Photovoltaic converters based on $Al_{0.1}Ga_{0.2}In_{0.7}Sb_{0.2}P_{0.8}$/InP heterostructures

© L.S. Lunin[1], M.L. Lunina[1], A.V. Donskaya[2]

[1] Southern Scientific Center of the Russian Academy of Sciences,
344006 Rostov-on-Don, Russia
[2] Platov South-Russian State Polytechnic University (NPI),
346400 Novocherkassk, Russia

E-mail: lunin_ls@mail.ru

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The optimal conditions for growing AlGaInSbP/InP(100) heterostructures by liquid-phase gradient epitaxy are revealed: temperature of 823 K, temperature gradient of 20 K/cm, zone thickness of 200 μm and supercooling of 5 K. The composition $Al_xGa_yIn_{1-x-y}Sb_zP_{1-z}$ was established by mass spectroscopy: $x = 0.1$, $y = 0.2$, $z = 0.2$ mol. fr. Using Raman spectroscopy, the presence of five modes of binary compounds has been proven: InSb, GaSb, InP, AlSb, GaP. The dependence of the structural perfection and photoluminescence on the presence of aluminum atoms (0.1 mol. fr.) in $Ga_{0.2}In_{0.8}Sb_{0.2}P_{0.8}$/InP heterostructures was studied. The spectral characteristics of the $Al_{0.2}In_{0.8}P/Al_{0.1}Ga_{0.2}In_{0.7}Sb_{0.2}P_{0.8}$/InP heterostructures showed a high quantum yield of about 95% in the wavelength range of $\lambda = 500-1100$ nm.

Keywords: growth kinetics, mass-spectroscopy, Raman spectroscopy, photoluminescence, external quantum yield.

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The development of electronics is closely related to advances in new materials, which include heterostructures based on multicomponent solid solutions of compounds $A^{III}B^{V}$. Their value lies in the possibility of forming structurally perfect heterojunctions, which is achieved by matching the lattice parameters and thermal expansion coefficients (TEC) of materials.

The solid solution of AlGaInSbP can be used as a full-fledged narrow-band solar cell on an indium phosphide substrate or as part of a cascade photoelectric converter (PEC) AlGaInSbP/GaAs/Ge/SiGe/Si. The temperature gradient zone recrystallization method (TGZR) has been chosen as a method for obtaining AlGaInSbP/InP(100) heterostructures, which makes it possible to control the thermodynamic and morphological state of the interphase boundaries, as well as the concentration of nonradiative recombination centers.

The aim of the paper is to study the quality of $Al_{0.1}Ga_{0.2}In_{0.7}Sb_{0.2}P_{0.8}$ layers and determine the optical output characteristics of the PEC based on $Al_{0.1}Ga_{0.2}In_{0.7}Sb_{0.2}P_{0.8}$/InP(100).

First of all, the kinetics of synthesis of AlGaInSbP layers was studied. It is known that the rate (υ) of growing solid solutions is influenced by the technological parameters of the (TGZR), such as the composition and thickness of the liquid zone (l), the temperature of the growth process (T) and its gradient (G). Initially, the dependence $\upsilon(l)$ was studied, which allows judging the mechanism of crystallization. Three growth modes were observed: kinetic $25 < l < 250\,\mu$m, mixed $250 < l < 350\,\mu$m, and diffusive $350 < l < 550\,\mu$m. It was found that the high aluminum content in the Al–Ga–In–Sb–P melt solution leads to a slowdown in the synthesis rate of AlGaInSbP layers. This is attributable to a decrease in the diffusion coefficients of aluminum atoms in the melt solution. As a result, defects are formed in the structure, which negatively affect the output characteristics of the PEC. In addition, with an increase in the concentration of Al in the liquid zone, the mixed crystallization regime shifts to the region of thin zones, which indicates the predominance of the diffusion mechanism of crystallization of the AlGaInSbP layer over the kinetic one. From a technological point of view, this means the complexity of growing AlGaInSbP thin films. For these reasons, the content of aluminum atoms in the liquid zone does not exceed 0.1 molar fraction. The temperature values in the process of growing the epitaxial layer and its gradient should be minimal in order to suppress the surface diffusion of active components and the high volatility of group V components, but sufficient to achieve uniform layered growth. Thus, optimal conditions for obtaining $Al_xGa_yIn_{1-x-y}Sb_zP_{1-z}$/InP(100) heterostructures were chosen: temperature $T = 823$ K, temperature gradient $G = 20$ K/cm, zone thickness $l = 200\,\mu$m and supercooling $\Delta T = 5$ K. In addition, since Al and P atoms are distributed unevenly in the layer with decreasing concentration from the heterogeneous boundary to the surface [1], an InAlPSb polycrystal was used as a feed for the melt solution.

The Raman scattering (RS) measurements were carried out using the inVia Raman Microscope (Renishaw) spectrometer at room temperature with a wavelength of 514 nm. It is known that, according to the selection rule, only longitudinal optical (LO) phonons are observed for crystals with a zinc blende structure when light is backscattered from a surface with an orientation (100). In accordance with Figure 1 the grown solid solution has a five-mode spectrum.

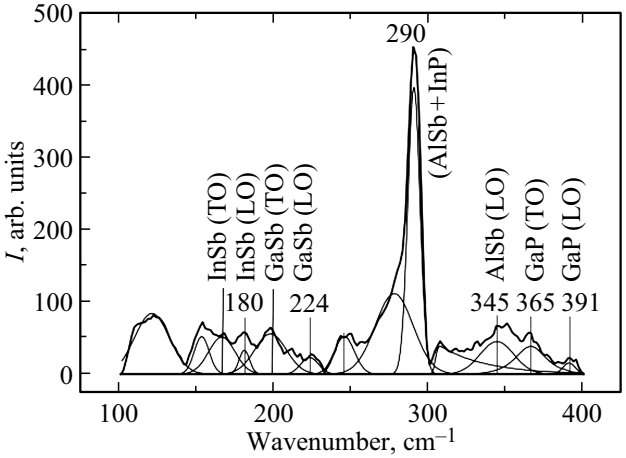

Figure 1. The RS spectrum from the AlGaInSbP layer.

Such modes as InSb, GaSb, InP, AlSb, GaP are clearly expressed. An analysis of the frequencies of the detected modes shows that there is a peak shift relative to the mode positions of the binary volume components. The LO-mode InSb is shifted towards lower frequencies (up to $180\,\mathrm{cm}^{-1}$), TO-mode manifests itself as a broadened peak with a lower wavenumber, as can be seen from the peaks of spectrum decomposition. A similar pattern is observed for the fluctuations of the binary component of GaSb and others. As a rule, such displaced modes in a solid solution are called localized, which arise due to the presence of some structural disorder in a real solid solution. In addition, we can assume the presence of peaks caused by the mixing of LO-TO modes of various components of the solid solution. An example of such mixing may be a high-intensity peak with asymmetric broadening at the base in region of $280-290\,\mathrm{cm}^{-1}$, which is probably formed by mixing AlSb and InP vibrations or a more complex mechanism with the possible presence of a triple phase. According to Ref. [2], the peak of oscillations of the longitudinal optical mode AlSb lies at $\omega = 344\,\mathrm{cm}^{-1}$, which coincides with the obtained result. According to the data from Ref. [3], the peak of the LO-phonons of GaP-oscillations of the binary component of the alloy is located at $\omega = 403\,\mathrm{cm}^{-1}$, and the TO-mode has an oscillation frequency of $365\,\mathrm{cm}^{-1}$. In the studied AlGaInSbP alloy, the GaP LO-phonon band is shifted to the lower frequency region — $\omega = 391\,\mathrm{cm}^{-1}$. Thus, the results of the RS on Figure 1 allow confirming the formation of a solid solution of AlGaInSbP, but it should be noted that the analysis is preliminary and requires additional studies to be performed in the future.

The luminescent properties of semiconductor structures directly depend on their quality, and in this regard, the data obtained by secondary ion mass spectrometry (SIMS) are analyzed. Mass spectra were obtained by etching the surface of the heterostructure with argon ions with an energy of 4 keV and a current density of $50\,\mu\mathrm{A/cm}^2$. Secondary particles were recorded with a Micromass PC100 quadrupole mass spectrometer in the multichannel ion monitoring mode, which is characterized by the exclusion of the background from the resulting picture.

The composition of the components in the solid phase of AlGaInSbP was determined by mass spectrometry. Let us consider the nature of the distribution of the components of group III over the thickness of the solid solution (Figure 2). The behavior of the In line from the heterogeneous boundary to the surface of the layer demonstrates a decrease in concentration from 35 to 33 %. The gallium line behaves like the indium line, varying from 10 to 13 %. Aluminum, due to the use of polycrystalline recharge, is distributed uniformly with composition fluctuations of ±1 %. If the behavior of metalloids is characterized by a uniform distribution over the depth of the layer, on its surface, and at a heterogeneous boundary, then the components of the V, group behave differently. At the heterojunction, there is a sharp increase in the concentration of P and a decrease in the proportion of Sb. The behavior of phosphorus and antimony lines is related to the peculiarity of the formation of chemical bonds of the V group elements. During the growth process, chemical bonds arise on the surface of the InP substrate between the P from the melt solution and the P contained in the substrate material. Since there are no Sb atoms in it, there are fewer In–Sb bonds. With a decrease in the content of phosphorus atoms in the depth of the epitaxial layer, vacancies are formed that are occupied by antimony atoms, which is why their concentration increases from 10 to 12 %. In general, there is no change in composition by more than 5 %, which means that the epitaxial layer is homogeneous.

The composition of the structure by elements is represented as: Al — 5 %, Ga — 10 %, In — 35 %, Sb — 10 %, P — 40 %. Considering that the sum of the molar fractions in sublattices is 1, it is possible to determine the exact composition of the solid solution $Al_{0.1}Ga_{0.2}In_{0.7}Sb_{0.2}P_{0.8}$.

The position of the heterojunction was determined by the criterion 16.86 % [4], based on the indium line, which

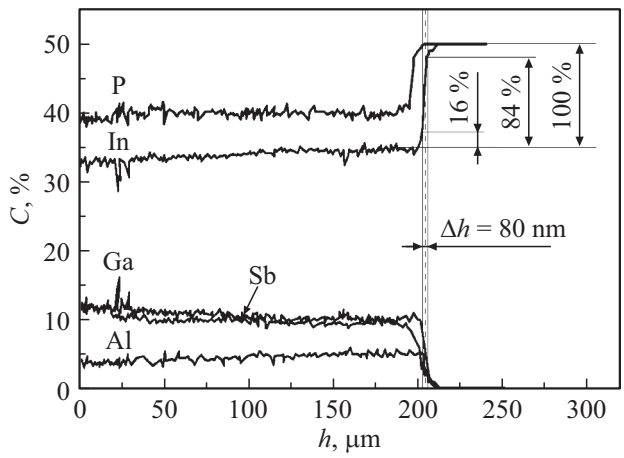

Figure 2. The SIMS profile of the AlGaInSbP/InP heterostructure. The value $h = 0$ corresponds to the surface layer.

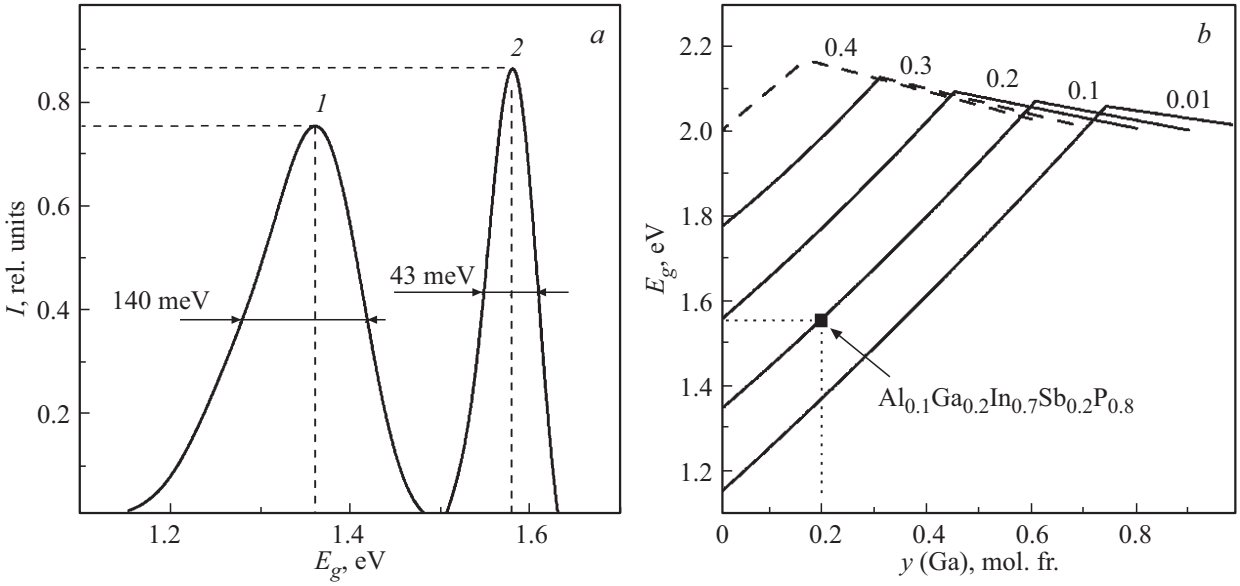

Figure 3. *a* — photoluminescence spectra of heterostructures $Ga_{0.2}In_{0.8}Sb_{0.2}P_{0.8}$/InP (peak *1*), $Al_{0.1}Ga_{0.2}In_{0.7}Sb_{0.2}P_{0.8}$/InP (peak *2*); *b* — width of the band gap of the solid solution $Al_xGa_yIn_{1-x-y}Sb_{0.2}P_{0.8}$ (values x are indicated above the curves; the dot indicates the composition of $Al_{0.1}Ga_{0.2}In_{0.7}Sb_{0.2}P_{0.8}$; dotted lines indicate thermodynamically unstable regions).

differs in minimal deviations from the direct dependence $C = 35\,\%$. We found the coordinates for the depth of the layer at which In changes by 16 % (left boundary of the heterojunction h_1) and by 84 % (right boundary of the heterojunction h_2) of its average concentration in the layer. Next, the position of the heterogeneous boundary was graphically determined as the arithmetic mean of h_1 and h_2. The thickness of the heterojunction was 80 nm, which is a satisfactory result in obtaining a high-quality structure.

Photoluminescent (PL) spectroscopy determined the quality and the band gap width E_g of $Al_{0.1}Ga_{0.2}In_{0.7}Sb_{0.2}P_{0.8}$/InP heterostructures. The optical properties of the heterosystem were studied in the spectral range of $0.2-2.0\,\mu$m. In order to minimize the evaporation of volatile components such as antimony and phosphorus, measurements were carried out at room temperature. The MDR-204 device was used as a monochromator, the excitation source was a laser with a power of 8.5 mW and a wavelength of 402 nm. The photoluminescence of the AlGaInSbP epitaxial layer was recorded with a germanium photodiode PD FDG (a photodetector with a germanium photodiode).

For comparison, the results for $Ga_{0.2}In_{0.8}Sb_{0.2}P_{0.8}$ are also presented in Figure 3, *a*, in addition to the photoluminescence spectrum of solid solutions of $Al_{0.1}Ga_{0.2}In_{0.7}Sb_{0.2}P_{0.8}$ synthesized on InP(100) substrates. It can be seen that both structures have a single peak associated with the edge of the spectrum. Studies have shown that with an increase in the number of components of the solid solution, the intensity increases *I* and the bandwidth of the radiation decreases by half the height of the peaks ΔE_g. These parameters determine the crystalline perfection of the epitaxial layer. In quad systems, the presence of one degree of freedom makes it possible to coordinate lattice constants (a) between the layer and the substrate. Therefore, the significant width of the PL spectral band at the half-height $\Delta E_g = 140$ meV (Figure 3, *a*, curve *1*) is determined by the absolute mismatch in the TEC (a) of the GaInSbP layer and the InP substrate ($\delta a = 6.4\,\%$). However, the selected composition of $Ga_{0.2}In_{0.8}Sb_{0.2}P_{0.8}$ solid solution with parameters $a = 5.91$ Å and $a = 5\,\mu\text{m}\,\text{K}^{-1}$ also has a slight mismatch in the lattice parameter with the InP substrate with the magnitude of $\delta a = 0.5\,\%$.

An additional chemical degree of freedom appears with the addition of Al to a four-component GaInSbP solid solution with E_g equal to 1.367 eV, due to which the TEC mismatch is eliminated. As a result, the peak shifts from the NIR range from $\lambda = 907$ nm to the visible range of $\lambda = 787$ nm, the radiation intensity increased to 0.87 rel. units, and ΔE_g decreased to 43 meV (Figure 3, *a*, curve *2*), which is associated with small fluctuations in composition over the thickness of the AlGaInSbP epislayer. The position of the peak *2* ($E_g = 1.578$ eV) corresponds to the theoretical data shown in Figure 3, *b* as a point. The peak shape *2* indicates straight-band energy transitions in the region of thermodynamic stability of heterostructures $Al_{0.1}Ga_{0.2}In_{0.7}Sb_{0.2}P_{0.8}$/InP.

The external quantum efficiency (EQE) is a quantitative assessment that makes it possible to determine the sensitivity range of a device made from a specific heterosystem. The external quantum efficiency was measured using a SolarTll monochromator with a reference silicon photodetector sensitive in the range of 320–1180 nm. Studied spectral characteristics of $Al_{0.2}In_{0.8}P/Al_{0.1}Ga_{0.2}In_{0.7}Sb_{0.2}P_{0.8}$/InP

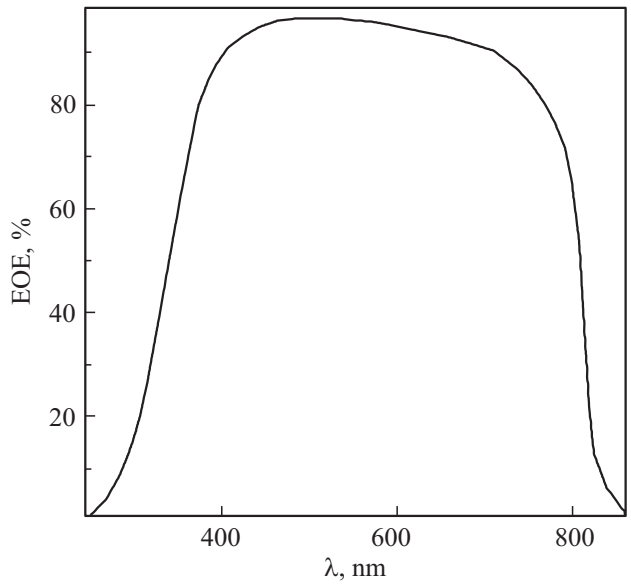

Figure 4. External quantum efficiency of $Al_{0.2}In_{0.8}P/Al_{0.1}Ga_{0.2}In_{0.7}Sb_{0.2}P_{0.8}/InP$ heterostructures.

heterostructures are shown in Figure 4. The composition of the wide-band window of $Al_{0.2}In_{0.8}P$ is selected in such a way as to use shorter-wavelength radiation from the edge of the spectrum $\lambda = 688$ nm. The active layer of $Al_{0.1}Ga_{0.2}In_{0.7}Sb_{0.2}P_{0.8}$ is consistent in the lattice parameter with the InP substrate and has a satisfactory degree of mismatch in the lattice parameter with window of $Al_{0.2}In_{0.8}P$ ($\delta a = 1.4\,\%$), therefore EQE has a high value of $\sim 95\,\%$ in the wavelength range of $\lambda = 400-800$ nm.

Studies of the structural perfection of $Al_{0.1}Ga_{0.2}In_{0.7}Sb_{0.2}P_{0.8}/InP(100)$ heterostructures revealed optimal technological parameters $T = 823$ K, $G = 20$ K/cm, $l = 200\,\mu$m and $\Delta T = 5$ K. The study of luminescent properties has shown that the transition to five-component solid solutions leads to an increase in intensity and a decrease in the radiation bandwidth by half the peak height. This fact indicates a higher crystal perfection. Measurements of spectral characteristics revealed a high value of the external quantum efficiency of $\sim 95\,\%$ in the spectral range of $\lambda = 400-800$ nm.

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Conflict of interest

The authors declare that they have no conflict of interest.

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