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Obtaining anisotypic heterostructures for a GaSb-based photovoltaic converter due to solid-phase substitution reactions

© G.S. Gagis, V.I. Kuchinskii, D.Yu. Kazantsev, B.Ya. Ber, M.V. Tokarev, V.P. Khvostikov, M.V. Nakhimovich, A.S. Vlasov, V.I. Vasil'ev

Ioffe Institute, St. Petersburg, Russia
E-mail: galina.gagis@gmail.com

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The possibility of manufacturing photovoltaic converter structures due to solid-phase reactions of substitution of Sb atoms in GaSb semiconductor wafers with As or P atoms, with simultaneous diffusion of Zn, is demonstrated.

Keywords: Solid-phase substitution reactions, photovoltaic converters, widegap window, $p-n$-junction, doping.

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In semiconductor device technology, along with epitaxial methods [1], diffusion methods are also used, for example, due to Zn diffusion to create the structures with $p-n$-junction based on n-GaSb for photovoltaic converters (PVC) [2]. However, diffusion methods make it possible to create structures not only with different types of doping, but also with near-surface regions that differ in the composition of the matrix material, for example, in the case of isovalent substitution in the crystal lattice $A^{\text{III}}B^{\text{V}}$ of the fifth group element B^{V} by the element C^{V}, which we demonstrated earlier [3]. The fifth group elements can be supplied to the $A^{\text{III}}B^{\text{V}}$ semiconductor wafer in the form of vapors, similar to how zinc is supplied during the diffusion doping process.

The main factors determining the progress of the solid-phase substitution reaction are the temperature in the reactor, the duration of the process, and the vapor pressure of the element C^{V}. In this paper we studied the processes of replacing Sb atoms with As or P atoms in GaSb wafers. The substitution was carried out at temperatures of $570-585^\circ$C for $27-35$ min.

Solutions-melts were used as sources of vapors of C^{V} elements, since the pressure of saturated vapor P_{C0} over a pure substance C^{V}, as a rule, is extremely high. Thus, at temperature of 580°C, the pressure P_{C0} over the pure substance C^{V} for arsenic is $5 \cdot 10^4$ Pa [4], and for red phosphorus — $4 \cdot 10^6$ Pa [5]. Over solutions-melts with an atomic concentration of the x_C^L component, the vapor pressure of the P_C component can be described by the expression [6]:

$$P_C = P_{C0}(x_C^L \gamma_C^L)^n,$$

where γ_C^L is activity coefficient of the component in the solution-melt, n is number of atoms in the vapor molecule C_n^{V}. For As and P the vapors are a mixture of C_2^{V} and C_4^{V} molecules, which complicates the expression for P_C [6]. However, in this paper we used the assumption that for $x_C^L < 0.1$ the probability of C_4^{V} molecules formation is extremely low, and we can assume that the vapor is entirely represented by C_2^{V} molecules.

Solutions-melts of Ga$-C^{\text{V}}$ type, containing As and P, provide too little solubility of the element C^{V}. Thus, according to [7], at 580°C the solubility of P and As in Ga is $x_{\text{P}}^L = 4 \cdot 10^{-5}$ and $x_{\text{As}}^L = 6 \cdot 10^{-3}$, which limits the vapor pressures of P_{P} to $\sim 1 \cdot 10^2$ Pa, P_{As} to ~ 2 Pa. The range of available vapor pressures can be expanded by using Sn$-$ZnSnC_2^{V} solutions-melts, in which the solubility of elements of the fifth group x_{P}^L, x_{As}^L reaches $\sim 5 \cdot 10^{-2}$ [8,9], which expands the range of available vapor pressures by two orders: P_{P} up to $\sim 1 \cdot 10^4$ Pa and P_{As} up to $\sim 1 \cdot 10^2$ Pa. Simultaneously with the delivery of C^{V} vapors, the delivery of Zn vapors is ensured. Thus, the near-surface layer of $\text{GaSb}_{1-x}C_x^{\text{V}}$ solid solution and the $p-n$ junction are formed simultaneously if the GaSb wafer has n-type doping, as in the case of GaSb : Te(001) used in this study. The penetration of C^{V} and Zn atoms can occur to different depth, which is demonstrated by studies using the secondary ion mass spectrometry (SIMS) method (Fig. 1, a). The formation of the $\text{GaP}_x\text{Sb}_{1-x}$ ternary solid solution in the near-surface regions of the GaSb wafers is confirmed by the Raman scattering spectra (Fig. 1, b). As can be seen from Fig. 1, b, the Raman scattering spectrum contains bands in the range $350-390\,\text{cm}^{-1}$, corresponding to GaP-type vibrations. There are no data on the dispersion of phonon modes of $\text{GaP}_x\text{Sb}_{1-x}$ solid solutions in the publications, however, based on general considerations and on the phonon dispersion data for $\text{GaAs}_{1-y}\text{P}_y$ solid solutions [10], we can conclude that the composition of the resulting $\text{GaP}_x\text{Sb}_{1-x}$ solid solution corresponds to $x \sim 0.7$. The GaSb-type vibrations of the $\text{GaP}_x\text{Sb}_{1-x}$ solid solution cannot be distinguished against the background of the GaSb substrate signal, but the presence of DATA and DALA acoustic modes witnesses the solid solution formation. The structures shown in Fig. 1 were fabricated by processing GaSb : Te(001) in P and Zn vapors obtained from Sn$-$ZnSnP$_2$ solutions-melts with $x_{\text{P}}^L = 5 \cdot 10^{-2}$ (Fig. 1, a) and $4 \cdot 10^{-2}$ (Fig. 1, b).

Method for forming heterostructures $p\text{-}A^{III}B^{V}_{1-x}C^{V}_{x}/n\text{-}A^{III}B^{V}$ with simultaneous diffusion of the fifth group element C^{V} and Zn can be used to obtain PVC with a wide-band window (WBW). Previously, WBW was fabricated from GaAs-based PVC and was $Al_zGa_{1-z}As$ ($z = 0.7-0.8$) layer formed by the epitaxial method [11]. As was shown in [11], the optimal thickness of the WBW up to 100 nm is sufficient to prevent the tunneling of charge carriers and, at the same time, does not prevent the passage of the short-wavelength part of the converted radiation. The WBW thicknesses mentioned in [11] are comparable with the thicknesses of near-surface regions of $GaSb_{1-x}C^{V}_{x}$, which can be obtained by the method of solid-phase substitution reactions [3].

At present, GaSb-based PVC structures used for infrared radiation conversion are fabricated without WBW, and the $p-n$ junction, as a rule, is formed by the method of two-stage zinc diffusion. Ultimately, the $p-n$ junction under the contacts lies at a depth of $1-1.5\,\mu$m [2], which is comparable to the results shown in Fig. 1, *a*.

In the present paper, during test structures manufacturing for PVC, the solutions-melts $Sn-ZnSnP_2$ with $x^L_P = 4\cdot10^{-2}$ or $Sn-ZnSnAs_2$ with $x^L_{As} = 3\cdot10^{-2}$ were used. The

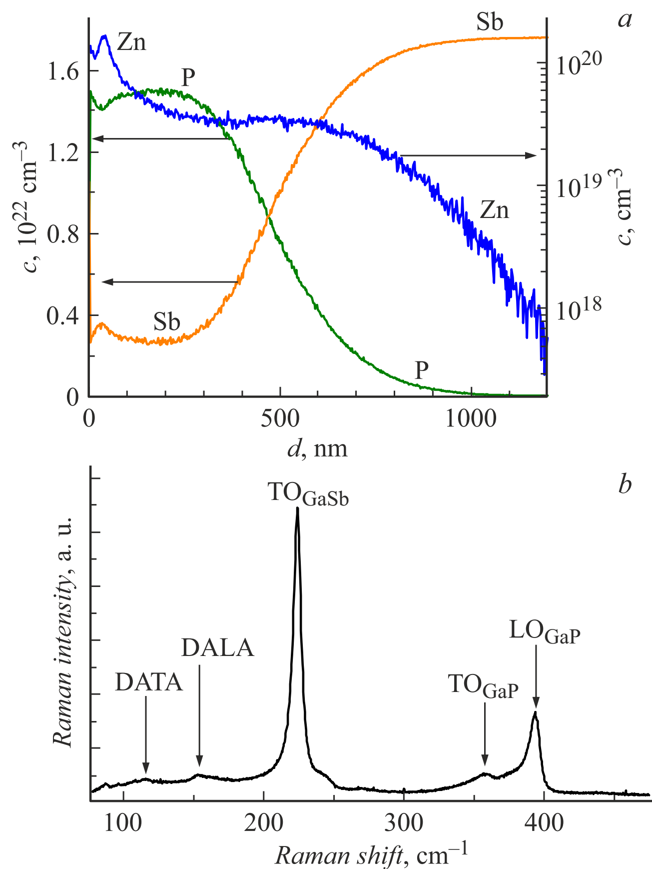

Figure 1. SIMS-measured profile of the volume concentration of components c vs. distance from the surface d (a), and the Raman scattering spectrum (b) for GaSb semiconductor wafers treated in phosphorus and zinc vapors.

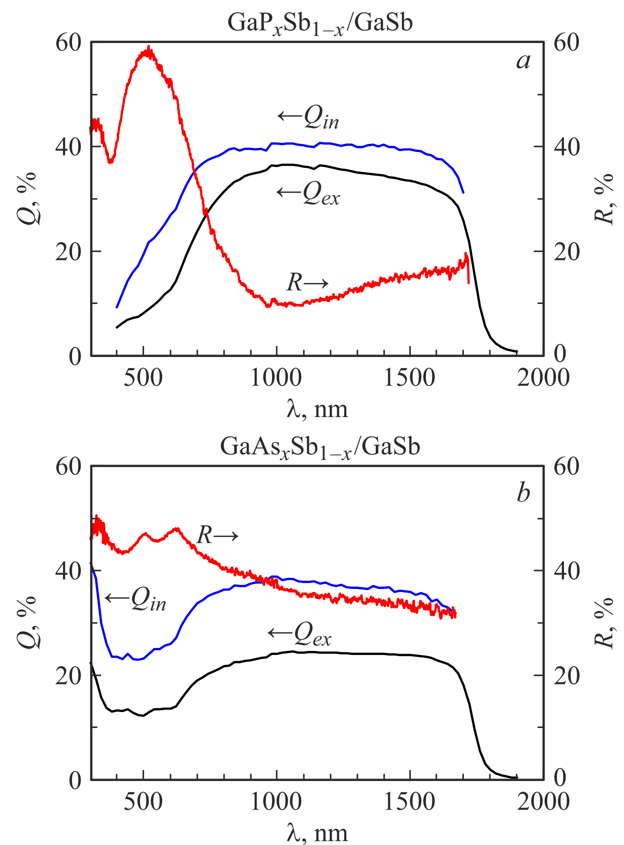

Figure 2. Quantum efficiency Q and the reflection coefficient R vs. the wavelength λ for structures obtained by processing GaSb wafers in Zn and P (a) and Zn and As (b).

dependence of the internal quantum efficiency Q_{in} on the wavelength λ was calculated based on the measurement data of the reflectance R and the external quantum efficiency Q_{ex}. The maximum $Q_{in} \sim 40\%$ was observed at wavelengths $\lambda = 800-1600$ nm in the $GaP_xSb_{1-x}/GaSb$ sample, obtained at 570°C (Fig. 2, *a*), and for the $GaAs_xSb_{1-x}/GaSb$ sample, obtained at 584°C (Fig. 2, *b*). These results are comparable with the results for GaSb-based PVCs obtained by two-stage zinc diffusion [2].

The results of this paper suggest that with further optimization of technologies of solid-phase substitution reactions, the proposed method will become one of the directions for improving the characteristics of GaSb-based PVCs.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] M. Razeghi, *MOCVD challenge. Survey of GaInAsP−InP & GaInAsP−GaAs for photonic and electronic device applications*, 2nd ed. (Taylor and Francis/CRC Press, 2010), p. 773. DOI: 10.1201/9781439807002
[2] V.P. Khvostikov, S.V. Sorokina, O.A. Khvostikova, M.V. Nakhimovich, M.Z. Shvarts, Semiconductors, **55**, 840 (2021). DOI: 10.1134/S1063782621100134.
[3] V.I. Vasil'ev, G.S. Gagis, V.I. Kuchinskii, V.G. Danil'chenko, Semiconductors, **49**, 962 (2015). DOI: 10.1134/S1063782615070234.
[4] D.W. Green, R.H. Perry, *Perry's chemical engineer's handbook. Section 2. Physical and chemical data*, 8th ed. (The McGraw−Hill Companies, Inc., N.Y., 2008).
[5] A. Smits, S.C. Bokhorst, Z. Phys. Chem., **91U** (1), 249 (1916). DOI: 10.1515/zpch-1916-9114
[6] N.D. Roenkov, Neorgan. materialy **11**, (6), 985 (1975) (in Russian).
[7] R.N. Hall, J. Electrochem. Soc., **110** (5), 385 (1963). DOI: 10.1149/1.2425770
[8] H. Borchers, B.G. Maier, Metall., **17** (8), 775 (1963).
[9] A.S. Borshchevsky and M.G. Vysotina, Neorg. materialy, **12** (4), 615 (1976). (in Russian)
[10] O. Pagés, J. Souhabi, A.V. Postnikov, A. Chafi, Phys. Rev. B, **80** (3), 035204 (2009). DOI: 10.1103/PhysRevB.80.035204
[11] V.M. Andreev, A.A. Vodnev, V.R. Larionov, T.P. Prutskikh, V.D. Rumyantsev, K.Ya. Rasulov, V.P. Khvostikov, FTP, **23** (4), 597 (1989). (in Russian)