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Peculiarities of Photosensitivity of n(GaAs)−p(GaAs)$_{1-x-y}$(ZnSe)$_x$(Ge$_2$)$_y$ Structures with Quantum Dots

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Abstract—The spectral photosensitivity of n(GaAs)-p(GaAs)$_{1-x-y}$(ZnSe)$_x$(Ge$_2$)$_y$ heterostructures in the photon energy range from 1.1 to 2.7 eV is studied. The peak sensitivity of the structure was found for a photon energy 2.62 eV, due to the impurity levels of ZnSe lying in the valence band of the solid solution.

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It is assumed that the impurity photovoltaic effect, which occurs in the case of absorption of photons with energies lower than the bandgap of the base semiconductor (E_g) of a solar phototransducer, and the reduction in energy losses caused by thermalization of high-energy photons [1, 2] is assumed to represent one of the most promising ways to improve solar cells. However, solving the problem of implementing the positive impurity photovoltaic effect is still at an early stage. It is closely related to the choise of impurities, rules of impurity level formation in the energy band, and the density and degree of filling of the impurity level. Thus, it is interesting to study the influence of molecular isovalent impurities on voltaic effects in multicomponent solid substitution solutions. Multicomponent solid solutions (SSs), in particular (GaAs)$_{1-x-y}$(ZnSe)$_x$(Ge$_2$)$_y$ SSs, are of special interest for solar energy along with traditional elementary group IV semiconductors and double semiconductor compounds of the A^{II}B^{VI} and A^{III}B^V types. Since the E_g of such SSs can vary widely, optoelectronic devices based on these materials can be developed for operation in the infrared and visible ranges [1−4].

This paper presents the results of experimental studies of multicomponent (GaAs)$_{1-x-y}$(ZnSe)$_x$(Ge$_2$)$_y$ SSs grown by liquid-phase epitaxy from a limited volume of tin solution melt by the technology described in [5]. Single-crystal plates of n-type conductivity GaAs with the (100) crystallographic orientation were used as substrates. The composition of the solution melt is determined based on experimental studies of the liquid-phase GaAs−Ge−ZnSe−Sn system and data [6−8]. Layers were grown by induced cooling in an atmosphere of purified hydrogen. Purification was performed using palladium. The induced cooling rate in the optimal mode was 1−1.5°/min. Crystallization of

layers was performed in the temperature range 730−640°C. Epitaxial layers had p-type conductivity. The thickness of layers was about 20 μm.

Since the periods of the crystal lattices of GaAs (5.646 μA), Ge (5.6576 μA), and ZnSe (5.661 μA) [9] do not differ significantly, a variband buffer layer with a varying composition of the SS consisting of GaAs, Ge$_2$, and ZnSe was used for further smoothing of the lattice parameters and smooth transition from the GaAs substrate to a (GaAs)$_{1-x-y}$(ZnSe)$_x$(Ge$_2$)$_y$ epitaxial layer with a high ZnSe content. These components are isovalent; i.e., the sums of the valences of the atoms of molecules of the components are equal. The conditions for the formation of the substitution of an SS in a multicomponent system of type A$_2$, AB, CD are presented in [10] as follows:

$$\Delta Z_i = (Z_A + Z_B) - (Z_C + Z_D) = 0, \quad (1)$$

$$\Delta r_i = (r_A + r_B) - (r_C + r_D) < 0.1(r_A + r_B), \quad (2)$$

where Z_i is the valence and r_i is covalent radius of atoms of the ith component.

Condition (1) shows the isovalence of components valid for GaAs−Ge$_2$, GaAs−ZnSe, and Ge$_2$−ZnSe systems, and condition (2) provides recombination passivity of impurities. In this case, mutual substitution of the SS molecular components do not lead to large deformation of the crystal lattice. The components of such a system can form a continuous substitutional solid solution in the form of (GaAs)$_{1-x-y}$(ZnSe)$_x$(Ge$_2$)$_y$, which is a stable solid phase.

The topography of the grown epitaxial layers was studied by AFM at the Institute of Ion-Plasma and Laser Technologies of the Academy of Sciences of Uzbekistan. Figures 1a and 1b show two- and three-

(a)

(b)
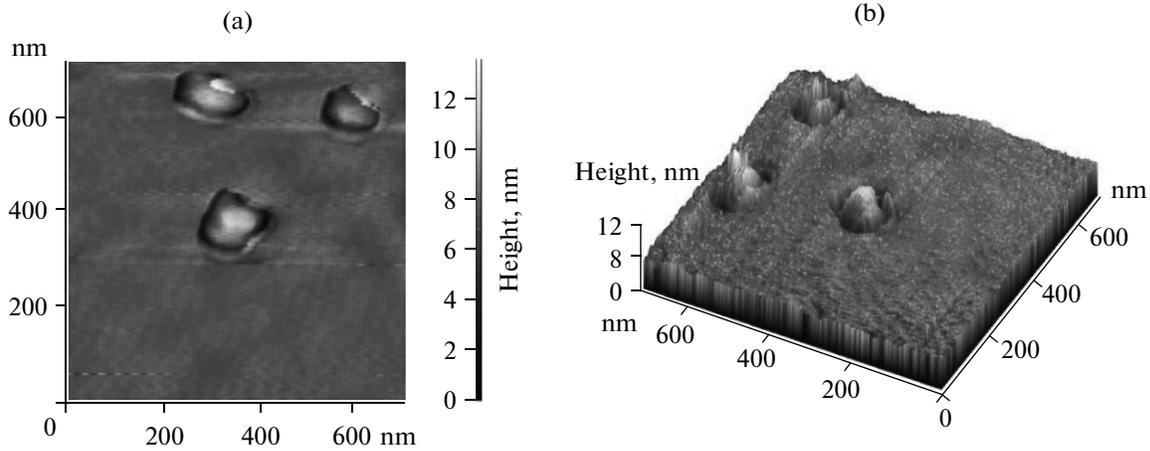
Fig. 1. Two- (a) and three-dimensional (b) surface image of epitaxial (GaAs)$_{1-x-y}$(ZnSe)$_x$(Ge$_2$)$_y$ film obtained using AFM. Image size is 700×700 nm^2, height of islands is ~12.6 nm, and width of islands is ~128−164 nm.

dimensional images of the surface and cleavage of the epitaxial layer (GaAs)$_{1-x-y}$(ZnSe)$_x$(Ge$_2$)$_y$. One can see from Fig. 1 that islands with a height ~12.6 nm and a width of ~128−164 nm are formed in the surface region of the film during growth. Apparently, these islands are formed from SS components, and they are quantum dots that create a local electrostatic field with anintensity of 10^7-10^9 V/cm at a distance of ~100−150 nm.

According to the Franz−Keldysh effect [11], such a strong local electric field should lead to a change in the band gap of the SS around the quantum dots; i.e., it is possible for local variband nanoscale structures to form [12].

Figure 2 shows the spectral dependence of photosensitivity of the n(GaAs)$-p$(GaAs)$_{1-x-y}$(ZnSe)$_x$(Ge$_2$)$_y$ structure at room temperature, measured with an optical spectrometer equipped with a Zeiss Jena mirror monochromator with quartz optics. It is possible to investigate samples in the photon energy range from 1 to 2.73 eV using these optics. One can see from Fig. 2 that the photoresponse increases dramatically from a photon energy of 1.2 eV, which confirms the active influence of the narrowband component (Ge$_2$) of SSs for the photovoltaic effect. It is known that the band gap of germanium $E_{g,\text{Ge}} = 0.67$ eV is less than $E_{g,\text{GaAs}} = 1.42$ eV, and $E_{g,\text{ZnSe}} = 2.70$ eV. However, the lack of completeness of Ge absorption is probably due to the small thickness of the Ge-enriched sublayer.

The maximum photosensitivity observed at a photon energy of 1.38 eV (Fig. 2), which may be due to width of buried (GaAs)$_{1-x-y}$(ZnSe)$_x$(Ge$_2$)$_y$ of the SS band gap. The decline in photosensitivity at photon energies greater than 1.38 eV is probably due to the depth of the separating barrier of the $p-n$ junction, which is determined by the thickness of the epitaxial layer, constituting in this case ~20 μm.

The diffusion length of minority carriers in the (GaAs)$_{1-x-y}$(ZnSe)$_x$(Ge$_2$)$_y$ layer determined in this

work was about 4.8 μm, which is much smaller than the depth of the separating barrier. This situation increases the recombination of photoinduced nonequilibrium charge carriers. Furthermore, Sn atoms partially embedded in the SS lattice from the tin solution melt create shallow donor levels [14] and assist recombination.

The photosensitivity spectrum of the investigated structure in the photon energy range from 2.4 to 2.7 eV has a peak sensitivity at 2.62 eV (Fig. 2). This peak is probably conditioned by the ZnSe broadband component. It is known that the covalent bond of the atoms of molecules in a pure ZnSe semiconductor material, expressed as $E_{g,\text{ZnSe}} = 2.70$ eV, is stronger than the Ga−As and Ge−Ge bond. However, when a ZnSe molecule replaces GaAs or Ge$_2$ molecules in a tetrahedral lattice of the SS, the Zn−Se bond weakens under the influence of surrounding Ga, As, and Ge atoms (Fig. 3).

This apparently causes the appearance of an ZnSe impurity energy band of located at $\Delta E_i = E_{\text{ph}} - E_{g\,\text{SS}}$ below the valence band of the (GaAs)$_{1-x-y}$(Ge$_2$)$_x$(ZnSe)$_y$ SS. Since ZnSe is direct-gap semiconductor and the
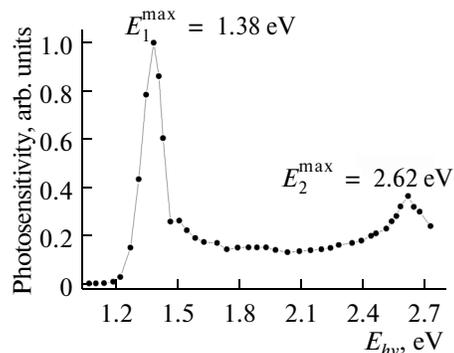
Fig. 2. Spectral photosensitivity of nGaAs$-p$(GaAs)$_{1-x-y}$(ZnSe)$_x$(Ge$_2$)$_y$ structures at room temperature.
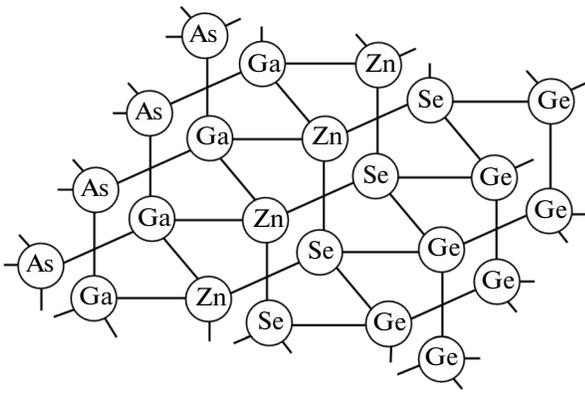
Fig. 3. Spatial configuration of tetrahedral bonds of molecules of continuous substitutional $(GaAs)_{1-x-y}(Ge_2)_x(ZnSe)_y$ solid solution.
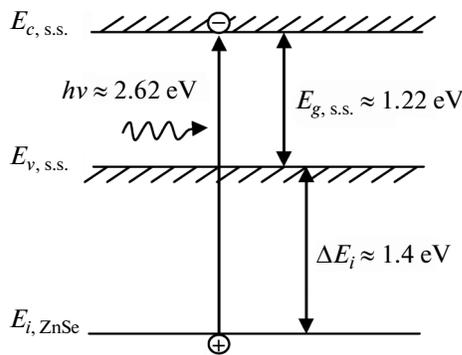
Fig. 4. Energy band diagram of $(GaAs)_{1-x-y}(ZnSe)_x(Ge_2)_y$ solid solution.

molar concentration of molecules in the ZnSe in SSs is $\sim 10^{20}$ cm^{-3}, this is additional evidence for the active participation of the Zn—Se bond in the photovoltaic effect at photon energies of $E_{ph} > 2.4$ eV.

CONCLUSIONS

Our studies of the photosensitivity spectra of nGaAs–p(GaAs)$_{1-x-y}$(ZnSe)$_x$(Ge$_2$)$_y$ heterostructures show that the $(GaAs)_{1-x-y}(ZnSe)_x(Ge_2)_y$ solid solution has a selective photosensitivity due to the ZnSe components in GaAs with different values of the ionization energy of the covalent bond of the corresponding molecules. The existence of impurity states in the band diagram of the solid solution is confirmed by the formation of island nanostructures, i.e., quantum dots. Such solid solutions can be used as a photoactive material for selective photodetector operation in the near infrared and visible regions.

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