FEATURES OF ELECTRIC AND PHOTOELECTRIC PROPERTIES OF $AgCd_{2-x}Mn_xGaSe_4$ SOLID SOLUTIONS

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Temperature dependences of the conductivity coefficient and the thermal electromotive force, as well as the spectral distribution of photoconductivity, of $AgCd_{2-x}Mn_xGaSe_4$ solid solutions with the isovalent substitution Cd→Mn have been studied. The results of x-ray phase analysis of the $AgCd_{2-x}Mn_xGaSe_4$ system testify that an extensive solid solution with the limiting composition $AgCd_{0.74}Mn_{1.26}GaSe$ emerges in it. The photoconductivity of $AgCd_{2-x}Mn_xGaSe_4$ alloys has been considered, and, by analyzing the position of intrinsic photoconductivity maximum, the band gap width at $T \approx 297$ K has been evaluated. Within the solid solutions range, the gap width increases from about 1.75 eV for pure $AgCd_2GaSe_4$ to 2.3 eV for the composition containing 40 mol% $AgCd_2GaSe_4$ and 60 mol% "$AgMn_2GaSe_4$". All the single-phase solid solutions turned out to be photosensitive with the multiplicity of conductivity variation at the 10^3-Lx illumination ranging from about 10 to 10^3, depending on the specimen composition.

1. Introduction

The onrush of modern microelectronics demands for searching novel semiconducting materials, the physical properties of which would expand the range of traditional semiconductor applications. Lately, the list of such materials was appended by complex single crystals of tetradic chalcogenide $AgCd_2GaS_4$, which demonstrate a high photosensitivity in the near infrared range of electromagnetic radiation [1–3]. In connection with the crystal lattice asymmetry and wide transparency windows, $AgCd_2GaS_4$ can be practically used as a basis for the fabrication of nonlinear elements for optoelectronic technique. To expand the application range of substances belonging to this tetradic phase, the electrical, optical, and photoelectric properties of solid solutions, obtained on the basis of $AgCd_2GaS_4$ by substituting one of the elements of this compound (Ag→Cu, Cd→(Zn, Mn), Ga→In, and S→(Te, Se)), were studied in works [4–8].

For the sake of searching for new complex semiconducting phases, we have synthesized and studied some properties of the related system $AgCd_{2-x}Mn_xGaSe_4$ with the isovalent Cd→Mn substitution. The results of x-ray phase analysis of the $AgCd_{2-x}Mn_xGaSe_4$ system testify to that an extensive solid solution emerges in it. Its limiting composition was determined from the variation of elementary rhombic cell parameters (Fig. 1) to be $AgCd_{0.74}Mn_{1.26}GaSe_4$. The specification of the crystal structure of the alloy with the aforementioned composition showed that the crystallographic position of Cd (4*b*) in the framework of spatial group $Pmn2_1$ is statistically populated with Cd and Mn atoms, i.e. the specimens belonging to this system are disordered alloys. A gradual substitution of cadmium by manganese results in a reduction of the elementary cell dimensions owing to a smaller tetrahedral ionic radius. At $x > 1.26$, the alloys contain three phases: $AgCd_{0.74}Mn_{1.26}GaSe_4$, $AgGaSe_2$, and MnSe. The initial composition of the system "$AgMn_2GaSe_4$" is biphase and contains $AgGaSe_2$ and MnSe (Fig. 2).

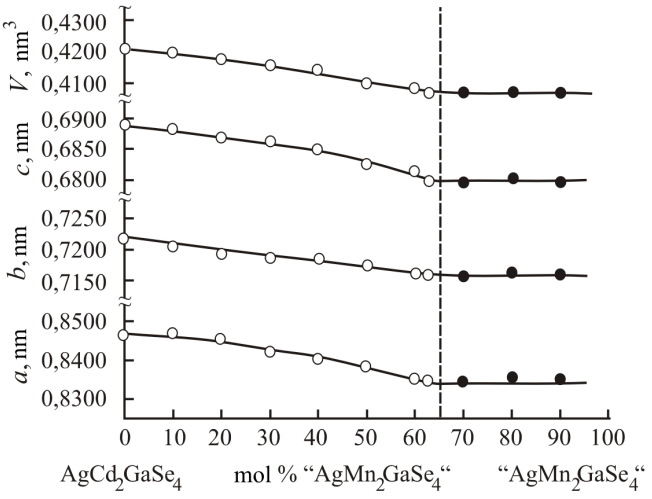

Fig. 1. Dependences of the lattice constants and the unit cell volume in $AgCd_2GaSe_4$–"$AgMn_2GaSe_4$" alloys on the solid solution content at 870 K

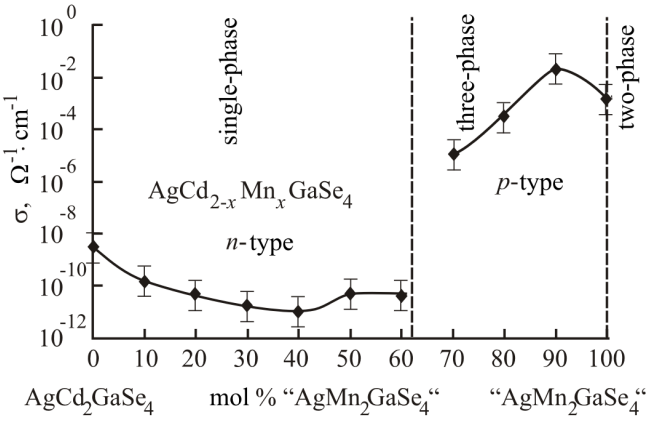

Fig. 2. Dependence of dark electroconductivity in solid solutions $AgCd_{2-x}Mn_xGaSe_4$ on their content at 293 K

2. Experimental Results and Their Discussion

In the present work, we studied the electric, photoelectric, and thermoelectric properties of alloys belonging to the system $AgCd_{2-x}Mn_xGaSe_4$ and synthesized by us. For this purpose, we fabricated specimens of 11 types with a content step of 10 mol% "$AgMn_2GaSe_4$".

The statistical character of the Cd-atom (the ionic radius $r_{Cd^{2+}} = 0.092$ nm) substitution by smaller Mn atoms ($r_{Mn^{2+}} = 0.080$ nm) gives rise to a violation in the periodicity of the electron potential energy in the lattice and, respectively, to the emergence of tails of the electron density of states in the semiconductor energy gap. At the same time, as the substances are complex phases, they are rich in structural defects of both the impurity and technological origins, which form energy levels in the forbidden gap. Therefore, one should expect that the spectrum of electron states in the alloys under investigation is similar to those in strongly defective, disordered, or amorphous semiconductors.

In Fig. 2, the dependence of specific dark electroconductance σ on the composition of $AgCd_{2-x}Mn_xGaSe_4$ system at 293 K is shown. In the single-phase range, the dark conductivity $\sigma \approx 10^{-10} - 10^{-11}$ $(\Omega \times \mathrm{cm})^{-1}$ and decreases with the growth of the "$AgMn_2GaSe_4$" content. Probably, one of the reasons for such a dependence may be an increase of the energy gap width in alloys, which agrees with the reduction of elementary cell dimensions at the isovalent substitution of Cd atoms by Mn ones. All the alloys of the system concerned belong to well-compensated semiconductors with a low (at the measurement error level) value of thermo-emf coefficient S in the single-phase range. For parent components of the alloy, $S = -96$ μV/K for $AgCd_2GaSe_4$ and +480 μV/K for "$AgMn_2GaSe_4$". A deep location of the Fermi level E_F in the energy gap is responsible for close contributions made to electroconductivity by the electron and hole components and, respectively, for a low S-value, which grows drastically near the three-phase region boundary. For specimens from the three-phase region, the experimentally determined values of thermo-emf coefficient were +29, +500, and +470 μV/K for compositions of 70, 80, and 90 mol% "$AgMn_2GaSe_4$", respectively.

The highest figures of merit $Z = S^2\sigma/\chi$, where χ is the specific heat conductance, are characteristic of three-phase alloys with large S-values.

The value of the quantity ZT is about 3×10^{-5} for the alloy with 90 mol % "$AgMn_2GaSe_4$" at a temperature of 293 K. From the aforesaid, it follows that alloys of the $AgCd_{2-x}Mn_xGaSe_4$ system cannot be promising materials for thermoelectrogenerators, for which the value of ZT falls within the interval $0.1 - 1$. But they can be a component of radiation-resistant temperature-sensitive thermoelements, where they would form a shoulder of the conductivity of p-type.

The temperature dependence of the electroconductivity for single-phase alloys belonging to the $AgCd_{2-x}Mn_xGaSe_4$ system, as well as for the majority of disordered semiconductors, has activation character [9] and is described by the exponential dependence

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \qquad (1)$$

at high temperatures from room one to $T \leq 400$ K. Here, E_a is the activation energy, and 400 K is the temperature, to which the specimens were heated up in our experiments. The determined values of the conductivity activation energy E_a for solid solutions with various compositions (Fig. 3) falls within the interval $0.4 - 0.63$ eV. The corresponding σ_0 turned out to be about 10^2 $(\Omega \times \mathrm{cm})^{-1}$, which, according to the criteria stated in work [9], testifies to the realization of the electroconductivity mechanism through the thermal excitation of charge carriers from the levels in the energy gap, which are located near the Fermi level, onto the level of delocalized states in the allowed energy band. Attention is attracted by a reduction of E_a at the transition to solid solutions with the content of the second component higher than 40 mol% (Fig. 3). In this content range, an insignificant growth of dark σ of the specimens is also observed (Fig. 2). On the basis of this fact, we may assume that cation sublattice defects related to cadmium ions play the dominating role in the specimens with low contents of

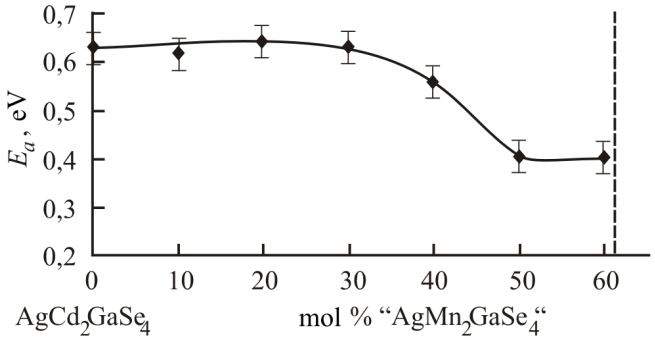

Fig. 3. Dependence of the electroconductivity activation energy in solid solutions $AgCd_{2-x}Mn_xGaSe_4$ on their content

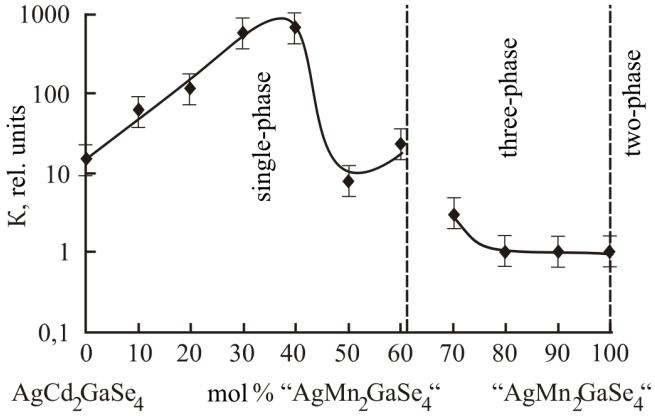

Fig. 4. Dependence of the electroconductivity variation multiplicity in the specimens at their illumination at 293 K with white light on their content

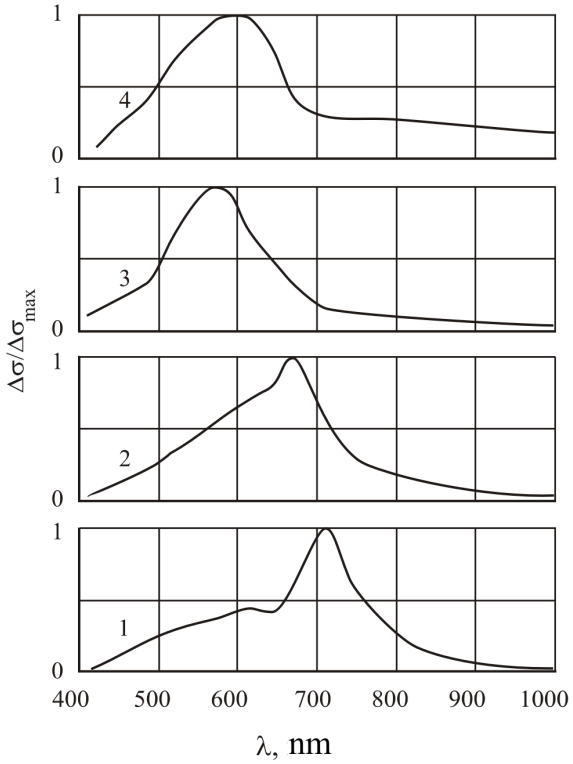

Fig. 5. Spectral distributions of photoconductivity of in solid solution $AgCd_{2-x}Mn_xGaSe_4$ at 293 K for specimens with various contents: (*1*) 100 mol% $AgCd_2GaSe_4$–0 mol% "$AgMn_2GaSe_4$", (*2*) 70 mol% $AgCd_2GaSe_4$–30 mol% "$AgMn_2GaSe_4$", (*3*) 60 mol% $AgCd_2GaSe_4$–40 mol% "$AgMn_2GaSe_4$", (*4*) 40 mol% $AgCd_2GaSe_4$–60 mol% "$AgMn_2GaSe_4$"

"$AgMn_2GaSe_4$" and define the E_a-value there, whereas defects associated with Mn ions dominate in specimens with the "$AgMn_2GaSe_4$" contents higher than 40 mol%.

All the specimens studied by us turned out to be photosensitive. In Fig. 4, the dependence of the conductivity variation multiplicity K of alloys at their illumination at room temperature with white light produced by a halogen lamp on the alloy component content is depicted. The light exposure of specimens was 10^3 lx. The parameter K was determined by the formula $K = \sigma_C/\sigma_T$, where σ_C and σ_T are the specific electroconductances of the specimen illuminated with light and in darkness, respectively. As Fig. 4 demonstrates, the most photosensitive ($K = 0.9 \times 10^3 - 1.0 \times 10^3$) were specimens with the content in the interval $30-40$ mol% "$AgMn_2GaSe_4$".

The reduction of photosensitivity for alloys with higher contents of the second component (more than 40 mol% "$AgMn_2GaSe_4$") is probably induced by the growth of their imperfection, when the content comes closer to the solubility limit. This conclusion is supported by a weak photosensitivity of three-phase alloys (Fig. 4) which are characterized by a considerably higher concentration of structural defects in comparison with single-phase ones. Similarly to what takes place in other semiconductors, the structural defects of a crystal lattice evidently play the role of effective centers for the fast recombination of nonequilibrium charge carriers in the bands. One may assume that the increase of the alloy imperfection near the solubility limit is responsible for the variations of E_a (Fig. 3) and σ (Fig. 2).

In Fig. 5, the spectral distributions of photoconductivity (PC) of $AgCd_{2-x}Mn_xGaSe_4$ alloys in the single-phase range at 293 K are presented. The characteristic feature of PC of specimens is a well degenerate maximum which is probably associated with the intrinsic PC. When the "$AgMn_2GaSe_4$" content increases, the intrinsic-PC maximum shifts toward the short-wave range: from 708 nm in pure $AgCd_2GaSe_4$ to 538 nm in alloys with the composition of 60 mol% $AgCd_2GaSe_4$ + 40 mol% "$AgMn_2GaSe_4$" (curves *1* to *3* in Fig. 5). The

further growth of the second component content gives rise to a smearing of the PC maximum without any notable shift of its position, which is typical of defect systems, and to the appearance of a conspicuous background given by impurity PC, probably, of the defect origin (curve *4* in Fig. 5). Making use of the intrinsic PC maximum for the evaluation of the energy gap width in the alloys, we may assert that it grows with increase in the "$AgMn_2GaSe_4$" content in the alloy from about 1.75 eV (curve *1* in Fig. 5) to 2.3 eV for alloys at the boundary of the single-phase solid solution existence range (curve *4* in Fig. 5), which agrees with x-ray diffraction data, namely, with a reduction of the elementary cell dimensions at the substitution of Cd atoms in the alloy by Mn ones.

Thus, on the basis of out research of electric, thermoelectric, and photo-electric properties of alloys belonging to the $AgCd_{2-x}Mn_xGaSe_4$ system, it was found that they are compensated semiconductors with a high photosensitivity in the range of the single-phase solid solution. The energy gap width in the alloys, which was estimated from the intrinsic PC maximum, grows, if Cd atoms in the solution are substituted by Mn ones.

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ОСОБЛИВОСТІ ЕЛЕКТРИЧНИХ ТА ФОТОЕЛЕКТРИЧНИХ ВЛАСТИВОСТЕЙ ТВЕРДИХ РОЗЧИНІВ $AgCd_{2-x}Mn_xGaSe_4$

В.В. Божко, Л.В. Булатецька, Г.Є. Давидюк, О.В. Парасюк, В.П. Сачанюк, А.П. Третяк

Р е з ю м е

Досліджено температурні залежності електропровідності, коефіцієнт термо-ерс та спектральний розподіл фотопровідності твердих розчинів $AgCd_{2-x}Mn_xGaSe_4$ з ізовалентним заміщенням Cd⇒Mn. Згідно із рентгенофазовим аналізом у системі $AgCd_{2-x}Mn_xGaSe_4$ спостерігається утворення протяжного твердого розчину, граничний склад якого є $AgCd_{0,74}Mn_{1,26}GaSe_4$. Проаналізовано фотопровідність сплавів системи $AgCd_{2-x}Mn_xGaSe_4$. По максимуму власної фотопровідності оцінено ширину забороненої зони при $T \approx 297$ K. У межах однофазного твердого розчину вона збільшується від $\sim 1,75$ еВ для 100 мол.% $AgCd_2GaSe_4$–0 мол.% "$AgMn_2GaSe_4$" до 2,3 еВ для 40 мол.% $AgCd_2GaSe_4$–60 мол.% "$AgMn_2GaSe_4$". Всі однофазні тверді розчини фоточутливі з кратністю зміни провідності, при освітленні 10^3 лк, що дорівнює $\sim 10^1 - 10^3$, в залежності від компонентного складу зразка.