisfactory agreement with U_0 found from the *I–V* characteristics of the same structures (Fig. 1).

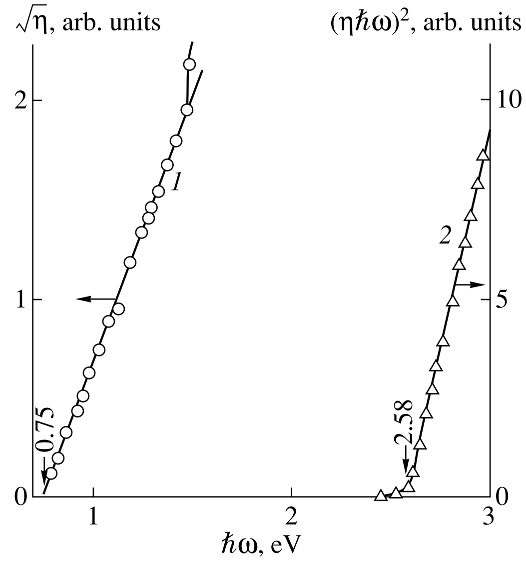

Fig. 4. Spectra of η in the coordinates (*1*) $\sqrt{\eta}$ – ħω and (*2*) $\sqrt{\eta}\,\hbar\omega$ – ħω. $In/CdGa_2Se_4$ structure, sample no. 6, $T = 300$ K.

Independently of the geometric characteristics of illumination, a fine structure in the form of three peaks at energies of 1.84, 2.0, and 2.05 eV is reproducibly manifested in the $\eta(\hbar\omega)$ spectra at photon energies above 1.5 eV. This structure can be attributed to photoactive absorption involving deep levels lying, respectively, at 0.74, 0.57 and 0.52 eV away from one of the unoccupied bands if account is taken of the $CdGa_2Se_4$ band gap $E_G = 2.57$ eV at $T = 300$ K, which was obtained from the optical absorption spectra [1, 5]. Detailed calculations of the band structure of $A^{II}B_2^{III}C_4^{VI}$ compounds have not be carried out yet, and, therefore, the nature of the fine structure of the $\eta(\hbar\omega)$ spectrum can also be attributed to the known weak pseudo-direct band-to-band transitions in $A^{II}B^{IV}C_2^{V}$ ternary semiconductors [6]. Evidently, further study is necessary to resolve this problem conclusively. Comparison of curves *1* and *2* in Fig. 3 shows that, if the $In/CdGa_2Se_4$ barriers are illuminated from the side of the In layer, the contribution of the long-wavelength structure to the photosensitivity of the barriers starts to vary significantly between different structures and ceases to be the principal one. For example, in some structures, photosensitivity is predominantly observed in the range of the fundamental absorption of $CdGa_2Se_4$ (Fig. 3, curve *1*). An exponential rise of photosensitiv-

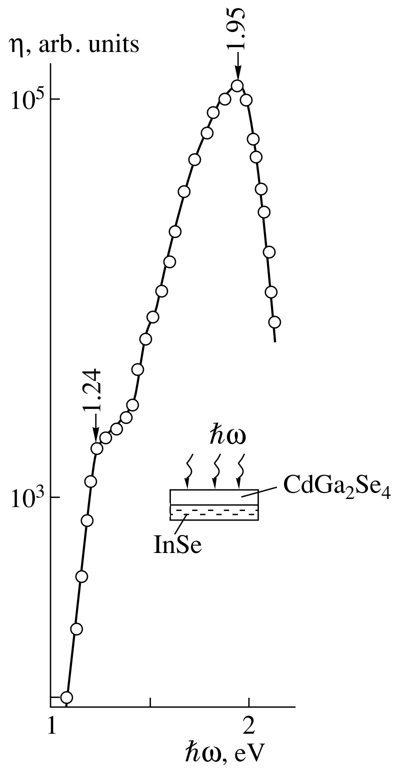

Fig. 5. The spectrum of the relative quantum efficiency of the photoelectric conversion η of InSe/$CdGa_2Se_4$ heterostructures exposed to unpolarized light at $T = 300$ K. Inset: schematic of the heterostructure and geometric characteristic of its illumination.

ity at $\hbar\omega > 2.4$ eV is characterized by a steep slope $S = \delta(\ln\eta)/\delta(\hbar\omega) \approx 20$ eV^{-1}, which, generally speaking, is typical of direct-gap semiconductors. As seen in Fig. 4 (curve *2*), the spectral dependence of quantum efficiency at $\hbar\omega > 2.6$ eV is linear in the coordinates $(\eta\hbar\omega)^2 - \hbar\omega$, which are typical of direct band-to-band transitions, and yields $E_G = 2.58$ eV upon the extrapolation $(\eta\hbar\omega)^2 \longrightarrow 0$, which is in good agreement with the data obtained from the analysis of the optical absorption in this crystal [5]. The increase in η at $\hbar\omega > E_G$ and the absence of a short-wavelength falloff in photosensitivity up to 3.6 eV, observed in the surface-barrier structures obtained, indicate a high efficiency of separation of photoexcited electron–hole pairs.

Along with the above-discussed example of the spectral dependence $\eta(\hbar\omega)$ achieved for the designed photoelectric converters, structures are also frequently obtained whose photosensitivity in the range $\hbar\omega < E_G$ is comparable with its value near E_G. A fine structure appears in the form of distinct peaks at $\hbar\omega \cong 1.84$, 2.0, 2.39, 2.70, and 3.0 eV in the η spectra of these structures. For the time being, there are no sufficient grounds for discussing the nature of these peaks. It is noteworthy, however, that the study of surface-barrier structures produced by standard technology reveals differences in their photosensitivity spectra. It seems natural to assign these differences to changes in the physical properties of $CdGa_2Se_4$ crystals, which, considering the data [1], can be presumably attributed to possible deviations from stoichiometry.

2. In the design of the first photosensitive structures based on n-$CdGa_2Se_4$ single crystals, we also used the method of bringing the cleaved (112) plane of these crystals into direct optical contact with the cleavage plane of lamellar n-InSe single crystals ($n \approx 10^{14}$ cm^{-3}, $U_n \approx 30$ cm^2 V^{-1} s^{-1}) at $T = 300$ K. The method used to fabricate these structures was similar to that employed in [7]. The heterostructure itself was produced after the deposition of current leads onto each of the semiconductor compounds. A single-crystal InSe wafer was mounted onto the surface of a microscope slide, and then a (112) mirror plane of $CdGa_2Se_4$ was pressed onto a freshly cleaved (001) mirror surface of InSe. Owing to the elasticity of n-InSe and the high surface quality of the contacting semiconductors, mild pressing and attrition of the adjoining surfaces provided a close optical contact of InSe and $CdGa_2Se_4$ [7, 8]. To fix the contact and ensure its long-term stability, $CdGa_2Se_4$ was pressed onto the (001) InSe surface with a spring. The heterostructure design is shown schematically in the insert in Fig. 5. As a rule, the heterostructures demonstrate rectification characterized by a factor $K \approx 2$–4 at the voltage $U \approx 50$ V, with the forward bias corresponding to the negative voltage applied to the n-InSe crystal. The linear approximation of the dark *I*–*V* characteristics has the form (1), with the U_0 and R_0 values close to those observed in surface-barrier structures based on the same crystals (see table). It is noteworthy that the parameters of the *I*–*V* characteristics in these structures are reproducible and show no degradation after InSe and $CdGa_2Se_4$ crystals are brought in contact. Figure 5 shows a typical spectral dependence of the relative quantum efficiency of photoelectric conversion in isotype n-InSe/n-$CdGa_2Se_4$ structures exposed to unpolarized light from the side of the wide-bandgap $CdGa_2Se_4$ component. These curves reproducibly demonstrate the known “window” effect with respect to the intensity of the optical radiation incident from the $CdGa_2Se_4$ side [4]. Indeed, the spectral position of the long-wavelength $\eta(\hbar\omega)$ edge corresponds to band-to-band transitions in the narrow-bandgap component of the heterostructure [3, 7], whereas the short-wavelength falloff of η at $\hbar\omega > 4.95$ eV (Fig. 5) is determined by the growing optical absorption in the $CdGa_2Se_4$ wafer, with a corresponding increase in the distance between the layer of photoexcited nonequilibrium carriers and the active region of the heterostructure. The predominance of heterostructure photosensitivity in the wide-bandgap component of the device results from the preferential localization of the active region in the bulk of $CdGa_2Se_4$, which is due to the difference in the doping level between the heterostructure components. Special attention should also be given to the close similarity between the $\eta(\hbar\omega)$ spectra of heterostructures (Fig. 5) and the spectra of surface-barrier structures illuminated from the side of the $CdGa_2Se_4$ wafer (Fig. 3, curve *3*). The reason for this coincidence is that the $\eta(\hbar\omega)$ spectra in both types of structures are defined by the photoactive absorption in the crystal of the $CdGa_2Se_4$ ternary compound. Due to the radiation absorption in bulk $CdGa_2Se_4$, the peak of voltage responsivity is red-shifted in heterostructures with respect to surface-barrier structures, and its magnitude appears to be lower than in $InSe/CdGa_2Se_4$ heterostructures (see table). For the same reason, the FWHM of $\eta(\hbar\omega)$ spectra in heterostructures is significantly narrower than in the surface-barrier structures fabricated on $CdGa_2Se_4$ of similar quality.

3. The photosensitivity to polarized radiation has been studied for the first time in surface-barrier structures oriented in the (112) plane. As seen in Fig. 6 (curves *1* and *2*), the photosensitivity of $In/CdGa_2Se_4$ surface-barrier structures exhibits a dependence of the quantum efficiency of photoelectric conversion, η, on the orientation of the electric field vector of the light wave $\boldsymbol{E}$ with respect to the tetragonal axis $\boldsymbol{c}$ of $CdGa_2Se_4$ single-crystal, which is typical of anisotropic crystals of ternary semiconductors [7, 9, 10]. Under illumination of the (112) plane and when the incident photon energy is fixed near the $CdGa_2Se_4$ band gap, the η polarization indicatrices follow Malus' law, so that in all cases $\eta^{\parallel} > \eta^{\perp}$, where the indices "$\parallel$" and "$\perp$" show the orientation of $\boldsymbol{E}$ with respect to $\boldsymbol{c}$. Figure 6 (curve *3*) shows a typical spectral dependence of the natural photopleochroism in $In/CdGa_2Se_4$ structures, calculated using the relation [9, 10]

$$P_N = (\eta^{\parallel} - \eta^{\perp})/(\eta^{\parallel} + \eta^{\perp}). \qquad (2)$$

The maximum coefficient of natural photopleochroism is observed near the energy of direct band-to-band *A*-transitions in $CdGa_2Se_4$ crystals, and its positive sign is in conformity with the selection rules for these transitions [11, 12]. It is necessary to emphasize that the maximum value $P_N^m \cong 12\%$ obtained in our study near the $CdGa_2Se_4$ E_G [1] can be raised by fabricating structures with a coplanar tetragonal axis on $CdGa_2Se_4$ wafers, because the orientation $\boldsymbol{E} \parallel \boldsymbol{c}$ is only partially accomplished in the structures on $CdGa_2Se_4$ wafers with (112) orientation. Special attention should be drawn to the fact that, in the range $\hbar\omega > E_G$, in which the allowed transitions from split-off subbands of the valence band come into play [1, 2], no P_N sign inversion is observed in the $In/CdGa_2Se_4$ structures under study, i.e., $\eta^{\parallel} > \eta^{\perp}$ (Fig. 6, curve *3*). This fact indicates that the influence of surface recombination is strongly suppressed in the best of the $In/CdGa_2Se_4$ structures obtained [9].

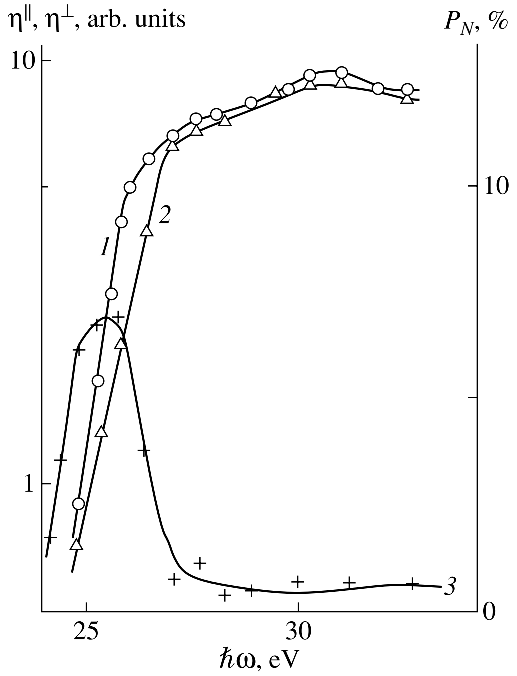

Fig. 6. Spectra of (*1*) $\boldsymbol{E} \parallel \boldsymbol{c}$, (*2*) $\boldsymbol{E} \perp \boldsymbol{c}$ photosensitivity, and (*3*) the coefficient P_N of natural photopleochroism of the $In/CdGa_2Se_4$ structure. $T = 300$ K, illuminated plane (112), sample no. 6.

Our study has demonstrated that $CdGa_2Se_4$ single crystals can find application in the design of photodetectors of unpolarized and linearly polarized radiation in a wide spectral range. The natural photopleochroism of structures based on $CdGa_2Se_4$ single crystals is selective and related to band-to-band *A*-transitions, similarly to the case of $A^{II}B^{IV}C^{V}$ and $A^{I}B^{III}C_2^{VI}$ ternary compounds [9, 10].

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