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# Phase separation effects in AlGaAsSb/GaSb alloys

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Layers of $Al_xGa_{1-x}As_ySb_{1-y}$ solid solutions on GaSb substrates were obtained by the MOVPE method. Three series of samples with an Al content of $x = 0.2$, 0.27 and 0.45 and different $y$ content providing both positive and negative lattice matching with the substrate were studied. Analysis of Raman scattering spectra showed the presence of phase separation effects for both Group V (Sb−As) and Group III elements a tendency towards preferential binding of As and Al atoms was detected.

**Keywords:** MOVPE, Raman scattering, AlGaAsSb, phase separation.

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The development of modern devices, such as thermophotovoltaic converters or certain types of avalanche photodiodes and lasers, occasionally requires the use of materials of the GaSb family [1–6]. This entails the need to model the band structure of a device and use materials with different band gap widths. The group of AlGaSb solid solutions serve as wide-band materials in the GaSb system. Unlike the GaAs−AlAs compounds with a maximum lattice parameter mismatch $\Delta a/a$ of $\sim 0.14\%$, the GaSb−AlSb pair has a mismatch of 0.72%, which may affect significantly the quality of layers due to the emergence of mismatch dislocations. The use of arsenic (i.e., the production of four-component solid solutions) appears to be the optimum way to compensate for strain and reduce the lattice parameter. However, although four components allow one to achieve ideal lattice matching, the application of such solid solutions is limited. Researchers are often forced to use digital and even positionally random solid solutions (primarily in the growth of compositions from the immiscibility region) [3–5]. In the present study, we report the results of examination of $Al_xGa_{1-x}As_ySb_{1-y}$ solid solutions (with a composition range providing a band gap of 0.72−1.4 eV; in what follows, these solutions are referred to as AlGaAsSb) via Raman spectroscopy and X-ray diffraction. Layers with both negative (the lattice parameter of the layer is smaller than that of the substrate) and positive (the contrary case) mismatch were investigated.

AlGaAsSb solid solutions were grown by metalorganic vapor-phase epitaxy (MOVPE) on GaSb (100) substrates at a temperature of 600°C and a reactor pressure of 100 mbar. The total $H_2$ flow through the reactor was 5.5 l/min. Arsine ($AsH_3$), trimethylantimony (TMSb), triethylgallium (TEGa), and trimethylaluminum (TMAl) were used as sources of arsenic, antimony, gallium, and aluminum, respectively. The main reason for using TMSb instead of stibine ($SbH_3$) is the poor stability of the latter, which decomposes over time during storage.

The ratio of molar flows of sources of group V and III elements in the gas phase in the process of growth of AlGaAsSb solid solutions was set to 2, and the fraction of flows of Al and As sources in the flows of groups III and V varied within the range of 0.1−0.9 (Al) and 0−0.02 (As).

The dependence of growth rate on the TMAl concentration in the gas phase (the V/III ratio was maintained at 2 by adjusting the TEGa flows, and the $AsH_3/(AsH_3+TMSb) = 0.016$ ratio was maintained constant) revealed that an increase in the molar fraction of TMAl led to a growth rate reduction, while the As concentration in the solid phase increased. The thickness of layers was no lower than 0.7−1.2 $\mu$m.

Figure 1, $a$ (curves *4*, *4'*) presents the Raman spectra of the $Al_{0.28}Ga_{0.72}As_{0.078}Sb_{0.922}$ sample. These spectra were measured at room temperature in the backscattering geometry from growth plane (001) in polarization $z(xy)z$ ($x \parallel [100], y \parallel [010]$) (curve *4*) and from a cleavage face — plane (110) — in polarization $z(x'x')z$ ($x' \parallel [001]$) (curve 4') with a spatial resolution no worse than 1.5 $\mu$m (a lens magnification of 80×). A single-frequency laser with an emission band at 532 nm was used for excitation. According to the selection rules, the scattering spectra should contain longitudinal modes in the former case and transverse modes in the latter case. The scattering spectrum features GaSb-type modes with frequencies of 222 and 227 $cm^{-1}$, which are denoted with subscript 1. Vibrations associated with Al atoms are visible in the 300−340 $cm^{-1}$ region. Two bands are seen clearly in this region. The splitting of the $LO_2$ band (emergence of an additional band denoted with subscript $2c$) was observed for all compositions studied here and for ternary AlGaSb solid solutions [7,8].

At first glance, it may seem that such behavior is caused by a violation of selection rules and the contribution of transverse modes to scattering; however, on the one hand, the preservation of selection rules for the GaSb mode and a significant (more than 1:10) polarization of the scattering signal are evident and, on the other hand, deconvolution

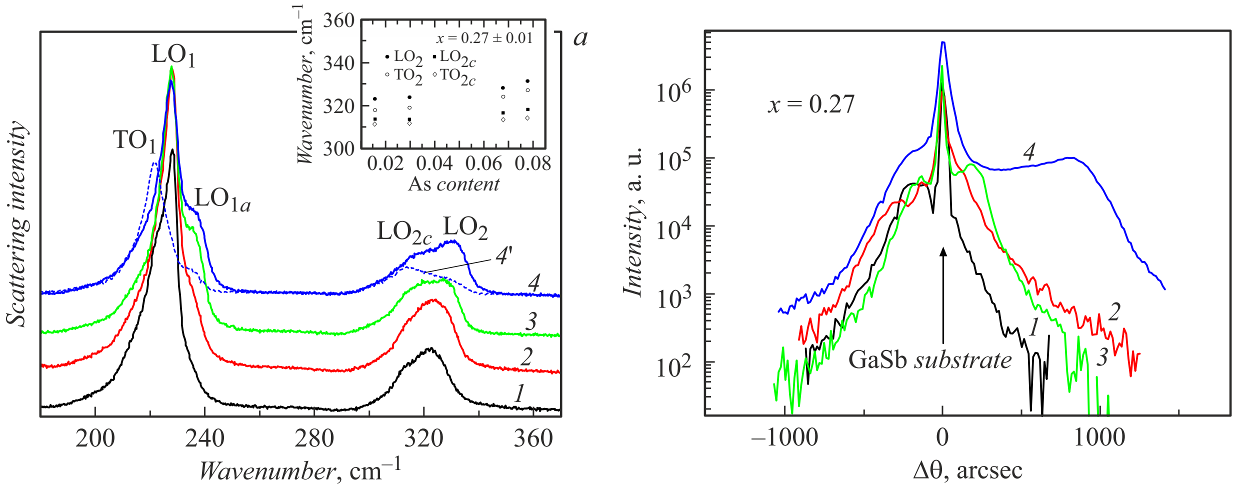

**Figure 1.** Raman spectra (*a*) and diffraction rocking curves (*b*) for a series of $Al_xGa_{1-x}As_ySb_{1-y}$ samples with $x = 0.27 \pm 0.01$, $y = 0.007$ (*1*), 0.03 (*2*), 0.068 (*3*), and 0.078 (*4*, *4'*). The inset shows the dispersion of phonon modes within the range of vibration frequencies of Al−Sb(As).

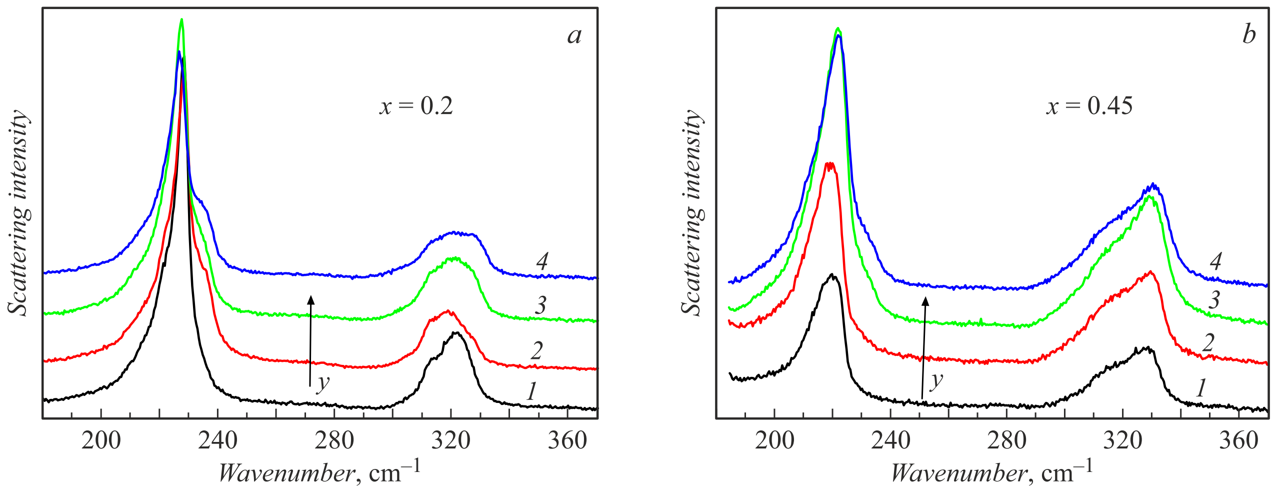

**Figure 2.** Raman spectra of $Al_xGa_{1-x}As_ySb_{1-y}$ layers with $x = 0.2$, $y = 0.008$ (*1*), 0.024 (*2*), 0.036 (*3*), 0.066 (*4*) (*a*) and $x = 0.45$, $y = 0.017$ (*1*), 0.048 (2), 0.083 (*3*), 0.118 (*4*) (*b*).

of the spectra by Lorentz functions reveals the presence of two longitudinal and two transverse vibrations in the indicated range (with the frequency of transverse vibrations always being lower than the frequency of longitudinal ones; see the inset in Fig. 1). Since the two-mode behavior is characteristic of both quaternary (AlGaAsSb) and ternary (AlGaSb) solid solutions, it may be assumed that the lower-frequency vibration is a localized longitudinal LO$_{2c}$-type vibration of AlSb.

The following changes induced by an increase in concentration of As in the solid solution may be noted (Fig. 1, *a*). An additional mode with a frequency of 234−238 cm$^{-1}$ (LO$_{1a}$ mode), which may be attributed to GaAs-type vibrations [9–11], emerges on the high-frequency slope of mode LO$_1$. The position of the dominant LO$_1$ mode remains unchanged. Slight shifts of the position of the maximum correlate with changes in the Al content in the solid solution ($x = 0.27 \pm 0.01$). A noticeable shift in vibration frequency of the LO$_2$ mode is observed in the region of frequencies of Al−Sb vibrations. The vibration frequency of the LO$_{2c}$ mode also increases, but within a significantly smaller range.

Thus, it is fair to assume that phase separation, which entails segregation of group V atoms (Sb and As), is observed in AlGaAsSb solid solutions. Just as in GaAsSb and GaInAsSb solid solutions (in the region of compositions close to GaSb), two phases are formed: one depleted in As atoms and one enriched with them. These phases may be designated as AlGaSb and AlGaAs (it is assumed here that both solid solution phases contain all four components, but tend to separate toward the indicated ternary compounds; in what follows, these are referred to as phases I and II).

The main phase (phase I) remains close to the AlGaSb ternary compound, which may explain the weak dispersion of the $LO_1$ mode. The formation of two phases is also seen in X-ray diffraction (Fig. 1, *b*). X-ray diffraction studies were performed using a DRON-2 setup (Ge (001) monochromator; $CuK_{\alpha 1}$; $\lambda = 0.154$ nm; 1 $\mu$m slits) in symmetric geometry. The figure presents the diffraction rocking curves for a series of samples with Al content $x = 0.27$. The presence of two phases in the solid solution is evident even at the minimum As concentration. As the As concentration increases, the lattice parameter of phase II decreases, while the lattice parameter of phase I remains virtually unchanged.

A similar behavior was observed for the other studied compositions with Al content $x = 0.2$ and 0.45 and As content $y = 0.007-0.067$ and $0.017-0.118$, respectively. Figure 2 shows a series of Raman spectra for the indicated solid solutions. It can be seen that the trends reported for $x = 0.27$ persist regardless of the Al content.

The behavior of bands evidently associated with As atoms warrants attention as well. The dispersion of band $LO_2$ is 2.5 times greater than the dispersion of the $LO_{1a}$ band. Such behavior is anomalous. This ratio in ternary solid solutions is 1.16 for AlGaAs and 0.94 for AlGaSb; i.e., the significant difference in dispersion of two phonon modes is inconsistent with the expected behavior. The same is true of the relative increase in intensity. This becomes clearly evident in the series of spectra of solid solutions shown in Fig. 2, *b*, which are characterized by the most profound compositional variation in the amount of Al in the solid phase: almost the entire increase in intensity is observed in the $LO_2$ band. This provides evidence in favor of the hypothesis that phase separation is found not only among group V elements, but also among the elements of group III with predominant formation of Al−As bonds: the higher the concentration of Al atoms in the growth zone (solid solution composition) is, the more likely is the binding of arsenic atoms with Al atoms. A probable explanation for this effect may be the difference in bond formation energies (of which the energy for Al−As is the highest). Together with the effect of local phase separation in group V, this leads to the emergence of a phase enriched in both arsenic and aluminum atoms.

Thus, the MOVPE growth of quaternary $Al_xGa_{1-x}As_ySb_{1-y}$ ($x = 0.2, 0.27, 0.45; y = 0.007-0.118$) solid solutions was studied. The high sensitivity of Raman spectroscopy in detection of phase separation in quaternary AlGaAsSb solid solutions was demonstrated. It was revealed that these solid solutions tend to phase separation with segregation of components towards Al(Ga)As and AlGaSb during growth under the specified conditions.

## Conflict of interest

The authors declare that they have no conflict of interest.

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