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Solid-phase substitution processes with phosphorus in InAs and InSb

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The processes of solid-phase substitution of atoms of the fifth group for phosphorus atoms in InAs semiconductor wafers at temperatures of 580–590°C and in InSb at 440–460°C using solutions of the Sn–ZnGeP₂ and Sn–CdGeP₂ melts as vapor sources have been studied. The formation of InP_xSb_{1-x} solid solution in InSb was confirmed by the Raman light scattering method.

Keywords: solid-phase substitution reactions, *p*–*n*-junction, doping, narrow-bandgap semiconductors.

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To create *p*–*n*-junctions in GaAs and GaSb in fabricating device structures, the method of zinc diffusion into an *n*-type substrate is at present widely used [1]. To perform this operation, arsenic and phosphorous vapors are often fed jointly with zinc vapors in order to compensate the loss of group V elements on the surface of an A^{III}B^V semiconductor wafer. For instance, the surface quality may be improved by passivating it with In and P atoms [2,3] or by treating only with P atoms [4], which can affect the process of further diffusion of zinc.

Previously we have conducted studies in which we succeeded in forming a near-surface layer of isovalent-substitution solid solution by feeding group V elements other than constituents of the GaAs or GaSb wafers [5,6]. As the sources of vapors of group V elements, melt solutions of zinc-containing ternary compounds in stannum were used: ZnSnP₂, ZnSnAs₂. As a result, diffusion of Zn and embedding of group V elements into the GaAs or GaSb wafers occurred simultaneously. Zinc penetrated into the GaSb wafer to the depth of up to 1000 nm, while the phosphorous penetration depth was 400–600 nm, so zinc diffused deeper than the group V element; therewith, as per our estimation based on the data from secondary-ion mass spectrometry (SIMS) and Raman light scattering spectroscopy, the near-surface phosphorous content in the GaP_xSb_{1-x} solid solution was $x = 0.7–0.8$ [6]. The method described in [5,6] seems to be practically applicable in creating structures comprising a wide-bandgap window and underlying *p*–*n*-junction, which are intended for photovoltaic converters. In this case, the role of the wide-bandgap window is played by the near-surface layer of the isovalent-substitution solid solution. A similar structure may be created in materials with narrower bandgaps, based on which IR devices can be fabricated.

In this work we studied the processes of substitution of group V atoms for phosphorous atoms in wafers

of intentionally undoped InSb(001) and of InAs(001):Sn. According to the calculations performed for 300 K based on the models described in [7], the InP_xAs_{1-x} solid solutions able to be formed in InAs have a wider bandgap E_g than that of InAs in the entire range of x , which is favorable for forming layers with wide-bandgap windows in the course of producing photoreceivers. As for the InP_xSb_{1-x} solid solutions, their dependence $E_g(x)$ has a local maximum in the range $x = 0.12–0.25$ eV; where $E_g = 0.10–0.11$ eV which is lower than in the original InSb semiconductor wafer ($E_g = 0.18$ eV).

To perform solid-state substitution, there were used methods and approaches we have described in detail in [5,6]. The substitution was performed during time $\tau = 15–60$ min. The operations were conducted at temperatures $t = 440–460^\circ\text{C}$ for InSb and $t = 580–590^\circ\text{C}$ for InAs. As the sources of phosphorous vapors, melt solutions Sn–ZnGeP₂, Sn–CdGeP₂ were used. The phosphorous vapor pressure above the melt solutions was estimated as in [5,6]; however, we regarded this method as insufficiently precise and, therefore, decided to estimate the vapor pressure based on experimental data [8] assuming that the vapor pressure above pure CdGeP₂ is created mainly by phosphorous vapors, while that above melt solution Sn–CdGeP₂ is proportional to the mole fraction of dissolved ternary compound CdGeP₂. To carry out simultaneous diffusion of zinc and phosphorous into InAs, melt solutions Sn–ZnGeP₂ in which atomic fraction of dissolved phosphorous was $x_P^I \approx 0.02$ were used as vapor sources; the phosphorous pressure estimate at $t = 590^\circ\text{C}$ was 10 Pa.

Fig. 1, *a* presents the SIMS data for the sample obtained by treating the InAs wafer at $t = 590^\circ\text{C}$ for $\tau = 15$ min. Under these conditions, zinc penetrates about 600 nm into the wafer while phosphorous diffuses not deeper than

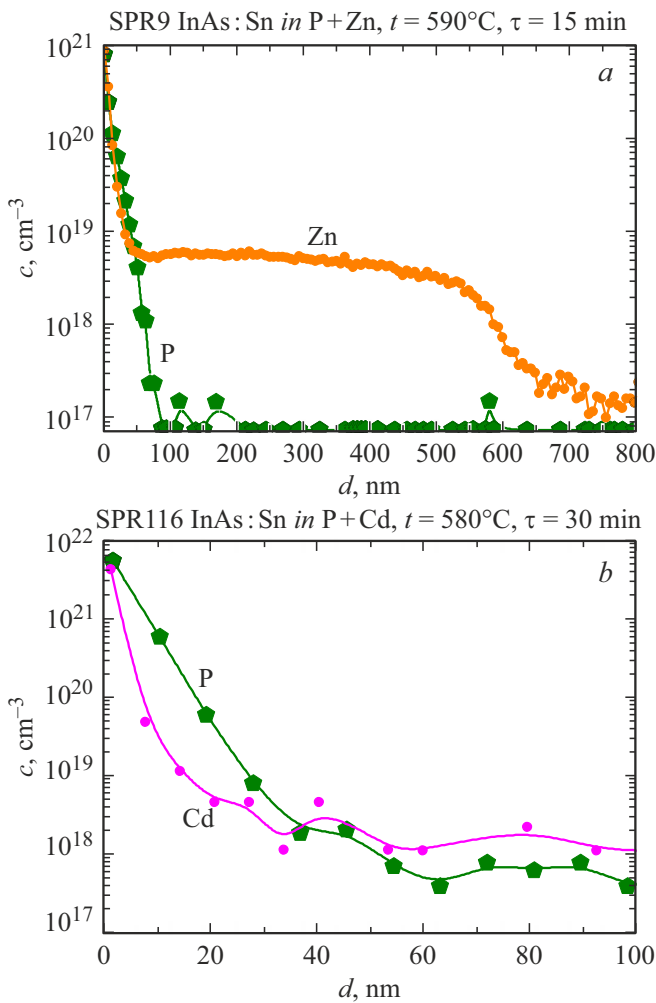


Figure 1. SIMS profile of the component concentrations c distribution along the layer depth d for InAs:Sn-based samples treated with vapors of melt solutions Sn–ZnGeP₂ (a) and Sn–CdGeP₂ (b).

100 nm. The zinc content remains close to 10^{19} cm^{-3} over almost the entire phosphorus penetration distance but is much higher in the near-surface regions, which negatively affects the devices performances [9].

In the case of such a distribution along the sample thickness, removal of the surface layer with excess zinc content inevitably results in removing the entire phosphorous-containing region. To make phosphorous penetrate to a larger depth and, at the same time, to prevent excess diffusion of zinc, it is reasonable to perform the phosphorous and zinc diffusions independently of each other in two separate manufacturing processes.

To ensure the phosphorous diffusion into InAs and InSb free of concurrent diffusion of zinc, melt solutions Sn–CdGeP₂ were used as vapor sources, where the phosphorous atomic fraction was $x_P^I = 0.07–0.08$, while the phosphorous vapor pressure estimate was $P_P = 15–25 \text{ Pa}$ at $t = 440–460^\circ\text{C}$ (for InSb) and $P_P = 50–180 \text{ Pa}$ at

$t = 580–590^\circ\text{C}$ (for InAs). Our investigation has shown that it is possible to fit conditions under which Cd penetrates into InAs to a shallower depth and in lower amounts than phosphorous (Fig. 1, b).

Fig. 2, a demonstrates a SIMS profile for sample SPR140 formed based on undoped InSb treated in phosphorous and cadmium vapors obtained from melt solution Sn–CdGeP₂. According to our estimates obtained from SIMS data, the phosphorous content in InP _{x} Sb_{1– x} near the surface of the created layer is $x = 0.15$ which corresponds to $E_g = 0.1 \text{ eV}$.

Fig. 2, b presents the sample SPR140 Raman spectrum measured in the backscattering geometry in the $z(xy)z$ polarization. The Raman spectrum exhibits a frequency shift of the In–Sb mode of the InSb-like type by ~ 0.5 and 1.5 cm^{-1} from its value in the bulk InSb for the transverse (TO) and longitudinal (LO) modes, respectively. Moreover, notice the appearance of new peaks related with acoustic modes DATA and DALA (their appearance is typical of solid solutions [10]) and peaks at frequencies 300 and 337 cm^{-1} which may be identified as In–P modes of the InP-like type in solid solution. These modes also exhibit a

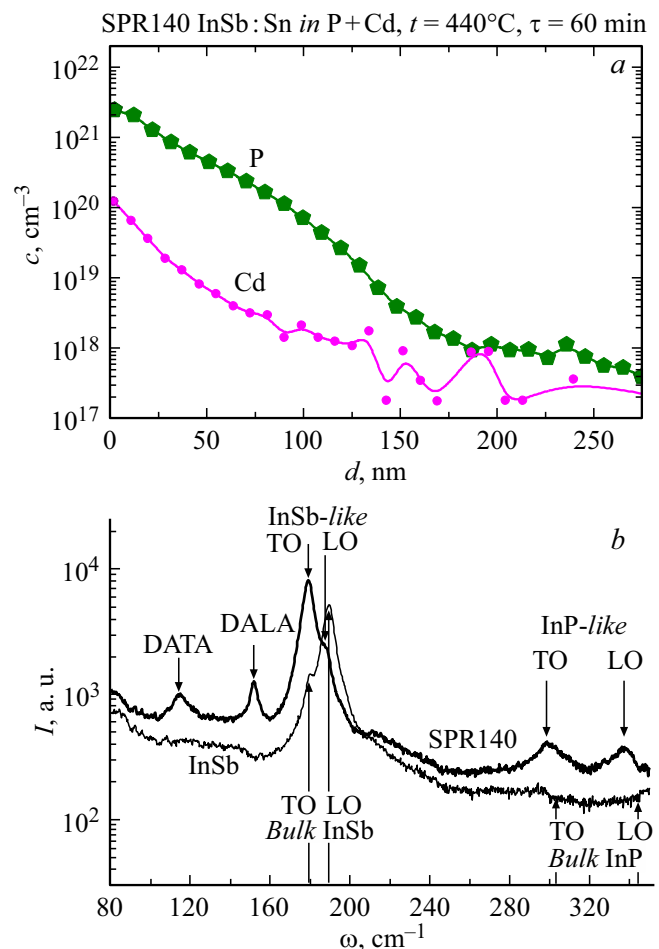


Figure 2. Investigation results for sample SPR140 prepared by treating InSb in P and Cd vapors. SIMS distribution profile of component concentrations c along depth d ; b — Raman spectrum for sample SPR140 and untreated InSb.

frequency shift by $\sim 4 \text{ cm}^{-1}$ (TO) and 6.5 cm^{-1} (LO) from the respective values in bulk InP. Thus, the Raman spectra evidence for formation of the $\text{InP}_x\text{Sb}_{1-x}$ solid solution. One can notice the intensity redistribution in the solid solution spectrum. The spectrum presented in Fig. 2, *b* shows that the band with maximal intensity is 178.9 cm^{-1} which is also broader than the respective one in bulk InSb. Taking into account that, as per the selection rules, the scattering spectrum is contributed by only LO optical modes, it can be said that mode 178.9 cm^{-1} is a screened longitudinal oscillation, which may be a sign of a high concentration of free charge carriers in the layer.

The performed studies of solid-phase reactions of substituting group V atoms with P atoms in InAs and InSb showed that, under the same process conditions, phosphorous better embeds into InSb and penetrates to larger depths. Earlier we have observed a similar situation in studying the phosphorous embedment into GaAs and GaSb [5]: under the chosen conditions, phosphorous penetrated into GaSb in significant amounts and to a larger depth than into GaAs. The data obtained allow one to expect that it is possible to extend the operating wavelength range of optoelectronic devices to $10\text{--}12 \mu\text{m}$ by creating the $\text{InP}_x\text{Sb}_{1-x}$ solid solution.

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Conflict of interests

The authors declare that they have no conflict of interests.

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