Photosensitivity of structures based on $A^{II}B^{III}C^{VI}_{4}$ monocrystals

I.A. Zharikov $^1$, V.Yu. Rud $^{1,2}$, Yu.V. Rud $^1$, E.I. Terukov $^3$, V.V. Davydov $^1$, N.N. Bykova $^4$

$^1$Peter the Great Saint Petersburg Polytechnic University, Saint Petersburg 195251, Russia
$^2$Department of Ecology, All-Russian Research Institute of Phytopathology, 143050, Moscow Region, Odintsovo district, B.Vyazyomy, Russia
$^3$Department of Solid State Physics, Ioffe Institute, Russian Academy of Sciences, St Petersburg 194021, Russia
$^4$Saint Petersburg State University of Economics, Saint Petersburg, 191023, Russia

Abstract. Monocrystals of ternary compounds of $A^{II}B^{III}C^{VI}_{4}$ semiconductors (HgGa$_2$S$_4$ and CdGa$_2$S$_4$) and various photosensitive structures based on them were investigated. The photoelectric properties of the structure obtained were studied using natural and linearly polarized light at 300 K. The results show that the structures created can find application as no polarized radiation photodetectors, and with allowance for high-triangular compression of the crystal lattice and linearly polarized radiation.

1. Introduction

The importance of the results of studying the fundamental properties of multicomponent semiconductors consists in the discovery of new nonlinear media with record values of nonlinear polarizability among them. For nonlinear optics, it is very important that when the atomic composition becomes more complicated with respect to elementary and binary semiconductor compounds, the efficiency of radiation conversion increases. In particular, the triple compound HgGa$_2$S$_4$ is of interest for the conversion of CO$_2$ laser radiation with an efficiency of up to 60%, as well as for recording radiation in the 10-12 μm transparency band of the atmosphere and for visualizing the spectra of fast processes in the 10-12 μm range. Since these substances have a large band gap (up to 4 eV), the development of technologies and instrument structures based on them can solve to some extent the problem of expanding the range of semiconductor electronics materials of the short-wave spectral range. It is important to note that the level of optical absorption in the region of their transparency slows down a wide application of these materials in nonlinear optics and photonics.

2. Results and discussion

Single crystals of ternary compounds of $A^{II}B^{III}C^{VI}_{4}$ semiconductors (HgGa$_2$S$_4$ and CdGa$_2$S$_4$) and various photosensitive structures based on them were investigated. The monocrystals were produced by directional crystallization of the triple melt compound close to the stoichiometry in a horizontally located boat made of glassy carbon (HgGa$_2$S$_4$), and also by the Bridgman-Stockbarger method from pre-synthesized single-phase polycrystalline ingots of this compound (CdGa$_2$S$_4$).

2.1 Structure on the basis of HgGa$_2$S$_4$ monocrystals

Monocrystals of HgGa$_2$S$_4$ were grown by directional crystallization of the triple melt compound close to the stoichiometry in a horizontally located boat made of glassy carbon. In the process of
slow directional cooling of the melt at rates of 0.1-0.3 °C/h, the axial temperature gradient is 1-3 °C/cm, which provides effectively suppressed crack formation, mass transfer and disturbances in the composition of the solid phase. The obtained bars with average dimensions of 10 × 15 × 200 mm were uniformly colored in a light orange color. The unit cell parameters of these crystals coincided with those known for \( \text{HgGa}_2\text{S}_4 \). Electrical measurements made on specially non-oriented single-crystal plates show that such crystals have a concentration of free electrons of \( 10^{12} \) cm\(^{-3} \) and a resistivity of \( 10^9 \) - \( 10^{10} \) Ω cm at \( T = 300 \) K. It should be noted that attempts to obtain crystals of mercury thiogallate have been carried out for a long time. However, the small size of crystals and their heterogeneity determines the need for further research to study the optical and photoelectric properties of such crystals [1].

The contact of vacuum-deposited layers of pure indium with a chipped or polished surface of \( \text{HgGa}_2\text{S}_4 \) reveals a clear straightening, with the throughput direction in Schottky barriers In / HgGa\(_2\)S\(_4\) always being realized with positive polarity of the external displacement on the semiconductor.

The rectification coefficient in the best barriers reached 15, and the reverse current increased with the power law and did not exceed \( (2-5) \times 10^4 \) A for \( U \leq 5 \) B and \( T = 300 \) K. When illuminated Schottky barriers, natural radiation generates a photovoltage and a semiconductor charges positively, which agrees with the direction of rectification. The voltage photosensitivity of the best Schottky barriers reaches 200 V/W at \( T = 300 \) K and dominates when illuminated by the barrier contact.

For all the Schottky barriers In / HgGa\(_2\)S\(_4\) obtained at the place of the short-wavelength decay typical for the case of illumination from the substrate side, \( \eta \), a sharp increase in the photosensitivity occurs at \( \hbar \omega > 2.3 \) eV during the transition to illumination from the barrier contact. In the range from 2.3 to 2.8 eV this growth is close to the root law, as evidenced by the rectification of the photosensitivity spectra in the coordinates \( (\eta \hbar \omega)^{1/2} \rightarrow 0 \). Extrapolation of this dependence \( (\eta \hbar \omega)^{1/2} \rightarrow 0 \) gives the value of the energy \( B_1 = 2.32 \) eV, which can be compared to indirect optical transitions in \( \text{HgGa}_2\text{S}_4 \). At \( \hbar \omega > 2.85 \) eV, the growth of the photosensitivity becomes close to the exponential one and can be characterized by the steepness \( s = \frac{\partial \left( \ln \eta \right)}{\partial \omega} / \hbar \omega \) \( \eta \hbar \omega \approx 12 \) eV\(^{-1} \), which gives grounds to compare it with the onset of direct interband transitions with an energy \( E_2 \approx 2.85 \) eV, which is close to the estimate of the bandgap width \( \text{HgGa}_2\text{S}_4 \) given in the literature [2]. The increase of \( \eta \) in the region \( \hbar \omega > E_2 \) up to 3.5 eV allows us to conclude that the obtained Schottky barriers are sufficiently effective in collecting pairs which photogenerated on the semiconductor surface.

2.2 Structure on the basis of \( \text{CdGa}_2\text{S}_4 \) monocrystals

\( \text{CdGa}_2\text{S}_4 \) monocrystals were grown by the Bridgman-Stockbarger method from pre-synthesized single-phase polycrystalline ingots of this compound. For the synthesis, binary components CdS and Ga\(_2\)S\(_3\) were used, which were loaded into cone-shaped crucibles of pyrolytic boron nitride with an internal diameter of \( \sim 16 \) mm and a length of 90 mm, and then crucibles filled with substance were placed in quartz ampoules. Ampoules were supplied with a quartz rod, with which they were attached to a mechanical vibrator. The pumped and sealed ampoule was placed in a single-zone vertical furnace, the temperature of which increased at a rate of \( \sim 100 \) °C/h to 1020-1050°C, at which it was kept for 3 hours with continuous vibrational stirring, after which the melt was cooled at a rate of \( \sim 100 \) °C/h to room temperature. After synthesis, the ampoule was transferred to a vertical two-zone furnace in which the growth of monocrystals was carried out. The temperature of the melt zone was set \( \sim 1030 \) °C, the annealing zone \( \sim 830 \) °C. The melt under these conditions was held for 24 hours, after which the ampoule with the melt dropped through the crystallization zone at a rate of \( \sim 0.26 \) mm/h at a temperature gradient of \( \sim 40 \) °C/cm. After the crystallization of the melt was completed, homogenizing annealing of the resulting crystals was usually carried out for 72 hours. The monocrystalline ingots (16 mm in diameter, 40 mm in
length) obtained in this method were transparent enough and homogeneously colored in a light yellow color.

In the absence of intentional doping, CdGa$_2$S$_4$ monocrystals grown by both methods indicated an electronic conductivity type and resistivity $\rho \approx 10^8$-$10^{10} \, \Omega \cdot \text{cm}$ at 300 K, with the highest-resistivity crystals obtained by the gas-phase method. An estimate of the concentration and Hall mobility of the CdGa$_2$S$_4$ monocrystals yielded $n \approx 10^8$-$10^9 \, \text{cm}^{-3}$ and $u_n \approx 1$-$10 \, \text{cm}^2 \, \text{V}^{-1} \cdot \text{s}$ at 300 K. Since CdGa$_2$S$_4$ monocrystals can only grow n-type conductivity, the method of planting various semiconductors for optical contact with each other was used to obtain heterostructures.

Mechanically, and then chemically polished plane of the single crystal CdGa$_2$S$_4$ was brought into contact with the surfaces of the newly obtained natural cleavages of the layered GaSe semiconductor compound with a hole concentration of $\approx 10^{14} \, \text{cm}^{-3}$ and a Hall mobility of $\approx 40 \, \text{cm}^2 \, \text{V}^{-1} \cdot \text{s}$ at $T = 300$ K. In Fig. 1 shows typical spectral dependences of the $\alpha (\hbar \omega)$ crystal of the CdGa$_2$S$_4$ crystal and $\eta (\hbar \omega)$ heterostructure from this crystal in linearly polarized radiation (LPI). It can be seen that in the LPI the spectrum of the optical absorption coefficient splits in such a way...
that \( \alpha^\parallel > \alpha^\perp \), as a result of which the spectrum is shifted in parallel to the short-wave region by \( \sim 80 \) meV with a transition from the polarization \( \mathbf{E} \parallel \mathbf{c} \) to \( \mathbf{E} \perp \mathbf{c} \). This means that indirect interband transitions are predominantly resolved in polarization \( \mathbf{E} \parallel \mathbf{c} \), as for uniaxial A²B¹V² crystals \([3,4]\). Polarization photosensitivity occurs only in heterostructures produced on \( \text{CdGa}_2\text{S}_4 \) (100) plates. The long-wavelength edge of the photosensitivity of heterostructures, determined by the interband absorption

\[ \text{Figure 2.} \] Spectral dependences of related quantum efficiency of photoconversion (curve 1- \( \mathbf{E} \parallel \mathbf{c} \), curve 2 – \( \mathbf{E} \perp \mathbf{c} \)) and coefficient of natural photopleochroism (curve 3) of \( \text{H}_2\text{O}/\text{n-CdGa}_2\text{S}_4 \) photoelectrochemical cell, \( T=300\text{K}, \) radiation from the side of \( \text{H}_2\text{O} \). Spectral resolution setup is 1 meV.

of GaSe when radiation enters it along the isotropic direction, as expected \([\text{]}\), is insensitive to the polarization of the radiation. Polarization photosensitivity occurs only at \( \hbar \omega > E_\sigma \) of gallium selenide and can be related to the anisotropy of photoactive absorption in \( \text{CdGa}_2\text{S}_4 \) crystals. This anisotropy turns out to be very peculiar. In polarized radiation, the spectrum \( \eta(\hbar \omega) \) splits (Fig. 1, curves 6 and 7) by \( \sim 80 \) meV, as does the \( \alpha(\hbar \omega) \) spectrum of the plate from which the heterostructure is obtained. In this case, a photoisotropic point at which \( \eta^\parallel = \eta \) is observed in the spectrum of \( \eta(\hbar \omega) \) at \( \hbar \omega_i \approx 2.76 \) eV, and below \( \hbar \omega_i \) when \( \eta^\parallel > \eta^\perp \), while above this energy, \( \eta^\parallel < \eta^\perp \). Consequently, only in the long-wave spectral region (\( \hbar \omega < \hbar \omega_i \)) the photosensitivity anisotropy agrees with the anisotropy of the optical absorption coefficient (Fig. 2), whereas in the region \( \hbar \omega > \hbar \omega_i \) the sign of the photosensitivity anisotropy \( \eta^\parallel > \eta^\perp \) becomes opposite to the dichroism of the optical absorption (\( \alpha^\parallel > \alpha^\perp \)).

This difference may be due to the fact that the photosensitivity of GaSe/CdGa₂S₄ heterostructures in the region \( \hbar \omega > \hbar \omega_i \) begins to be determined by the optical transmission of the CdGa₂S₄ plate because the radiation \( \mathbf{E} \perp \mathbf{c} \) slightly absorbed in CdGa₂S₄ still continues to
contribute to the photosensitivity of the heterostructure, whereas the absorption depth in CdGa$_2$S$_4$ radiation with polarization E $\parallel$ c is already shorter than the diffusion displacement length of the photoholes in the CdGa$_2$S$_4$ plate.

Direct photoelectrochemical contact of CdGa$_2$S$_4$ with H$_2$O, like solid structures, reveals rectification and photovoltaic effect. Straightening in the structures of H$_2$O/CdGa$_2$S$_4$ at U~10 V reaches $10^3$, and under their illumination a photocurrent arises. Among the photoelectrochemical (PHCN) cells we obtained, the H$_2$O/CdGa$_2$S$_4$ cells showed the highest photosensitivity, with the photocell always having a negative potential, which agrees with the direction of rectification. The main results of this cycle are shown in Fig. 2 and are as follows. When the photocell is illuminated from the electrolyte side along the normal to the photoelectrode (100) plane, the long-wavelength photosensitivity edge in the region of indirect optical transitions exhibits the same polarization dependence as the optical absorption coefficient of CdGa$_2$S$_4$. This dependence consists in shifting the long-wave part of the spectra $\eta(h\omega)$ to the short-wavelength region with a change in the polarization E $\parallel$ c by E $\perp$ c because the inequality $\eta > \eta^\parallel$ is satisfied.

In the case of GaSe/CdGa$_2$S$_4$ heterostructures, the short-wavelength photodisparity drop due to the effect of optical absorption in CdGa$_2$S$_4$ turned out to be opposite to the inequality $\alpha^\parallel > \alpha^\perp$. And only in the PHCN, where it was possible to exclude the influence of absorption by the CdGa$_2$S$_4$ crystal on the photoconversion process, the anisotropy of $\alpha$ and $\eta$ was found to be consistent. A correspondence between the absorption and photoconversion process has been achieved for the PHCN, as a result of which the inequality $\eta^\parallel > \eta$ is satisfied.

The shift of the spectra of $\eta(h\omega)$ with a change in the polarization of the radiation from E $\parallel$ c to E $\perp$ c by $\approx 70$-80 meV (Fig. 2, curves 1, 2) can be a consequence of the removal of degeneracy in the free band and its splitting due to the natural tetragonal compression in CdGa$_2$S$_4$ crystals. In the region of indirect interband transitions in CdGa$_2$S$_4$, the natural photoleochrom coefficient $P_{\eta}$ turned out to be positive and reaches a maximum value of $\approx 50\%$ near the photon energy $\approx 2.7$ eV (Fig. 2, curve 3), which is close to the energy of indirect interband transitions in CdGa$_2$S$_4$. With increasing $\hbar\omega > 2.9$ eV (Fig. 2, curve 3), the natural photoleochroism coefficient remains low ($P_{\eta}$=$0$) up to 3.4 eV. This may be a consequence of competition between optical transitions with opposite selection rules and only with an approach to the energy of direct optical transitions does the amplitude of the negative coefficient of photoleochrom increase to $\approx 20\%$. This means that direct interband transitions in CdGa$_2$S$_4$ are predominantly resolved in the polarization E $\perp$ c. Unfortunately, detailed theoretical calculations of the band structure of CdGa$_2$S$_4$ crystals are currently not available [5,6,7,8], which makes it impossible to compare now our results with the theory.

3. Conclusions

Presented here results open up new opportunities for structures based on anisotropic semiconductors HgGa$_2$S$_4$ and HgGa$_2$S$_4$ as the photodetectors of natural and linearly polarized radiation. Also we show that the Shottky barriers can be used for monitoring the optical quality of HgGa$_2$S$_4$ monocrystals as wide-band photodetectors.

References

[1] Levine B F, Bethea C G, Kasper H M, Thiel F A, 1976 IEEE Journal Quantum Electron QE 12 367
[2] Shay J L, Tell B, Kasper H M, and Schiavone L M. 1972 Physics Review B 3 5003.
[3] Bairamov B Ch, Rud’ V Yu, Rud’ Yu V 1998 MRS Bull 23 91.
[4] Shpunt V Ch, Rud’ Yu V, Tsendin K D 1993 Journal Technical Physics 19 13 41
[5] Kesamanly F P, Rud’ V Yu, Rud’ Yu V 1999 Semiconductors 5 483
[6] Rud’V Yu, Rud’ Yu V, Shpunt V Ch, Terukov E I 2016 *Optical Memory & Neural Networks (Information Optics)* **25** 1 40

[7] Myazin N S, Smirnov K J, Davydov V V, Logunov S E 2017 Journal of Physics: Conference Series. **929**-1 012064

[8] Rud V Yu, Rud Yu V, Terukov E I 2016, *J. Opt. Technol.* **83**-5-275