Epitaxial growth and investigation of GaP/GaP(As)N heterostructures on Si (100) 4° substrates

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Abstract This article demonstrates the phased creation of heterostructures containing GaPN and GaPAsN layers on Si substrates grown by molecular-beam epitaxy. A technique of preparing a silicon surface for epitaxial growth, the creation of a GaP initial layer, and optical studies of GaPN and GaPAsN layers are described. It is shown that high-quality GaP(As)N epitaxial layers can be created on Si substrates by molecular-beam epitaxy.

1. Introduction
Nowadays heterostructures based on dilute nitrides are of great interest in the world, since they open the possibility of integrating silicon technology and AlIBV technology for creating light emitting devices, solar cells and integrated circuits [1-4]. Addition of nitrogen in GaP modifies conduction band and makes the GaP1-xNx compound direct-gap, besides addition of nitrogen leads to lattice matching of the Si and GaP1-xNx. However, during the epitaxial growth of AlIBV compounds on Si substrates, many defects and dislocations arise, such as anti-phase domains, misfit and threading dislocations etc. That is why the preparation of the silicon surface and the growth of the initial layer are important stages in the creation of heterostructures on Si substrates.

2. Pre-growth preparation of silicon substrates
The pre-growth preparation of substrates is one of the most important step in the formation of structures of molecular-beam epitaxy (MBE) technology for opto- and microelectronics, since the presence of chemically pure, structurally perfect, atomically smooth surface is a prerequisite for producing epitaxial layers of device quality.

Based on the methods proposed in the works [5,6] the method of preparation of Si (111) substrates was developed.

The procedure of the chemical treatment of substrates consists of the following operations (HNO3 ~ 70%; HF ~ 46%; H2O2 ~ 30%; NH4OH ~ 28%; HCl ~ 36%; distilled deionized water with a resistance of at least 15MOhm·cm):

1. Washing off traces of organic contaminants by boiling first in CCl4, then in acetone.
2. Oxidation of the upper layer of silicon in boiling nitric acid and bleeding of the formed SiO2 in a solution of hydrofluoric acid (HF: H2O = 1: 3) for 20-30 seconds (this operation is repeated several times).
3. Boiling in a peroxide-ammonia solution (NH4OH: H2O2: H2O = 1: 1:3) for 10 minutes, followed by removal of contaminants together with silicon oxide in a solution of hydrofluoric acid.
4. Formation on the surface of a thin protective oxide by boiling in peroxide-acid solution (HCl: H2O2: H2O = 3: 1: 1) for 10 minutes.
5. Final washing with deionized water and drying with ethanol in centrifuge.

Samples prepared in this way were immediately loaded into the MBE chamber, where they were before the final stage of pre-epitaxial preparation in the conditions of ultra-high vacuum (UHV). In UHV conditions, chemically prepared substrates were sequentially degassed in a growth module at 450°C for 60 minutes and 750°C for 40 minutes.
3. Epitaxial growth of GaP initial layer
The growth of the GaP initial layer was carried out on VEECO GEN III MBE on silicon substrates. To overcome the problem of the formation of antiphase regions during the growth of AlIIIBV compounds on silicon, vicinal silicon substrates were used with misorientations at 4° relative to the (001) surface in the [110] direction.

The GaP semiconductor initial layer was formed by sequential deposition of Ga and P monolayers on a silicon substrate.

During the opening of the shutter of the Ga source, gallium atoms accumulate on the epitaxial surface. When the Ga shutter is closed and the P shutter opens, the accumulated gallium is consumed by the growth of the GaP film. In each cycle, a significant part of the time, the GaP film grows in metal-enriched conditions. The time to hold the growth surface under a stream of phosphorus atoms is selected in such a way that all the accumulated gallium reacts with phosphorus. After all the metal is consumed to form a GaP film, the surface goes into a phosphorus-stabilized state, and each new cycle begins with the deposition of gallium on the phosphorus-stabilized surface. The GaP initial layer consisted of 30 periods of Ga and P monolayers at characteristic thicknesses of monolayers of 0.13 nm and 0.19 nm, respectively. Further, a 200-nm-thick GaP buffer layer was grown on top of the initial layer (figure 1).

![Figure 1. SEM image of GaP/Si heterostructure with GaP initial layer](image)

It is seen that dislocation cones are formed in the initial layer, but then annihilate and do not penetrate in surface of the buffer layer.

4. Low-temperature photoluminescence of GaP(As)N layers
GaP (As) N layers were grown on GaP and Si substrates by MBE (table 1).

| № sample | layer/substrate           |
|----------|---------------------------|
| 1        | GaP$_{0.918}$As$_{0.007}$N$_{0.000}$/GaP |
| 2        | GaP$_{0.993}$N$_{0.007}$/GaP          |
| 3        | GaP$_{0.994}$N$_{0.006}$/Si           |
| 4        | GaP$_{0.937}$As$_{0.047}$N$_{0.010}$/GaP |
Photoluminescence (PL) spectra recorded at cryogenic temperature, 10 K, for the samples given in table 1 are shown on figure 2.

![Figure 2. The PL spectra of GaPN / GaP, GaPAsN / GaP and GaPN / Si heterostructures at T = 10 K](image)

Starting from temperatures close to the temperature of liquid nitrogen, 80 K, and at lower temperatures, PL spectra are split into a series of lines (samples 1, 2 and 3). The effect was most distinctly in the study of a sample with the lowest molar fraction of nitrogen (sample 1). The most intense emission line, designated NN₁, is associated with the recombination of carriers through a localized state formed by the closest pair of nitrogen atoms. In a general form, the possible nitrogen pairs are designated NNᵢ, for i = 1 nitrogen atoms are located at the nearest anion positions [7]. The peaks with lower energy associated with the state of NN₁ are its phonon replicas, including optical longitudinal and transverse phonons (LO and TO, respectively), acoustic phonons (LA, TA), and local phonon vibrational modes (LVM). Replicas associated with different phonons are indicated in figure 2 by symbols corresponding to specific phonons.

Additionally, at a temperature of 10 K to the right of the most intense series of phonon replicas associated with the pair NN₁, a pair of NN₃ lines and associated replicas arise. The energy position of the observed lines NN₁ and NN₃, as well as the energy distance between the phonon lines, are in good agreement with the known energy values of these lines in GaPN [7]. The presence of arsenic in moderate concentrations in sample 1 does not affect the energy position of the observed lines NN₁ and NN₃. In addition, on the spectra of samples 1, 2 and 3 to the left of the phonon replicas, a shoulder is observed associated with optical transitions between the E-band and the top of the valence band. An example of the decomposition of the observed spectrum into possible component spectra for sample 2 is shown in figure 3.
Figure 3. An example of the decomposition of the observed integral PL spectrum (2) into possible component spectra (2' and 2'') for sample 2 at T = 10 K.

The change in the mutual arrangement of the bottom of the E band relative to the level of the pair NN1, which is in a clearly fixed position, leads to an energy shift of the PL related to the transitions between the bottom of the E subband and the top of the valence band. As a result, the shape of the integrated PL spectrum, which we observe, is modified. For example, one can note the difference between the spectra of samples 1 and 2. The energy distribution of the levels of nitrogen pairs NNi and isolated nitrogen atoms in GaP and the subband E of GaPN solid solution is shown schematically in figure 4.

Figure 4. The energy distribution of the levels of nitrogen pairs NNi and isolated nitrogen atoms in GaP and the subband E of GaPN solid solution.
For samples with a small fraction of nitrogen (samples 1, 2 and 3), the energy gap between E-bottom and the NN1 level is small and radiative recombination is carried out on both channels. For sample 4, with a higher fraction of nitrogen, the energy gap increases and the PL spectrum (see figure 2) is determined only by optical transitions between the E-bond and the top of the valence band.

In general, the photoluminescence spectra allow us to conclude that the molecular beam epitaxy is suitable for the creation of GaPN and GaPAsN layers both on the surface of gallium phosphide and on the surface of silicon. Critical fall PL signal intensity when replacing a GaP substrate to the Si substrate is not observed.

5. Conclusion
This article demonstrates the phased creation of heterostructures containing GaPN and GaPAsN layers on Si substrates grown by molecular-beam epitaxy. A technique of preparing a silicon surface for epitaxial growth, the creation of a GaP initial layer, and optical studies of GaPN and GaPAsN layers are described. It is shown that high-quality GaP(As)N epitaxial layers can be created on Si substrates by molecular-beam epitaxy.

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