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Influence of GaAs Molecules on the Photosensitivity of pSi−n(GaSb)$_{1-x}$(Si$_2$)$_x$ and nGaAs−p(InSb)$_{1-x}$(Sn$_2$)$_x$ Heterostructures

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Received July 7, 2016

Abstract—The spectral dependences of heterostructures pSi−n(GaSb)$_{1-x}$(Si$_2$)$_x$ ($0 \leq x \leq 0.07$) and nGaAs−p(InSb)$_{1-x}$(Sn$_2$)$_x$ ($0 \leq x \leq 0.05$) alloyed by GaAs molecules are studied. The ionization energy of GaAs molecules in the studied structures is assessed and its dependence on the width of the band gap and parameter of the lattice of the basic semiconductor are found.

The semicentennial history of photovoltaic [1, 2] and thermo-photovoltaic [3, 4]—semiconducting conversion of solar energy and thermal emission of hot bodies into electricity—prove the long-term relevance of the related studies and developments. In spite of the achievements in the development of photo conversion systems, the extensive application of solar photo conversion systems is being held back due to their comparatively high cost [5]. Increasing the photo converters' efficiency based on the available low-cost semiconducting materials is the critical task. In this respect, the growth of solid solutions of the elemental semiconductors and semiconducting binary compounds with high photoelectrical parameters on the available silicon substrates and the studies on the photoelectrical properties are both of fundamental and applied interest.

The low efficiency value of the single junction solar cells is conditioned for wide-band gap materials by the semiconductors' transparency in the long-wave region; and for the narrow-band gap materials, it is due to the thermalization of the hot electrons generated by the high-energy photons of the solar spectrum. Increasing the efficiency of the solar element in the short wave region may be achieved by semiconductor alloying with the isovalent molecules of the wideband semiconductors. The molecules of the wideband semiconductor meeting the conditions of the formation of solid solutions with solvent [6] in a low-dimensional semiconductor with the energy levels $E_i \geq 2E_g$ (E_g is the width of the band gap of the basic semiconductor) located in the valence band may contribute to the generation of two hole-electron pairs for the high-energy photons [7]. The energy levels of the impurity molecules are determined, firstly, by the interaction of these molecules with the solvent atoms, and secondly, by the structural and electro-physical parameters of the solvent and soluble molecules: the lattice parameter, covalent radius, band gap width, and electro-negativity. The accumulation of the experimental data concerning the interaction of impurity molecules and the solvent and revelation of the dependences of the energy parameters of the impurity molecules on the other fundamental parameters of the solvent will allow intentionally using impurity molecules for expanding the spectral region of the photo-receivers' sensitivity and increasing the photo-converters' efficiency.

The dependences of the ionization energy of the impurity GaAs molecules on the width of the band gap and the parameters of the lattice of the basic semiconductor based on the GaAs, GaSb, and InSb.C compounds were studied. For this purpose, the spectral dependences of the heterostructures' photo-sensitivity pSi−n(GaSb)$_{1-x}$(Si$_2$)$_x$ ($0 \leq x \leq 0.07$) [8], nGaAs−p(InSb)$_{1-x}$(Sn$_2$)$_x$ ($0 \leq x \leq 0.05$) (Fig. 1) alloyed by the GaAs molecules were studied. The heterostructures were grown on the pSi and nGaAs substrates of the solid solutions n(GaSb)$_{1-x}$(Si$_2$)$_x$, p(InSb)$_{1-x}$(Sn$_2$)$_x$, correspondingly, by the LPE method from the tin solution melt. During the growth of the epitaxy layers, the solution melt was dissolved by the GaAs. The grown epitaxy layer was ~10 μm thick. The mole content of the GaAs in solid solutions was ~0.5%. The GaAs molecules, replacing the molecules of the base semiconductor, are part of the solid solution as one component; however, at such a content, they may be considered as an isovalent additive with localized energy levels in the band diagram of the solid solution.
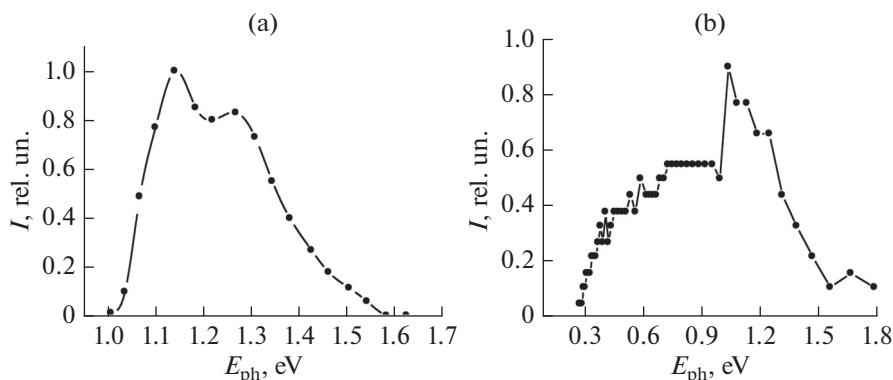
Fig. 1. Spectral dependences of the photosensitive heterostructures $p\text{Si}{-}n(\text{GaSb})_{1-x}(\text{Si}_2)_x$ ($0 \le x \le 0.07$) (a) and $n\text{GaAs}{-}p(\text{InSb})_{1-x}(\text{Sn}_2)_x$ ($0 \le x \le 0.05$) (b) alloyed by the isovalent GaAs molecules.
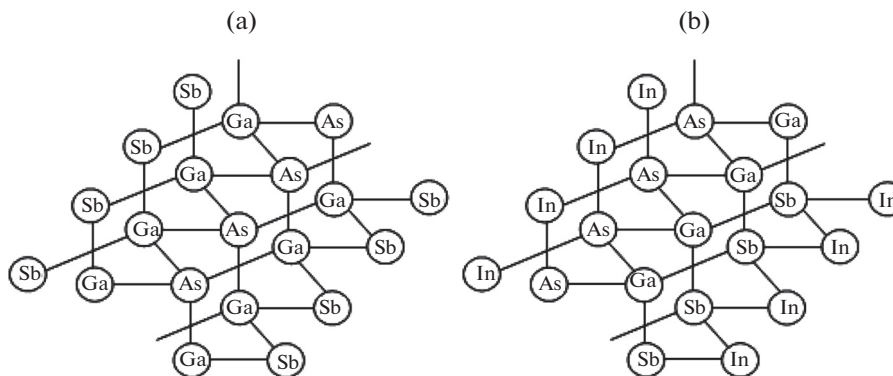

Fig. 2. Tetrahedral bonds GaSb (a) and InSb (b) with isovalent replacement impurities of the GaAs molecules.

The ionization energy of the GaAs molecules in the $(\text{GaSb})_{1-x}(\text{Si}_2)_x$ and $(\text{InSb})_{1-x}(\text{Sn}_2)_x$ solid solutions was assessed by the red edge of the sensitivity peak which appeared due to the generation of hole-electron pairs featuring covalent GaAs bonds and are found in the short-wave region of the spectral dependence of the photo-sensitivity of the studied structures (Fig. 1).

In the $(\text{GaSb})_{1-x-y}(\text{Si}_2)_x(\text{GaAs})_y$ ($0 \le x \le 0.07$, $0 \le y \le 0.005$) solid solution, the mole content Si_2 is 7%; therefore, the crystal lattice is characterized mainly by the properties of the binary component GaSb, just as $(\text{InSb})_{1-x-y}(\text{Sn}_2)_x(\text{GaAs})_y$ ($0 \le x \le 0.05$, $0 \le y \le 0.005$) is characterized by the properties of InSb. In these solid solutions, the isovalent molecules replace the GaSb and InSb molecules at the lattice point, respectively (Fig. 2). As can be seen from Fig. 2a, two types of covalent bonds, Ga–Sb and Ga–As, are available in the solid $(\text{GaSb})_{1-x-y}(\text{Si}_2)_x(\text{GaAs})_y$ ($0 \le x \le 0.07$, $0 \le y \le 0.005$) solution around molecules Ga–As. The difference of the sum of atoms covalent radius of molecules GaSb and GaAs is ~7%:

$$\Delta r = |r_{\text{Ga}} + r_{\text{Sb}} - (r_{\text{Ga}} - r_{\text{As}})|$$
$$= |2.64\,\text{Å} - 2.45\,\text{Å}| = 0.19\,\text{Å} \qquad (1)$$
$$\approx 0.072(r_{\text{Ga}} + r_{\text{Sb}}),$$

as well as the differences of the values of the electro-negativity by the Pauling scale of atoms of the molecules Ga–As $- \Delta\chi_{\text{GaAs}} = |\chi_{\text{Ga}} - \chi_{\text{As}}| = 0.37$ and GaSb $- \Delta\chi_{\text{GaSb}} = |\chi_{\text{Ga}} - \chi_{\text{Sb}}| = 0.24$, are close; therefore, the Ga–As molecules do not strongly deform the crystal lattice and are not active recombination centers.

The energy of the disconnection of the covalent bonds Ga-Sb and Ga-As in the corresponding semi-conducting material is determined by the width of the band gaps of these semiconductors: $E_{g,\,\text{GaSb}} = 0.72$ eV and $E_{g,\,\text{GaAs}} = 1.43$ eV. Therefore, the observed growth of the heterostructure sensitivity $p\text{Si}{-}n(\text{GaSb})_{1-x}(\text{Si}_2)_x$ (Fig. 1a) at the photons' energy of $E_{\text{ph}} \ge 1.2$ eV is conditioned by the disconnection of the covalent bonds Ga–As. The energy of the ionization of the Ga-As molecules in the solid solution $(\text{GaSb})_{1-x}(\text{Si}_2)_x$ ($0 \le x \le 0.07$), which is $E_{i,\,\text{GaAs}} \approx 1.2$ eV, may be evaluated based on the red edge of the photosensitivity peak in Fig. 1a. The change of the value $E_{i,\,\text{GaAs}}$ from $E_{g,\,\text{GaAs}}$,
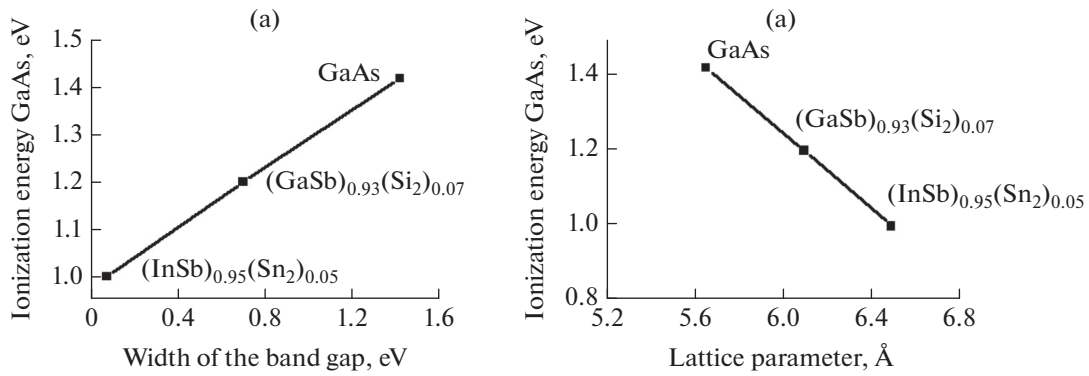
Fig. 3. Dependences of the ionization energy of the isovalent impurity GaAs molecules on the width of the band gap (a) and lattice parameter (b) of the semiconducting materials.

seems to be conditioned by the difference of the covalent radiuses $r_{GaAs} = r_{Ga} + r_{As} = 2.45$ Å and $r_{GaSb} = r_{Ga} + r_{Sb} = 2.64$ Å ($r_{GaAs} < r_{GaSb}$). The distance of the covalent bond Ga–As increases to more than 2.45 Å; this leads to a decrease of the disconnection energy of the covalent bond Ga–As from 1.43 eV, characteristic for the pure GaAs semiconductor, to 1.2 eV in the solid solution $(GaSb)_{1-x-y}(Si_2)_x(GaAs)_y$ ($0 \leq x \leq 0.07$, $0 \leq y \leq 0.005$ because the Ga–As molecules conform into the crystal lattice GaSb during the molecular replacement.

It is seen in Fig. 2b that four types of bonds, Ga–As, Ga–Sb, In–As, and In–Sb, are available in the solid solution $(InSb)_{1-x-y}(Sn_2)_x(GaAs)_y$ ($0 \leq x \leq 0.05$, $0 \leq y \leq 0.005$) around the GaAs molecules. The difference of the sum of the covalent radiuses of the molecules of the GaAs and InSb atoms is ~14.6%.

Value Δr is determined as

$$\begin{aligned} \Delta r &= \left| (r_{In} + r_{Sb}) - (r_{Ga} + r_{As}) \right| \\ &= \left| 2.87 \text{ Å} - 2.45 \text{ Å} \right| \\ &= 0.42 \text{ Å} \approx 0.146 \left| (r_{In} + r_{Sb}) \right|. \end{aligned} \quad (2)$$

However, the difference of the sum of the covalent radiuses of the molecules GaAs and GaSb, GaAs and InAs, as well as InSb and GaSb, InSb and InAs, is less than 9%:

$$\begin{aligned} \Delta r &= \left| (r_{Ga} + r_{As}) - (r_{Ga} + r_{Sb}) \right| = 0.19 \text{ Å}, \\ \Delta r &= \left| (r_{Ga} + r_{As}) - (r_{In} + r_{As}) \right| = 0.24 \text{ Å}, \\ \Delta r &= \left| (r_{In} + r_{Sb}) - (r_{Ga} + r_{Sb}) \right| = 0.23 \text{ Å}, \\ \Delta r &= \left| (r_{In} + r_{Sb}) - (r_{In} + r_{As}) \right| = 0.19 \text{ Å}. \end{aligned} \quad (3)$$

Due to such bonds, the elastic strain energy of the crystal lattice of the solid solution $(InSb)_{1-x-y}(Sn_2)_x(GaAs)_y$ ($0 \leq x \leq 0.05$, $0 \leq y \leq 0.005$) will be insignificant. The difference of the values of the the electro-negativity of the atoms of these molecules has close values: $\Delta\chi_{GaAs} = |\chi_{Ga} - \chi_{As}| = 0.37$, $\Delta\chi_{GaSb} = |\chi_{Ga} - \chi_{Sb}| = 0.24$, $\Delta\chi_{InAs} = |\chi_{In} - \chi_{As}| = 0.4$, $\Delta\chi_{InSb} = |\chi_{In} - \chi_{Sb}| = 0.27$; therefore,

the shares of the ionic compounds of the polar covalent bonds of these molecules are comparable. Because the difference of the electro-negativity of the values of the molecules of the atoms for all components of the solid solution is $\Delta\chi < 0.6$, the chemical bonds may be considered covalent.

The disconnection energies of the covalent bonds In–Sb, In–As, Ga–Sb, and Ga-As in the corresponding semiconducting material are $E_{g, InSb} = 0.18$ eV, $E_{g, InAs} = 0.35$ eV, $E_{g, GaSb} = 0.72$ эB, and $E_{g, GaAs} = 1.43$ eV, respectively. Therefore, the growth of the photosensitivity of the pSi–$n(GaSb)_{1-x}(Si_2)_x$ heterostructure (Fig. 1b) at photon energies of $E_{ph} \geq 1.0$ eV is conditioned by the disconnection of the covalent bond Ga-As, whose energy is higher than that of the others. The ionization energy of the GaAs molecules in the solid solution $(InSb)_{1-x-y}(Sn_2)_x(GaAs)_y$ ($0 \leq x \leq 0.05$, $0 \leq y \leq 0.005$), which is $E_{i, GaAs} \approx 1.0$ eV, may be evaluated in Fig. 1b based on the red edge of the photosensitivity peak. The change of the $E_{i, GaAs}$ value, as in the case of the solid solution $(GaSb)_{1-x-y}(Si_2)_x(GaAs)_y$ ($0 \leq x \leq 0.07$, $0 \leq y \leq 0.005$), is conditioned by the difference of the covalent radiuses $r_{GaAs} = 2.45$ Å and $r_{InSb} = 2.87$ Å ($r_{GaAs} < r_{InSb}$). Because $r_{InSb} = 2.87$ Å $> r_{GaSb} = 2.64$ Å, this leads to a higher elongation of the covalent bond Ga-As in the solid solution $(InSb)_{1-x-y}(Sn_2)_x(GaAs)_y$ compared to the solid solution $(GaSb)_{1-x-y}(Si_2)_x(GaAs)_y$, which results in a decrease of the atom interacting forces of the GaAs molecules and therefore to a higher decrease of the disconnection energy of the covalent bond Ga–As.

Because the disconnection energy of the covalent bond Ga–As is more than the width of the band gaps of the studied solid solutions, the energy levels of the impurity molecules Ga–As stay within the valent region of the solid solutions. Figure 3 shows the dependences of the ionization energy of the impurity Ga–As molecules on the width of the band gaps (E_g) and lattice parameter (a) of the basic semiconductor. Figure 3a shows that with a decrease of E_g a decrease

of $E_{i,\,GaAs}$ is observed. Analysis of Fig. 3a shows that dependence $E_{i,\,GaAs}$ on E_g is linear; extrapolation of this dependence on a straight line gave the following type of functional dependence:

$$E_{i,\,GaAs}\,(eV) = 0.98 + 0.31 \cdot E_g\,(eV). \qquad (4)$$

The change of $E_{i,\,GaAs}$ in different semiconductors seems to be conditioned by the deformation of the Ga−As molecules under the influence of the surrounding atoms of the crystal lattice. For the purpose of minimizing the potential energy of the elastic strains of the crystal lattice the impurity molecules conform to the lattice; this results in a change of the distance between atoms Ga and As, as shown above. Therefore, the interacting forces and interacting energy of the atoms of the GaAs molecules change; as a result, the disconnection energy of the Ga−As bond will change. This is proved by the decrease of $E_{i,\,GaAs}$ with an increase of the lattice parameters of the semiconducting materials; this is shown in Fig. 3b. The experimental points given in Fig. 3b cover the straight line. The extrapolation of these points gave the following empirical expression of the $E_{i,\,GaAs}$ dependence on the lattice parameter:

$$E_{i,\,GaAs}\,(eV) = 4.27 - 0.504a\,(\text{Å}). \qquad (5)$$

Taking into account the differences of the crystal lattice types and shares of the covalent and ion bonds in the elementary semiconductors and semiconducting compounds $A^{IV}B^{IV}$, $A^{III}B^{V}$, and $A^{II}B^{VI}$, as well as the interacting forces of the ion cores with valent electrons, we assume that dependences (4) and (5) seem to be appropriate only in the case when the GaAs molecules are in solid solutions based on the semiconducting compounds $A^{III}B^{V}$. However, analysis of the experimental data and theoretical studies afford grounds for considering that a decrease of the ionization energy of the impurity isovalent molecules of elementary semi-

conductors and semiconducting compounds $A^{III}B^{V}$ and $A^{II}B^{VI}$ with a decrease of the band gap width and an increase of the lattice parameter of the basic semiconductor is characteristic of all semiconducting materials.

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Translated by E. Grishina

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