Formation of $A^3B^5$ ternary solid solutions on GaSb plates by solid-state substitution reactions

V I Vasil'ev$^{1,2}$, G S Gagis$^1$, K K Soboleva$^3$, V I Kuchinskii$^{1,2}$

$^1$ Ioffe Physical-Technical Institute of the Russian Academy of Sciences, St Petersburg, Russia
$^2$ St Petersburg Electrotechnical University "LETI", St Petersburg, Russia
$^3$ St Petersburg State Polytechnical University, St Petersburg, Russia

E-mail: giman@mail.ioffe.ru

Abstract. A method of ultra-thin GaAsSb and GaPSb solid solutions layers formation by supplying vapors of As or P to heated GaSb crystal plates is proposed.

1. Introduction

The paper [1] described that conversion efficiency of solar radiation into electricity in tandem solar cells composed of mechanical-joined upper photovoltaic converter (PC) based on GaAs and lower PC on the basis of GaSb is much higher than that in solar cells including only single GaAs-based PC. In this case, the presence of wide-bandgap optical window (WOW) on surface of each of PC element plays essential role [2]. WOW is the ultra-thin layer of solid solution isomorphous with the device structure and having wider bandgap comparing to the underlying layers. The nowadays layers of $A^3B^5$ solid solutions are obtained by epitaxial methods: liquid phase epitaxy, metal-organic chemical vapor deposition and molecular beam epitaxy. As this takes place, the crystal lattice of solid solution layer is completely made of components arriving at the crystal surface. Previously we have shown [3] that GaAsP ternary solid solution on the heated GaAs surface can be formed by solid-state substitution at which the solid solution forms in near-surface layer of GaAs plate at the expense of partial replacement of arsenic atoms by phosphorous atoms delivered to a crystal surface as vapors, at that this solid solution plays the role of WOW. The work describes the results of the processes of solid-state substitution in GaSb plates to obtain GaAsSb and GaPSb WOW on GaSb surfaces. In addition the possibility of simultaneous formation of WOW for GaSb and zinc diffusion implementing for p-n-junction creation in a single technological process has been considered.

2. Experiment

WOW epilayers and p-n-junctions were formed in GaSb:Te(100) plates. Thicknesses and compositions of obtained wide-bandgap layers are determined by three factors: a temperature, a duration of process and partial pressures of vapors of delivered elements. Processes were carried out at temperatures 520 - 580 °C. This temperature range is favorable for elements diffusion into crystal structure and subsequent solid-state substitution reactions. Phosphorous and arsenic vapor sources were unsaturated solutions-melts of ZnSnAs$_2$ and ZnSnP$_2$ in tin. The same solutions-melts were zinc vapors sources. Components concentration of the fifth group in the used solutions-melts were 0.01 - 0.05 atomic fractions. In doing so, concentrations of zinc were two times lower - 0.005 - 0.025 atomic fractions. The pressure values of the elements of the fifth group were estimated using data of saturated vapor pressures of arsenic and phosphorous at the temperatures of carrying out the process and taking...
into account the activity of these components in solutions-melts. Estimated values of pressures amounted up to 10^3 Pa for phosphorous and up to 10 Pa for arsenic. Solutions-melts and GaSb plates were in the closed graphite cassette. Processes were carried out in a bowed hydrogen quartz reactor to prevent material oxidation. Durations of processes were from 5 to 30 minutes.

Properties of the obtained samples were investigated using secondary ion mass-spectrometry (SIMS) method and photoluminescence (PL) measurements.

3. Results and discussion

Surfaces of obtained layers had mirror-smooth morphology, which indicated the absence of clusters and erosion processes.

Figure 1 shows the variation of arsenic concentration in crystal depth for the sample obtained by GaSb processing at 580 °C in arsenic vapors emitted from solution-melt containing 0.01 atomic fractions of arsenic. The shape of the curve indicates the absence of differed composition phases that is the evidence of formation of solid solution with continuous variation of composition from the surface into the depth of the sample.

Concentration of arsenic on this sample surface amounted 0.02 atomic fractions (3.5·10²⁰ cm⁻³), and its decrease deep into crystal had exponential shape, with reduction up to 10¹⁸ cm⁻³ occurring at 18 nm depth. As it can be seen in figure 1, zinc diffusion takes place much deeper than diffusion of arsenic, which provides p-n-junction formation outside the solid solution layer placed close to the surface.

According to calculations done using the paper [4] data, the bandgap value of GaAsₓSb₁₋ₓ solid solution becomes greater than the bandgap value of GaSb at x > 0.52 and for bandgap value of GaPₓSb₁₋ₓ solid solution the same increase occurs at x > 0.23.

As evident from our investigations, the proposed method allows to obtain high concentrations of introduced components at increasing processing time and vapor pressures. Figure 2 gives the results of SIMS measurements for the sample obtained at processing GaSb at 580 °C in phosphorous vapors emitted from solution-melt containing about 0.04 atomic fractions of phosphorous, the process duration was 30 minutes. GaPₓSb₁₋ₓ solid solution formed at the depth up to 1200 nm, phosphorous concentration on the surface reaching x = 0.8 and smoothly decreasing deep into crystal from the surface.
These GaP$_x$Sb$_{1-x}$ solid solutions with compositions $x = 0.2 – 0.8$ seemingly cannot exist because of extensive miscibility gap. Nevertheless, in the articles [5, 6] the possibility of obtaining negative lattice-mismatched (about $10^{-3}$) solid solution layers up to 50 nm thickness with compositions inside miscibility gap was demonstrated. The elastic deformation arising from the negative lattice mismatching stabilizes crystal lattice and prevents phase decomposition. It is GaAs$_x$Sb$_{1-x}$ and GaP$_x$Sb$_{1-x}$ solid solutions that have negative value of lattice-mismatching to GaSb, and in the cases when their thickness does not exceed 50 nm the defectless solid solution layer formation can be suggested. Figure 2 demonstrates that there are the signs of phase decomposition in the region closed to the surface (below 40 nm). The phase decomposition on larger depths is hampered due to stabilizing influence of crystal lattice and presence of elastic deformation.

Crystal defects are known to decrease essentially PL intensity, whereas a layer formed without any defect can either demonstrate its own PL or play WOW role that results in significant increase of PL intensity of the underlying layer. WOW is transparent for underlying layer radiation and at the same time is a barrier which prevents carriers migration on the surface where probability of their nonradiative recombination is great [2].

Previously we demonstrated the possibility of WOW obtaining on GaAs plates by supplying phosphorous vapors to their surfaces [3], therewith in the increase of PL intensity up to 25 times compared with PL intensity of unprocessed control GaAs plates was achieved. The given work demonstrates that PL intensity increase due to WOW effect was achieved as great as 5 times for GaSb processed in arsenic vapors. The same value was obtained for GaSb samples processed in phosphorous vapors. In this case one should take into account that PL-intensity decreases due to zinc doping process. The effect of increase of PL intensity without any change of spectrum shape in combination with SIMS data attest that the elements of the fifth group supplied to GaSb plate surface are embedded into crystal lattice instead of Sb atoms. In cases when the thicknesses of solid solutions layers and concentrations of embedded components are such that defectless conjunction with primary crystal
becomes impossible, PL intensity increase due to WOW effect is either less intensive or entirely does not occur.

4. Conclusion
The experiments demonstrated that owing to solid-state substitution reactions it is possible to form GaAsSb or GaPSb solid solutions in the near-surface region of GaSb crystals which are continuous with primary crystal and play WOW role. Therewithin, in spite of the high zinc doping level of the structure, the effect of PL intensity increase due to WOW formation was observed.

References

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