Synthesis and characterization of GaPN/GaP heterostructures grown on silicon (001)

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Abstract. III-V compound semiconductor heterostructures grown on Si wafers are one of the promising materials in modern optoelectronics. The most promising candidate providing lattice matching with Si is III-phosphide-based alloys diluted with nitrogen. In this work, we study the effect of growth conditions on the structure and optical properties of GaP₁₋ₓNx/GaP/Si planar heterostructures synthesized by plasma assisted molecular beam epitaxy. A series of samples with a maximum impurity nitrogen content as high as 5.05% was synthesized. The morphological, structural and optical properties of heterostructures are studied with scanning electron microscopy and optical spectroscopy. All of the samples demonstrate a broad photoluminescence (PL) response in the red wavelength region at room temperature (RT). The most efficient RT PL is obtained with the samples grown under a high nitrogen gas flow through a nitrogen plasma cell.

1. Introduction

Heterostructures based on dilute nitride alloys of gallium phosphide on silicon are one of the most promising systems for creating light-emitting devices operating in the visible (yellow to red) spectral range and highly efficient multi-junction solar cells [1]. Gallium phosphide has a small lattice mismatch with silicon at 0.37%. However, this is an indirect-gap semiconductor material (band gap ~2.26 eV at 300 K) [2], which limits its use in optoelectronic devices. The incorporation of nitrogen atoms into solid solutions of III group semiconductor phosphides leads to a significant change in the band structure and properties of the starting material, while the observed decrease in the band gap is accompanied by a decrease in the crystal lattice parameter. The incorporation of nitrogen into the GaP₁₋ₓNx solid solution already at x ≥ 0.005 creates strongly localized acceptor-like levels and makes this material quasi-direct bandgap [3].

2. Experiment

Diluted GaP heterostructures were synthesized with the use of a Veeco GEN-III molecular beam epitaxy (MBE) machine equipped with a phosphorus valved cracker and a valved inductively-coupled nitrogen plasma source. The growth technique was reported in detail previously [4]. Elemental fluxes were controlled via measurement of their beam equivalent pressure (BEP). Ga BEP was maintained at 1.2x10⁻⁷ Torr (corresponding to a 0.35 mm/h planar GaP growth rate). According to the previous results [5], a P/Ga BEP ratio of 6 was chosen for all of the growth runs. To control the effective N flux, the plasma emission intensity I (a.u.) was measured, while its mass flow was set with a controller.
and maintained from 0.3 to 1.1 sccm depending on the sample number. The plasma source was maintained at a constant RF input power of 450 W with an automatic impedance matcher.

Structural characterization and calculation of the N content were performed by analysing X-ray diffractometry data (not presented here). The effect of N incorporation on the crystallinity of the GaP$_{1-x}$N$_x$ alloys and their optical properties at RT were studied by Raman micro-spectroscopy (RS) and photoluminescence (PL) spectroscopy with the use of a a Horiba LabRam HR800 micro-Raman spectrometer in backscattering geometry. A schematic representation of the studied heterostructures is presented in figure 1.

Table 1. Calculated N content in the samples with the corresponding growth parameters.

| Sample | N flow, sccm | Intensity of plasma emission, a. u. | N content, % |
|--------|-------------|------------------------------------|-------------|
| #2     | 0.3         | 6.3                                | 2.98        |
| #3     | 0.5         | 7.3                                | 3.08        |
| #4     | 0.8         | 7.5                                | 3.04        |
| #5     | 0.8*        | 7.2*                               | 5.05        |
| #6     | 1.1         | 7.3                                | 3.07        |
| #7     | 1.1**       | 7.3**                              | 3.66        |

* — growth rate reduced by half,
** — open valve of the Veeco N plasma source.

Figure 2 shows SEM tilted images of the sample cleaved edges. The surface morphology of the GaP/Si reference sample (figure 2 (a)) is rather atomically smooth and is formed by GaP (001) terraces. This effect is most likely associated with the annihilation of APDs formed at the initial growth stage, which affects the surface morphology, as was demonstrated previously [4].
Typical SEM images of samples containing 3.07%, 3.66% and 5.05% N atoms are shown in figure 2 (b–d), respectively. It is clearly seen that the surface of these samples is rougher compared to the GaP/Si heterostructure (figure 2 (a)), which indicates a tendency to 3D growth under the presence of nitrogen.

**Figure 2.** SEM images of (a) GaP/Si reference sample 1, (b–d) GaP<sub>1–x</sub>N<sub>x</sub>/GaP/Si heterostructures.

### 3. Optical properties

The optical characterization was carried out at RT (300K) with a 532 nm diode-pumped solid-state laser providing near bandgap excitation of GaP and GaP<sub>1–x</sub>N<sub>x</sub>. Figure 3 shows the Raman spectra of dilute nitride heterostructures. All of the presented spectra show the existence of vibrational modes related to Si and cubic GaP, which were previously discussed in [4]. The spectra are normalized to the intensity of the TO-LO vibrational mode of Si.

**Figure 3.** Room temperature Raman spectra of heterostructures containing GaP<sub>1–x</sub>N<sub>x</sub> solid alloy obtained in backscattering geometry.
Raman bands at 520.7 cm$^{-1}$ and a broad plateau at 930–980 cm$^{-1}$ can be attributed to the (TO-LO) and two-phonon (2TO-) phonon modes of the Si substrate, respectively [6]. A pronounced scattering signal at 367, 403 and 785 cm$^{-1}$, which is seen in figure 3, can be attributed to the longitudinal optical (LO$_1$), transversal optical (TO$_1$) and two-phonon longitudinal (2LO$_1$) vibrational modes of the GaP lattice, respectively [7]. The appearance of the low-energy tail seen in figure 3 (black curve) is related to the intense PL emission in the sample with 3.07% of incorporated nitrogen.

As can be seen in figure 3, an additional vibrational mode (labeled as X) appears in the GaP$_{1-x}$N$_x$ RS spectra between the TO$_1$ and LO$_1$ GaP-like Raman bands [8], [4], [9], [10], [11], and it is not observed at RS of GaP/Si structure (not presented here). This peak is characterized by increasing intensity with N content (see figure 3) and can be attributed to disorder-activated optical phonons due to clustering of N into the GaP matrix [11].

The appearance of the optical vibrational phonon mode at 500 cm$^{-1}$ (marked as LO$_2$ in figure 3) can be attributed to the longitudinal Ga-N bond vibration into the GaP matrix and is related to the two-mode behavior typical of solid alloys [8] as its integral intensity increases with N content. As can be seen in figure 3, the integral intensity of the two-phonon 2LO$_1$ GaP-like mode also increases with N content. The appearance of such two-phonon modes is typical of solid alloys due to the enhancement of the second-order Raman scattering with an increase in structural disorder [12].

Then, we have studied room temperature (RT) PL properties of the synthesized dilute nitride heterostructures. PL was excited by a diode laser operating in the cw-regime ($\lambda = 532$ nm). All the samples, which contain nitrogen atom impurities of nitrogen atoms, demonstrated a bright photoluminescence signal, which is evidence of direct band-gap transitions in dilute nitride GaP$_{1-x}$N$_x$ alloys [13]. Figure 4 (a) shows the representative PL spectra of the samples containing 3.07, 3.66 and 5.05% of N. The spectral position of the PL intensity maximum for these samples is in the range from 1.85 eV to 1.9 eV for these structures. The PL peak position demonstrates a redshift with an increase in N content from 3.07% up to 5.05% (see figure 4 (b)). All the spectra have a broad PL line with a full width at half maximum of more than 300 meV. The PL spectra contain several lines in the spectral range from ~1.4 to ~2.2 eV. The intensities of the PL signal for the samples are compared in figure 4 (b). The highest PL intensity was obtained for the sample synthesized at the highest gas flow of 1.1 sccm (table 1) having 3.07% of N.

![Figure 4](image_url)

**Figure 4.** (a) RT PL spectra of samples # 2, #4 and # 6, (b) dependencies of the PL intensity and the PL peak position on the N content for all of the synthesized GaP$_{1-x}$N$_x$ samples.
We believe that the ion concentration in inductively coupled nitrogen plasma for a given input RF power correlates with the gas flow rate and increases as gas flow rates go down [14]. Ionized species can have high kinetic energy and thus can damage the growing dilute nitride films. This can be a reason for an order of magnitude lower intensity found for the sample grown at 0.3 sccm. We suppose that ion bombardment leads to the formation of point defects which act as non-radiative recombination centers and highly reduce the PL intensity.

The PL intensity damping is also observed for the N content above 3.07% (figure 4 (b)), which corresponds to the degradation of the structural quality as a result of defect formation in the highly lattice-mismatched GaP$_{1-x}$N$_x$ layer [15]. We assume that there in a transition from planar growth to growth of 3D islands in samples with a high nitrogen content, which can be driven by stress induced by lattice mismatch and non-optimal growth conditions.

4. Conclusions

In this work, planar heterostructures were synthesized by plasma-assisted molecular beam epitaxy (MBE-PA N). It was possible to achieve a maximum concentration of impurity nitrogen of 5.05 % in GaP$_{1-x}$N$_x$. The appearance of additional vibrational modes in the Raman spectra in solid solutions of GaP$_{1-x}$N$_x$ was shown. A broad RT PL response in the red wavelength region was observed. The maximum intensity of the photoluminescence signal was observed in the samples with an impurity nitrogen concentration of ~3% grown at a high nitrogen gas flow through a nitrogen plasma cell. A further increase in the nitrogen concentration dramatically impairs the crystalline and optical quality as a result of the defect formation induced by lattice mismatch and non-optimal growth conditions.

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