FEATURES OF ELECTRIC, THERMOELECTRIC, AND PHOTOELECTRIC PROPERTIES OF $\operatorname{AgCd_2GaS_{4-x}Se_x}$, $\operatorname{AgCd_{2-x}Zn_xGaS_4}$, $\operatorname{Ag_{1-x}Cu_xCd_2GaS_4}$, $\operatorname{AgCd_2Gal_{1-x}In_xS_4}$, AND $\operatorname{AgCd_2GaS_{4-x}Te_x}$ SOLID SOLUTIONS

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Solid solutions $AgCd_2GaS_4 - AgCd_2GaSe_4$, $AgCd_2GaS_4 AgZn_2GaS_4$, AgCd₂GaS₄—CuCd₂GaS₄, AgCd₂GaS₄- $AgCd_2InS_4, \ and \ AgCd_2GaS_4 - AgCd_2GaTe_4 \ are \ photosensitive$ materials, the photoconductivity maxima of which fall into the spectral region 500-800 nm, the specific value being determined by the type and composition of the solution. The experiments showed that most photosensitive turned out the solid solutions ${\rm AgCd}_{2(1-x)}{\rm Zn}_{2x}{\rm GaS}_4$ with $x=0.2\div0.3$: at illuminance of 10^3 Lx, their photoconductivity becomes about 300-500 times higher. By their physical properties, the solid solutions under consideration are similar to their electron analogs, CdS—-CdSe alloys. Similarly to the case of binary semiconductor alloys, an abrupt change of the energy position of centers, which are responsible for optical activity of specimens, occurs in the range of 30-50 mol.% of the second component. A model that explains the features of photoelectric properties of the solid solutions concerned has been suggested.

1. Introduction

One of the challenging technological problems in the creation of new substances is the synthesis and the study of semiconducting compounds, the properties of which make them suitable to be applied in thermo- and optoelectronics, nonlinear optics, etc. Recently, scientific articles have reported about the synthesis of ternary and quaternary chalcogenide compounds, which places them among other promising materials of electronic technique, such as CuGaSe₂, CuInSe₂, and CuIn_{1-x}Ga_xSe₂ [1].

In this article, we report the results of our researches of the crystal structure and the physical properties — the specific conductivity, the thermoelectric coefficient, and the spectral distribution of photoconductivity — of specimens belonging to the systems AgCd₂GaS₄—AgCd₂GaSe₄, AgCd₂GaS₄—AgZn₂GaS₄, AgCd₂GaS₄—CuCd₂GaSe₄, AgCd₂GaSe₄—AgCd₂InSe₄, and AgCd₂GaSe₄—AgCd₂GaTe₄ which are electronic analogs to alloys of binary semiconductors of A^{II}B^{VI} group.

2. Experiment

Specimens were synthesized from elements of high purity (not lower than 99.99 wt.%). The technology was described in more details in work [2]. The specimens obtained were studied making use of the X-ray phase analysis at a DRON 4-13 diffractometer (CuK α emission). In Fig. 1, we show schematically the dependences of the crystal lattice types of the solid solutions under investigation on their composition. For physical experiments, we fabricated specimens possessing the form of rectangular parallelepipeds (0.2— 0.4)×(1-2)×(3-5) mm³ in dimension. The specimen surfaces were ground and polished with diamond pastes. For photoelectric studies, the surfaces were additionally etched in a 10% solution of H_2O_2 in HNO_3 . Thin copper wires, welded with the help of an electric arc onto the specimen surface, served as contacts in the electric measurements. Occasionally, contacts were prepared of a gallium-indium eutectics by its rubbing into the

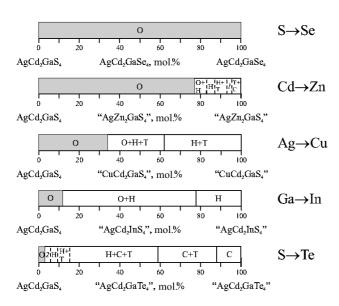


Fig. 1. Phase contents of the cross-sections (from top to bottom) $AgCd_2GaS_4$ — $AgCd_2GaSe_4$, $AgCd_2GaS_4$ — $AgZd_2GaSe_4$, $AgCd_2GaS_4$ — $AgCd_2GaSe_4$, $AgCd_2GaSe_4$ — $AgCd_2GaSe_4$, $AgCd_2GaSe_4$ — $AgCd_2GaSe_4$

specimen surface. The ohmic behavior of contacts persisted in wide ranges of temperature and voltage.

3. Experimental Results

3.1. Solid solutions of the $AgCd_2GaS_4-AgCd_2GaSe_4$ system

The $AgCd_2GaS_{4(1-x)}Se_{4x}$ system forms a continuous series of solid solutions within the whole interval of the component content (Fig. 1, the first row). The basic results of the researches of the solid solutions belonging to this system were presented in work [2]. The solid solutions $AgCd_2GaS_{4(1-x)}Se_{4x}$ are analogous, by their physical properties, to their electronic analogs, alloys of the $CdS_{1-x}Se_x$ system. Similarly to the alloys of binary semiconductors, they change smoothly, almost linearly, the width of their energy gap as the content varies. In the interval $x = 0.3 \div 0.5$, a sharp variation of the energy position of centers, which are responsible for the main maximum of impurity-induced photoconductivity, takes place (Fig. 2, curve 1), similarly to the variation of the energy position of the centers of slow recombination in $CdS_{1-x}Se_x$ solid solutions (Fig. 2, curve 3) [3].

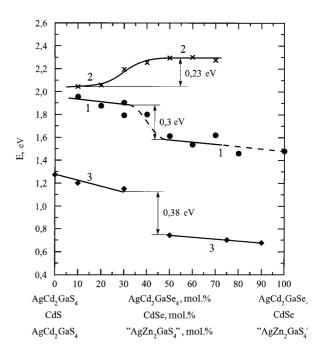


Fig. 2. Dependences of the energy position of the maxima of impurity-induced photoconductivity in $\operatorname{AgCd_2GaS_{4(1-x)}Se_{4x}}$ (1) and $\operatorname{AgCd_2(1-x)}\operatorname{Zn_{2x}GaS_4}$ (2) solid solutions on their composition content. The dependence of the optical energy of hole ionization from the centers of slow recombination on the composition content of $\operatorname{CdS_{1-x}Se_x}$ solid solutions (3) [3]

Therefore, we consider defects in the cation sublattice to be responsible for both the maximum of impurity-induced photoconductivity in the $\operatorname{AgCd_2GaS_{4(1-x)}Se_{4x}}$ solutions and the centers of slow recombination in $\operatorname{CdS_{1-x}Se_x}$ alloys.

Judging from the sign of their thermoelectric coefficient, all $AgCd_2GaS_{4(1-x)}Se_{4x}$ solid solutions belong to semiconductors with the n-type conductivity. The dark conductivity σ of these solutions within the whole interval of solubility is 10^2-10^3 times lower, depending on the composition content x, than that of its components (AgCd₂GaS₄ and AgCd₂GaSe₄), and amounts to $10^{-10} - 10^{-11} \ \Omega^{-1} \text{cm}^{-1}$ at $T \approx 300 \ \text{K}$. It may be due to the availability of technological defects of both the donor and acceptor types in the crystal lattice, which emerge, when solid solutions are formed, and stabilize the position of the Fermi level near the energy gap middle point. Various point defects, their clusters, or other damages of the bulk structure of the crystal lattice can play the role of such defects. As a rule, structural defects in semiconductors are the effective centers of recombination of nonequilibrium current carriers [4]. This fact explains lower photosensitivity of the

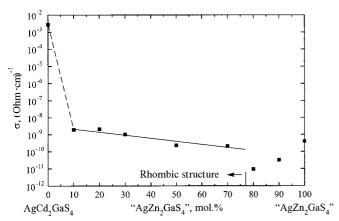


Fig. 3. Dependence of the specific dark conductivity σ of the ${\rm AgCd}_{2(1-x)}{\rm Zn}_{2x}{\rm GaS}_4$ solid solution on its composition content at $T\approx 300~{\rm K}$

 ${\rm AgCd_2GaS_{4(1-x)}Se_{4x}}$ solid solutions in comparison with that of their components. An exposure of the specimens to white light with the illuminance $E=10^3$ Lx causes the growth of their conductivity by a factor $k=10\div 20$. The concentration of fast recombination centers with a defective origin in binary photoconductors with weak photosensitivity is $N\geq 10^{18}~{\rm cm^{-3}}$ [5]. Applying this criterion to solid solutions under investigation, we may state that the concentration of the corresponding centers in them is not lower than the quoted value.

The thermoelectric material quality Q depends on the parameters, which are included into the formula

$$ZT = \frac{S^2 \sigma}{\kappa} T,\tag{1}$$

where S is the Seebeck constant or the thermoelectric coefficient, σ the specific conductivity, and κ the general heat conduction coefficient caused by both the heat conductivity of the crystal lattice and that of the electron subsystem. Perspective thermoelectric materials are multicomponent compounds which have low values of the lattice heat conductivity. The modern electronic industry demands thermoelectric materials with high Q. Now, $ZT \approx 1$ for the best of them.

The individual components, $\operatorname{AgCd_2GaS_4}$ and $\operatorname{AgCd_2GaSe_4}$, of the $\operatorname{AgCd_2GaS_4(1-x)Se_4x}$ solid solutions possess, according to our measurements, the thermoelectric coefficient $S \approx 500$ and $300~\mu\text{V/K}$, respectively. After the solid solution having being formed, the value of the thermoelectric coefficient diminishes to the response limit of our devices. Such a behavior of S is typical of compensated semiconductors with close contributions of electrons and holes to conductivity. Small values of S and σ , and, accordingly,

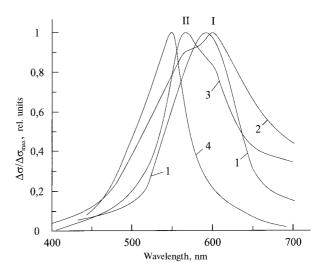


Fig. 4. Spectral distribution of the photoconductivity of $AgCd_{2(1-x)}Zn_{2x}GaS_4$ alloys at $T \approx 300$ K and various composition contents x = 0.1 (1), 0.2 (2), 0.3 (3), and 0.5 (4)

of the Q-factor ZT evidence for the inefficiency of employing the $\mathrm{AgCd_2GaS_{4(1-x)}Se_{4x}}$ solid solutions as thermoelectric materials.

3.2. Solid solutions of the $AgCd_2GaS_4-AgZn_2GaS_4$ system

The $AgCd_2GaS_4$ -based solid solutions in the $AgCd_{2(1-x)}Zn_{2x}GaS_4$ system exist within the interval $x=0\div 0.75$ (Fig. 1, the second row). Therefore, the physical properties of the specimens of the $AgCd_{2(1-x)}Zn_{2x}GaS_4$ alloy were analyzed only within this interval.

Judging from the sign of their thermoelectric coefficient, all $\operatorname{AgCd}_{2(1-x)}\operatorname{Zn}_{2x}\operatorname{GaS}_4$ solid solutions belong, similarly to the solutions considered in the previous case, to semiconductors with the *n*-type conductivity and possess low $S \approx -(20 \div 40)~\mu\text{V/K}$ and σ (Fig. 3), which evidences for their affinity to compensated semiconductors with a high concentration of technological defects of both the donor and acceptor types. Moreover, as *x* increases, their specific conductivity decreases, presumably due to the growth of the energy gap width (Fig. 3). The solid solutions of the $\operatorname{AgCd}_{2(1-x)}\operatorname{Zn}_{2x}\operatorname{GaS}_4$ system cannot be perspective materials for the thermionic technique, but all of them appeared photosensitive both at 300 and 77 K within the range of solubility.

If x is low (\leq 0.2), the position of the photoconductivity maximum ($\lambda_M \approx 600$ nm) little

differs from that of the analogous maximum in the $\operatorname{AgCd_2GaS_{4(1-x)}Se_{4x}}$ solid solutions with the same percentage of the second component (Fig. 2, curves 1 and 2; Fig. 4, peak I). It seems that the same defects, as in the case of the alloys of the $\operatorname{AgCd_2GaS_{4(1-x)}Se_{4x}}$ system with low x, are now responsible for the maximum of the impurity-induced photoconductivity in the $\operatorname{AgCd_2(1-x)}\operatorname{Zn_{2x}GaS_4}$ solutions with low x.

Below the composition content x=0.2, the position of the photoconductivity maximum practically does not change (Fig. 2, curve 2). In specimens with $x=0.2\div0.5$, there occurs a reconstruction of the photoconductivity spectrum. In the short-wave vicinity of the maximum at $\lambda_M \approx 600$ nm (Fig. 4, peak I), there appears a maximum of photoconductivity at $\lambda_M \approx 560$ nm (Fig. 4, peak II); this testifies to the formation of new photosensitive centers which exist together with the old ones. As x grows further, these new centers of photosensitivity, which are responsible for peak II, become dominating, and the position of peak II slowly shifts towards the short-wave range, probably due to the increase of the energy gap width of the solid solution (Fig. 2, curve 2; and Fig. 4).

Concerning the nature of a center of the impurity-induced photosensitivity, which was caused by a defect in the cation sublattice of alloys on the basis of binary semiconductors, its energy position depends on the nearest environment, namely, the anions in the first coordination sphere [7]. In the $AgCd_2GaS_{4(1-x)}Se_{4x}$ alloys, where the increase of x is accompanied by the replacement of Se ions for S ones, the variation of the maximum position of the impurity-induced photosensitivity is probably stimulated by a replacement of a selenium for a sulphur in the environment of the defect in the cation sublattice which is responsible for photoconductivity [2].

In the $\operatorname{AgCd}_{2(1-x)}\operatorname{Zn}_{2x}\operatorname{GaS}_4$ alloys, the occupation of the anion sublattice by sulfur ions remains constant as x increases, but the occupation of the cation sublattice changes. The concentration of Zn atoms increases, and the concentration of Cd atoms decreases. We may suppose that, in this case, the variation of the position of the photoconductivity maximum is governed by the replacement of Cd atoms by Zn ones at more distant lattice points around the defect which is responsible for photoconductivity. Since their influence on the ionization energy of the photosensitive center is not so dramatic as that of the atoms of the first coordination sphere, the displacement of the maxima at the photoconductivity spectrum reconstruction in the specimens of the $\operatorname{AgCd}_{2(1-x)}\operatorname{Zn}_{2x}\operatorname{GaS}_4$ system will

be shorter than that in the $\operatorname{AgCd_2GaS_{4(1-x)}Se_{4x}}$ one, which is really observed in the experiment (Fig. 2, curves 1 and 2). We note that the peak is shifted towards the short-wave range, contrary to the previous case ($\operatorname{AgCd_2GaS_{4(1-x)}Se_{4x}}$), where it is caused by the influence of the anions in the first coordination sphere possessing the effective charge of the other sign ("minus") rather than the atoms of the cation sublattice ("plus").

The photosensitivity of the $\operatorname{AgCd}_{2(1-x)}\operatorname{Zn}_{2x}\operatorname{GaS}_4$ solid solutions is by almost one order of magnitude higher than the photosensitivity of the specimens of the $\operatorname{AgCd}_2\operatorname{GaS}_{4(1-x)}\operatorname{Se}_{4x}$ system, especially in the range of the photoconductivity spectrum reconstruction $(x=0.2 \div 0.3)$ and, being exposed to white light with the illuminance E=10 Lx, their conductivity variation ratio achieves the values $k\approx 300 \div 500$ at $T\approx 300$ K.

Multiphase specimens with x>0.75 also turned out photosensitive.

Thus, the solid solutions belonging to the $AgCd_{2(1-x)}Zn_{2x}GaS_4$ system are photosensitive materials with the maxima of photoconductivity in the visible range of the electromagnetic spectrum (540 nm $\leq \lambda \leq$ 600 nm), depending on the composition content of the solution.

3.3. Solid solutions of the $AgCd_2GaS_4-CuCd_2GaS_4$ system

For the $Ag_{1-x}Cu_xCd_2GaS_4$ solid solutions, the composition content range $x = 0 \div 0.34$ corresponds to the single-phase state (a rhombic elementary cell) of a specimen (Fig. 1, the third row). The specific dark conductivity of the solid solutions is $\sigma \approx 10^{-9} \ \Omega^{-1} \text{cm}^{-1}$ at $T \approx 300$ K and practically does not depend on the alloy content, which may evidence for a minor change of the energy gap width in the $Ag_{1-x}Cu_xCd_2GaS_4$ alloys as the composition content of the solid solutions varies. Thermoelectric measurements testify to that, in the whole range of the existence of solid solutions, they are semiconductors with the n-type conductivity and the small thermoelectric coefficient $[S \approx -(20 \div 60)]$ $\mu V/K$ at $T \approx 300$ K], i.e. they also belong, as well as the systems considered above, to semiconductors with a large degree of compensation caused by technological defects of both the donor and acceptor types.

The solid solutions of the $Ag_{1-x}Cu_xCd_2GaS_4$ system possess low photosensitivity with the conductivity variation ratio no more than $k \approx 10$ (at $T \approx 300$ K) when being exposed to white light with the illuminance $E = 10^3$ Lx.

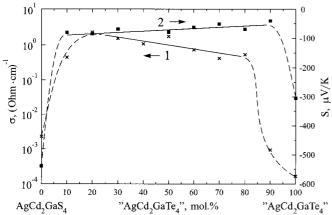


Fig. 5. Dependences of the specific dark conductivity (1) and the thermoelectric coefficient (2) of the ${\rm AgCd_2GaS_{4(1-x)}Te_{4x}}$ solid solution on its composition content at $T\approx 300~{\rm K}$

An interesting feature of the researched material is the fact that, above x = 0.3, the maximum position in the spectral distribution of photoconductivity practically does not change and corresponds to $\lambda_M \approx 760 \text{ nm}$ (1.63 eV). It is known [8] that, in Cu-doped CdS single crystals which are electronic analogs of the solid solutions under investigations, there exist the socalled "copper" centers of photosensitivity which are copper atoms that substitute Cd ones at the points of the cation sublattice (Cu_{Cd}). The energy depth of the Cu_{Cd} centers, reckoned from the bottom of the conduction band, is about 1.5 eV. One may assume that the $Ag_{1-x}Cu_xCd_2GaS_4$ solid solutions also involve the defects of such a type, namely, if some extra points of the cadmium sublattice are occupied by copper atoms (Cu_{Cd}). The impurity-induced photoconductivity of the $Ag_{1-x}Cu_xCd_2GaS_4$ solid solutions is caused by the excitation of electrons from the "copper" centers (Cu_{Cd}) into the conduction band. Since the energy gap width of the $Ag_{1-x}Cu_xCd_2GaS_4$ solid solutions practically does not change with the variation of their composition content, the position of the photoconductivity maximum in the solid solutions remains constant.

Application of the high-resistance solid solutions of the $Ag_{1-x}Cu_xCd_2GaS_4$ system with low photosensitivity in modern electronics is problematic.

$3.4.~Solid~solutions~of~the~AgCd_2GaS_4-AgCd_2InS_4~system$

The phase composition of the $AgCd_2Ga_{1-x}In_xS_4$ solutions is shown in Fig. 1 (the fourth row).

In the composition content range $x = 0 \div 0.6$, the alloys of the AgCd₂Ga_{1-x}In_xS₄ system belong to high-

resistance materials with $\sigma \approx 10^{-9} \ \Omega^{-1} \mathrm{cm}^{-1}$ at $T \approx$ 300 K. Above x = 0.7, the growth of σ is observed, which reaches the maximal value $\sigma \approx 1 \Omega^{-1} \text{cm}^{-1}$ for alloys with x = 0.8 and afterward remains practically constant. In the whole range of concentration, the specimens of the $AgCd_2Ga_{1-x}In_xS_4$ system belong to semiconductors with the n-type conductivity and the thermoelectric coefficient $S \approx -(100 \div 150) \, \mu V/K$ for high-resistance specimens. In the range $x \ge 0.6$, S grows and reaches the value $S \approx -250 \ \mu \text{V/K}$ which afterward remains practically constant. The temperature dependence of σ for the specimens of high-resistance solutions is described by the exponential dependence, which is characteristic of disordered semiconductors [9]. In the solutions with low-resistance compositions, σ weakly changes with temperature, and the solutions are not photosensitive. The $AgCd_2Ga_{1-x}In_xS_4$ solutions of other compositions possess low photosensitivity (k < 10 at $E = 10^3$ Lx).

We believe that single-phase low-resistance alloys $(\sigma \approx 1~\Omega^{-1} {\rm cm}^{-1})$ with high x, for which $S \approx -250~\mu{\rm V/K}$, may have the highest practical importance. Using the value $\kappa \approx 10^3~{\rm cal/(cm \cdot s)}$ for ternary and quaternary compounds [10], we can estimate the parameter ZT for $T \approx 300~{\rm K}$. Such estimations show that ZT = 0.005 for the specimens of low-resistance AgCd₂Ga_{1-x}In_xS₄ solutions. It is much less than the relevant value for the most efficient thermo-materials fabricated on the basis of compounds of Bi, Te, and Sb.

3.5. Solid solutions of the $AgCd_2GaS_4-AgCd_2GaTe_4$ system

The composition content ranges, where multi- and single-phase alloys of this system exist, are presented in Fig. 1 (the fifth row). Photo- and thermoelectric measurements show that the alloys belonging to the ${\rm AgCd_2GaS_{4(1-x)}Te_{4x}}$ system have no photosensitivity, being semiconductors with the n-type conductivity. In the composition content range $x=0.1\div0.85$, the alloys are low-resistance with $\sigma=(1\div3)~\Omega^{-1}{\rm cm^{-1}}$ and $S\approx-100~\mu{\rm V/K}$ at $T\approx300~{\rm K}$ (Fig. 5). The temperature dependences of σ for such alloys possess the features of metallic conductivity, i.e. σ decreases to some extent as the temperature grows. The value of the parameter ZT, calculated by us for low-resistance solutions, equals $ZT\approx0.001$ at $T\approx300~{\rm K}$.

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ОСОБЛИВОСТІ ЕЛЕКТРИЧНИХ, ТЕРМОЕЛЕКТРИЧНИХ І ФОТОЕЛЕКТРИЧНИХ ВЛАСТИВОСТЕЙ ТВЕРДИХ РОЗЧИНІВ $\operatorname{AgCd}_2\operatorname{GaS}_{4-x}\operatorname{Se}_x$, $\operatorname{AgCd}_2\operatorname{GaS}_{4-x}\operatorname{Te}_x$ AgCd $_2\operatorname{GaS}_{4-x}\operatorname{Te}_x$

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Резюме

 $AgCd_2GaS_4-AgCd_2GaSe_4$, $AgCd_2GaS_4-$ Тверді розчини "AgZn₂GaS₄", AgCd₂GaS₄—"CuCd₂GaS₄", AgCd₂GaS₄— "AgCd₂InS₄" і AgCd₂GaS₄—"AgCd₂GaTe₄" є фоточутливими матеріалами з максимумом фоточутливості в області 500—800 нм, положення якого визначається типом і складом розчину. Найвищу фоточутливість виявляють тверді розчини ${\rm AgCd_2GaS_4}$ —" ${\rm AgZn_2GaS_4}$ ", у складі яких 20—30 мол.% "AgZn $_2$ GaS $_4$ ". При освітленості 10^3 лк їх фотопровідність зростає у 300—500 разів. За фізичними властивостями тверді розчини подібні до своїх електронних аналогів — сплавів системи CdS-CdSe. Як і в сплавах бінарних напівпровідників, у цих сплавів з вмістом другої компоненти 30—50 мол.% спостерігається різка зміна енергетичного положення центрів, відповідальних за оптичну активність зразків. Запропоновано модель, яка пояснює особливості фотоелектричних властивостей твердих розчинів.