Effect of growth conditions at MOCVD on thickness uniformity of GaInAsP epilayers obtained on InP

A E Marichev, R V Levin, B V Pushnyii, G S Gagis, V I Vasil'ev, M P Scheglov, D Yu Kazantsev, B Ya Ber, T B Popova, E P Marukhina

Ioffe Institute, St. Petersburg, Polytehnicheskaya 26, 194021, Russia

E-mail: segregate1@yandex.ru

Abstract. Ga$_{1-x}$In$_x$As$_y$P$_{1-y}$ epitaxial layers with compositions $x = 0.77 – 0.87$, $y = 0.07 – 0.42$ and thicknesses 620 – 850 nm were grown by MOCVD method on InP substrates. Temperature, pressure and gas mixture composition were held constant during growth procedure. Secondary-ion mass spectrometry showed change of V-group elements composition $y$ through epilayers thicknesses by value $\Delta y$ up to 0.08. Reducing $\Delta y$ value down to 0.01 – 0.02 was achieved by optimizing the composition of gas mixture to reduce lattice mismatch between the layer and the substrate. The obtained data allow us to conclude that the deformations arising due to lattice mismatch between the forming layer and the growth surface result in varying the content of V-group elements through epilayer thickness.

1. Introduction

At present, there is growing interest in wireless power transmission systems including a laser and a photovoltaic converter (PVC). Solid-state YAG:Nb-laser is interesting because of its high power (up to 10 kW) and relatively compact size [1]. Operating wavelength of such laser is of 1064 nm (photon energy is of 1.165 eV). Ga$_{1-x}$In$_x$As$_y$P$_{1-y}$ solid solutions lattice-matched to InP and having bandgap values $E_g = 1.05 – 1.15$ eV are seen as suitable materials for the PVC of this radiation. Figure 1 shows the properties of Ga$_{1-x}$In$_x$As$_y$P$_{1-y}$ solid solutions calculated using parameters from [2] and expressions from [3]. It can be seen in figure 1 that the required bandgap value and lattice-matching to InP correspond to Ga$_{1-x}$In$_x$As$_y$P$_{1-y}$ compositions $x = 0.79 – 0.84$, $y = 0.3 – 0.47$. Ga$_{1-x}$In$_x$As$_y$P$_{1-y}$ solid solutions lattice-matched to InP are mainly used for waveguide or barrier layers for lasers with working wavelengths 1.3 [4] μm and 1.55 μm [5]. The quality of solid solution for active layers for PVC and photodetectors has higher requirements than those for waveguide or barrier layers of radiation sources. For efficient conversion of radiation, the active regions of PVC must be of sufficient thickness (from 500 nm and thicker). The distribution of components on the epilayer thickness should be uniform to achieve a high degree of crystalline perfection of the thick epitaxial layer. However, the non-uniformity of V-group elements content through the thicknesses of InAsPb epilayers obtained on InAs by metal-organic chemical vapor deposition (MOCVD) was observed in [6] by secondary ion mass spectrometry (SIMS), though gas flows remained constant during epilayer deposition. The non-uniformity in [6] was greater for greater lattice-mismatch between the epilayer and the substrate and was explained by elastic strains influence on V-group components incorporation. The elastic strains appear when epilayer of a slightly different equilibrium value of lattice constant is grown coherently on a single-crystal substrate [7]. Here, the equilibrium value of the lattice constant, also known as the
relaxed lattice constant value, is the value that the epitaxial layer could have if it could be separated from the substrate, which deforms epilayer crystal lattice. The fact that elastic strains can affect embedding of V-group elements was reported in [8] for GaAsP solid solutions grown on GaAs.

As regards GaInAsP lattice-matched to InP, there are well-researched methods of its growing by MOCVD at reduced pressure in the range of compositions \( y > 0.46 \) [9], but the study of the homogeneity of the content of the matrix elements (Ga, In, As, P) through epilayer thickness was almost no attention paid. However, for compositions \( y < 0.44 \), which are compositions of interest for PVC, an area-nonhomogeneity in the V-group elements content was observed [10], so, it is reasonable to expect the same heterogeneity through the thickness. In present work, we obtained data indicating such thickness heterogeneity of V-group elements distribution.

2. Experiment

The epitaxial growth was carried out on an AIX200 setup by AIXTRON at temperature of 600°C and low pressure of 0.1 atm. The hydrogen with dew point lower than -100°C was used as carrier gas, total flow of hydrogen through reactor was of 5 L/min. Structures were grown on InP(100):Sn substrates misoriented on 4° and with doping level \( n = (1-3) \cdot 10^{18} \text{ cm}^{-3} \). Triethylgallium TEGa and trimethylindium TMIn kept at temperature of 17°C were precursors of III-group elements, arsine AsH₃ and phosphine PH₃ were precursors of V-group elements. In epitaxial process InP buffer layers were formed before GaInAsP layers deposition, the molar flows of the precursors during InP buffer layer growth were \( X_{\text{AsH}_3} = 7813 \mu\text{mol/min} \) and \( X_{\text{TMIn}} = 25.64 \mu\text{mol/min} \), the deposition of buffer layers lasted 10 – 20 min. The growth of each Ga₁ₓInₓAsᵧP₁₋ᵧ epilayer lasted 60 minutes, the values of molar flows of precursors during this time were kept constant, nevertheless, SIMS showed change of V-group elements composition \( y \) through epilayers thicknesses, the composition variations \( \Delta y \) were different for different gas mixture compositions. The gas mixture compositions for studied in present work epilayers is listed in table 1.

Measured by the X-ray microanalyser "Camebax" compositions of obtained Ga₁ₓInₓAsᵧP₁₋ᵧ solid solutions were in the range \( x = 0.77 - 0.87, \ y = 0.07 - 0.42 \) (figure 1, table 1), used accelerating potential of 10 kV corresponds to averaging of the composition of GaInAsP at a depth of 500 nm from the layer surface.

The structures of epitaxial layers were studied by X-ray diffractometry method using a 3-crystal high-resolution X-ray spectrometer, where germanium crystals with orientation (001) in the reflex of type (004) of CuKα₁ were used as a monochromator and analyzer. The diffraction curves were recorded in the (020)-scan mode near the peak of InP substrate \( \theta_{\text{InP}} \) (figure 3, table 1).
Table 1. Properties of obtained Ga$_{1-x}$In$_x$As$_y$P$_{1-y}$/InP structures

| No. | Molar flows of precursors, µmol/min | “Camebax” | Data from SIMS | XRD |
|-----|-----------------------------------|-----------|----------------|-----|
|     | $X_{\text{TMIn}}$ | $X_{\text{TEGa}}$ | $X_{\text{AsH}_3}$ | $X_{\text{PH}_3}$ | $x$ | $y$ | Layer thickness, nm | $\Delta y$, $(\Delta a/a)_\perp$, $10^{-3}$ |
| No.1 | 17.63 | 2.043 | 15.63 | 1696 | 0.87 | 0.07 | 620 | 0.01 | $-13 \pm 2$ |
| No.2 | 17.63 | 2.043 | 15.63 | 848  | 0.86 | 0.22 | 740 | 0.06 | $-7 \pm 2$ |
| No.3 | 17.63 | 2.043 | 31.25 | 1696 | 0.86 | 0.42 | 770 | 0.08 | $+4 \pm 2$ |
| No.4 | 17.63 | 2.043 | 17.86 | 1696 | 0.85 | 0.30 | 850 | 0.01 | $-4 \pm 0.7$ |
| No.5 | 13.62 | 3.064 | 31.25 | 1696 | 0.77 | 0.41 | 620 | 0.02 | $-9 \pm 0.6$ |

3. Results and discussion

Unlike studied in [6, 8] InAsPSb and GaAsP solid solutions, Ga$_{1-x}$In$_x$As$_y$P$_{1-y}$ contains two components in III-group sublattice: Ga and In, that gives possibility for III-group elements contain $x$ variation. But according to the SIMS data, for obtained in this work Ga$_{1-x}$In$_x$As$_y$P$_{1-y}$ epilayers, the content of III-group elements $x$ remained constant through the epilayer thickness, while the content of V-group elements $y$ varied by the amount $\Delta y$. For samples No.1 – No.3 changes were monotonous (figure 2a). For samples No.4 and No.5 arsenic content $y$ first gradually increased to the middle of the layer, and again decreased to its surface (figure 2b).

Figure 2. The SIMS-profiles for samples No.3 (a) and No.4 (b).

Some connection was observed between the $\Delta y$ values and the shapes of the x-ray diffraction (XRD) curves. Samples No.4 (figure 3a) and No.5 (figure 3b) with slight composition variation
$\Delta y \leq 0.02$ have a clearly expressed layer peaks of X-ray reflection, that allow analyzing the layer structure according to lattice parameter changing in the [001] direction:

$$(\Delta a/a)_\perp = (a_{\text{GaInAsP}} - a_{\text{InP}})/a_{\text{InP}}$$

where $a_{\text{GaInAsP}}$ and $a_{\text{InP}}$ - lattice constants of GaInAsP epilayer and InP substrate in the [001] direction.

Sample No. 3 with high heterogeneity of V-group elements composition $\Delta y = 0.08$ has a wide blurred profile of the XRD curve (figure 3a) with a number of oscillations in the angle range from $(\Delta a/a)_\perp = 0$ to $(\Delta a/a)_\perp = +6 \cdot 10^{-3}$. According to SIMS data, arsenic content $y$ in Ga$_{1-x}$In$_x$As$_y$P$_{1-y}$ epitaxial layer of sample No.3 (figure 2a) increases from the heterointerface with InP to the surface. Covalent radius of arsenic atom is greater than that of phosphorus atom [11], therefore, the increase in arsenic content $y$ should increase the lattice constant. In this case $(\Delta a/a)_\perp > 0$, therefore, the mismatch between Ga$_{1-x}$In$_x$As$_y$P$_{1-y}$ layer and InP becomes higher. Such a change in the properties of the epitaxial layer through the thickness can be explained by the fact that in the initial stages of growth the influence of the InP on growing GaInAsP layer for the sample No.3 leads to decreasing $| (\Delta a/a)_\perp |$ in comparison with that in the absence of this influence. But as the moving away from the heterointerface with InP, the influence of InP become weaker, and the composition of the gas mixture in this case contributes to the formation of a solid solution with higher values of $| (\Delta a/a)_\perp |$.

**Figure 3.** X-ray diffraction curves for samples No.3, No.4 and No.5.

An even greater broadening of XRD curve profile (see table 1) and lower peak intensity characterizes the structure of the sample No. 1 with relatively small $\Delta y = 0.01$. It can be conditioned by its poor quality.

The photoluminescence (PL) measurements carried out at 77 K in 0.85 – 1.24 µm wavelength range (1.00 – 1.46 eV) allowed us to evaluate the quality of samples. PL of sample No.1, was extremely weak and PL for sample No.5 was virtually absent, what can mean their poor quality. For samples No. 2 - 4 PL was quite intense.

The quality of samples obtained essentially depends on lattice mismatch between epilayer and substrate $(\Delta a/a)_\perp$. It is known that Ga$_{1-x}$In$_x$As$_y$P$_{1-y}$/InP(100) heterostructures grown at temperatures 580 - 650 °C have good quality if their $(\Delta a/a)_\perp$ at room temperatures falls into range from $-4 \cdot 10^{-3}$ to $+2 \cdot 10^{-3}$ [12, 13]. At room temperature this range is shifted to negative values direction because the specific difference in the thermal expansion coefficients of GaInAsP and InP.
Since the lattice mismatch creates elastic strain, and those, in turn, affect the embedding the V-group elements, the gradient of the composition $\Delta y$ should be associated with the value $(\Delta a/a)_{\perp}$: the greater $| (\Delta a/a)_{\perp} |$, the higher the value of $\Delta y$. But for sample No.1 the SIMS method showed the relative uniformity of the composition through Ga$_{1-x}$In$_x$As$_y$P$_{1-y}$ layer thickness despite the high value $| (\Delta a/a)_{\perp} | = 1.3 \cdot 10^{-2}$. Perhaps this is due to the fact that a large number of misfit dislocations appear near the heterointerface in the initial stages of growth resulting in relaxation of elastic deformations, so, the further composition of the epitaxial layer of sample No. 1 is determined only by the gas mixture, thus, the influence of the InP is practically absent. For samples No. 4 and No. 5 the $| (\Delta a/a)_{\perp} |$ value first decreases, then increases according to arsenic content $y$. Changing of $y$ can be caused by elastic deformations in the growing layers.

4. Summary
The data obtained in present work allow us to conclude that the content of chemical elements in the V-group sublattice of the deposited GaInAsP layer is determined not only by the composition of the gas mixture, temperature and pressure, but also by the influence of the growth surface crystalline structure. The growth surface has a certain chemical composition and lattice parameter, that contributes to the formation of the certain chemical bonds, which favors the embedding ones chemical elements and makes it difficult the embedding others. The atoms of V-group are more undergone to this effect due to the fact that they can form volatile molecules (dimers and tetramers) which leave the growth surface. If the chemical elements come from gas mixture exactly in those ratio that is necessary for the formation of the epitaxial layer with the same lattice constant as that of the growth surface, then the layer composition remains constant as deposition occurs. If the composition of the gas mixture does not provide the formation of a layer lattice-matched to a growth surface, the elastic deformations arises and determine the preferable chemical bond length for subsequent monolayers. These bonds lengths may differ from that for the previous layer. As a result, the deposited epitaxial layer has a variable composition through the thickness. In the case of significant differences of lattice constants of the deposited layer and the growth surface, the growing layer elastic deformations vanish due to formation of misfit dislocations near the heterointerface with InP.

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