Raman measurements of dilute nitride alloys GaP(As)N grown on GaP substrates

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Abstract. The structural properties of GaP(As)N dilute nitrides alloys grown on GaP substrates by molecular-beam epitaxy are investigated. The samples were studied by Raman scattering and high-resolution X-ray diffraction. In this work the impact of lattice mismatch of GaP(As)N layer and GaP substrate on the form of the spectrum of Raman scattering of samples was detected. It was shown that the addition of arsenic in solid solution GaPAsN can compensate the elastic stresses in the crystal lattice, and we can estimate the lattice mismatch between epitaxial layer GaP(As)N and GaP substrate by the intensity ratio of LO/TO phonon peaks.

1. Introduction

Dilute nitrides materials (InGaPAsN)/GaP with lattice constant close to silicon are very promising for creating lasers, light-emitting diodes (LED), solar cells and detectors for integration on silicon wafers. Recently the yellow-orange light-emitting diodes based on GaP/GaPN heterostructures were demonstrated. Compared with commercial LEDs based on quantum wells AlInGaP, these LEDs have a higher stability of emission wavelength with increasing injection current [1] and a low specific thermal resistance [2].

The electrically pumped diode laser based on Ga(PAsN)/GaP material system which operates at low temperatures [3] and at room temperature [4] was realized. But GaP(As)N dilute nitrides alloys have unusual properties which are not fully understood. Therefore, this paper investigates structural properties of GaP(As)N/GaP heterostructures.

2. Experiment

The structural properties of GaP(As)N dilute nitrides alloys grown on GaP substrates by molecular-beam epitaxy were investigated. Samples were grown on epi-ready GaP (100) substrates. The concentration of As and N in GaP(As)N layers shown in table 1.

The compositions of the layers were calculated using the BAC-model from the data obtained from the photoluminescence spectra and high-resolution X-ray diffraction. Calculations are shown in previous papers [5,6].
Table 1. The characteristics of the samples 1-3.

| No | Concentration | Concentration | $\text{LO}_X/\text{TO}_T$, | Lattice mismatch, % |
|----|---------------|---------------|-----------------|------------------|
| 1  | 0,7           | 0             | 0,25            | 0,23             |
| 2  | 1,6           | 4,7           | 0,33            | 0,14             |
| 3  | 0,5           | 7,7           | 0,37            | 0,11             |

3. Results and discussion

Structural features of the samples were studied using Raman scattering with excitation energy 2,33 eV (figure 1).

Figure 1. Raman spectra of dilute nitride alloys GaP(As)N grown on GaP substrates

The Raman spectrum is dominated by the longitudinal (LO$_T$) and symmetry-forbidden transverse (TO$_T$) and phonon modes at 404 and 365 cm$^{-1}$, respectively. Also we observe addition phonon line LO$_X$ (between LO$_T$ and TO$_T$ modes) at 386 cm$^{-1}$. Calculation of the intensity ratios of are shown in Table 1.

Increasing intensity of additional phonon mode LO$_X$ and symmetry-forbidden phonon line TO$_T$ from the third sample to the first may be explained by relaxation of the momentum conservation rules and the symmetry selection rules, respectively. In paper [7] increasing intensity of LO$_X$ mode and LO$_X$/TO$_T$ ratio with increasing of N concentration in GaP$_{1-x}$N$_x$ layers. But in our case increasing of nitrogen concentration in GaPAsN layers does not lead to increasing of LO$_X$/TO$_T$ ratio.

Therefore samples were studied by high-resolution X-ray diffraction (XRD). Diffraction rocking curves were obtained using a DRON-8 X-ray diffraction system with a BSV 29 highly focused X-ray tube. The anode material was copper with Ka1 radiation line ($\lambda = 1,5405$ Å). Characteristic XRD rocking curves near the symmetric GaP (004) reflection are on figure 2.
Figure 2. Characteristic XRD rocking curves near the symmetric GaP (004) reflection of epitaxial layers GaP(As)N with different nitrogen concentration.

For samples with GaP(As)N layer on GaP substrate, the presence of two diffraction peaks and a series of lines of thickness oscillations are characterized. The maxima correspond to the diffraction on lattice of GaP and the diffraction on elastically strained lattice of GaP(As)N layer. Presence of thickness oscillations demonstrates high quality of heterointerfaces of such layers. Addition of nitrogen in GaP(As)N decreases lattice constant of solid solution and therefore peaks corresponding to XRD of the layers of samples 1 and 2 shifted toward larger angles $2\Theta$ relatively substrate GaP. However for the sample 3 diffraction peak from GaPAsN layer shifted to the left relatively Bragg angle of GaP substrate. This is due to the fact that addition of arsenic in GaPNAs leads to growth of lattice constant and the compensation of elastic stresses caused by the embedding of nitrogen. At certain ratios of nitrogen and arsenic concentrations we can achieve complete matching of the lattice constants of the quaternary solid solution GaPAsN and GaP substrate.

The lattice mismatch of GaP(As)N layers and GaP substrates was calculated by angular distance between diffraction peaks (table 1). We can see that during the growth of ternary solid solution GaP$_{0.993}$N$_{0.007}$ (sample 1) the mismatch is maximum (0.23%). By adding the arsenic (samples 2 and 3) the mismatch decreases. The smallest mismatch observed in the sample with the highest concentration of arsenic – 7.7% (sample 3). However, it is obvious that a further increasing of arsenic concentration in the solid solution GaPAsN the lattice mismatch will increase.

By XRD and Raman scattering data we can build a dependence between the magnitude of the lattice mismatch of layers GaPAsN and GaP and $LO_X/TO_\Gamma$ ratio (figure 3).
Figure 3. Dependence of lattice mismatch of GaP(As)N layers and GaP substrate on \( \text{LO}_{X}/\text{TO}_{\Gamma} \) phonon peak ratio.

As the increasing the mismatch of lattice constants of growing layer and substrate, the ratio \( \text{LO}_{X}/\text{TO}_{\Gamma} \) decreases linearly and symmetry-forbidden phonon line \( \text{TO}_{\Gamma} \) intensity increases. This may be due to the reducing of crystal symmetry of solid solution GaP(As)N caused by addition of nitrogen. By adding the arsenic in solid solution the ratio of \( \text{LO}_{X}/\text{TO}_{\Gamma} \) increases and intensity of \( \text{TO}_{\Gamma} \) phonon line decreases. This is due to the fact that the addition of arsenic in solid solution GaPAsN can compensate the elastic stresses in the crystal lattice, and by the intensity ratio of \( \text{LO}_{X}/\text{TO}_{\Gamma} \) phonon peaks we can estimate the lattice mismatch between epitaxial layer GaP(As)N and substrate GaP.

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References
[1] M. Kaneko, T. Hashizume, V.A. Odnoblyudov, C.W. Tu. J. Appl. Phys., 101, 103 707 (2007)
[2] S. Adachi, J. Appl. Phys. 54, 1844 (1983)
[3] B. Kunert, S. Reinhard, J. Koch, M. Lampalzer, K. Volz, and W. Stolz, phys. stat. sol. (c) 3, 614–618 (2006)
[4] B. Kunert, A. Klehr, S. Reinhard, K. Volz, and W. Stolz, Electron. Lett. 42, 601 (2006)
[5] A.A.Lazarenko, E.V. Nikitina, E.V. Pirogov, M.S. Sobolev, Semiconductors, Volume 48, Issue 3, pp 392-396 (2014)
[6] A.A.Lazarenko, E.V. Nikitina, M.S. Sobolev, E.V. Pirogov, D.V. Denisov, Semiconductors, Volume 50, Issue 4 (2015)
[7] A. Pulzara-Mora et al. / Vacuum 80 (2006) 468–474