GaPN/GaP nanowire-polymer matrix: photoluminescence study

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Abstract. This study is devoted to the investigation of the optical properties and composition of GaPN/GaP nanowire heterostructure. Nanowire arrays were grown on Si substrate (111) by the plasma-assisted molecular beam epitaxy. Polydimethylsiloxane membrane encapsulation was used to obtain the free-standing NW arrays. The morphology of GaPN/GaP NW was investigated with scanning electron microscopy. The optical properties of the GaPN nanowire arrays were determined at the He temperature (5K) with photoluminescence spectroscopy. Analysis of photoluminescence response allowed us to conclude that the incorporation of nitrogen atoms during the growth occurs both in the nanowires and in the parasitic islands with different content. Direct bandgap-like behaviour of the GaPN/GaP nanowires demonstrates the potential of nanowire-polymer matrix practical application in future optoelectronic devices.

1. Introduction

The development of flexible optoelectronic devices and nano-sized light-emitting sources is one of the main goals of modern semiconductor technology [1]. Since 2008, there has been a relatively large number of works on the creation of nanowire flexible inorganic light-emitting devices [2-4]. However, there is still the so-called green window problem. Therefore, in order to create light-emitting devices operating in the visible green range, a nitrogen diluted gallium phosphide compound is considered. III-V nanowires (NWs) based on the ternary GaPN solid alloy form a promising platform thanks to the possibility of the bandgap engineering in the 1.7 - 2.2 eV range [5, 6]. In this paper, we report PL properties of new material for nanowire-based flexible light-emitted devices based on GaPN/GaP nanowire-polymer matrix.

2. Growth and structure

GaPN/GaP NW heterostructure arrays were grown on vicinal (4°) silicon (111) substrates within self-catalyzed vapor-liquid-solid (VLS) approach by plasma-assisted molecular beam epitaxy (PA-MBE) using Veeco GEN-III MBE machine equipped with the Riber RF-plasma (13.56 MHz) activated nitrogen source. Si (111) wafers were cleaned by the modified Shiraki technique ended by the boiling
in 35% nitric acid water solution to form a dense surface silicon oxide layer. After loading and degassing the substrate was annealed at 870°C, which is 10°C lower than the temperature required to thermally deoxidize silicon. The growth temperature was measured by both thermocouple and pyrometer and was equal 730°C during the growth process. Ga flux was kept constant and equivalent to the 0.4 ML/s growth rate of planar GaP/(111), calibrated by reflection high energy electron diffraction (RHEED), and corresponds to Ga beam equivalent pressure (BEP) equal to the $8 \times 10^{-8}$ Torr. The synthesized sample represents GaPN/GaP heterostructured NWs consisting of GaPN segment grown on GaP stem and schematically shown in figure 1 (c). The growth time of the GaP stem and GaPN segment was equal. P/Ga BEP ratio was kept constant during the growth of GaP and GaPN and equal 18. The growth was not interrupted during the plasma ignition. As a reference, GaP NWs were grown at the same growth conditions but without nitrogen flux.

The structure and morphology were studied using scanning electron microscopy (SEM) (Zeiss SUPRA 25-30-63). According to SEM analysis, the morphology of the GaP NW was almost identical to GaPN/GaP NW samples, we conclude that used nitrogen flux does not affect the nanostructure morphology and preserves self-catalytic growth.

Figure 1 shows SEM images of the studied epitaxial NW arrays. Both vertical NWs and 3D- nanoscale islands with flat (111) facets are formed at chosen growth conditions. In Figure 1 (b) clearly seen that the NWs and 3D- islands are hexagonal in cross-sections, it means that they are following the Si (111) substrate crystallographic orientation. The NWs are rather uniform in size for both studied samples and have a length of about 5.8 μm. The average diameter of a single NW ~80 nm. The lateral shape of the 3D islands is very different from island to island, but their average height is practically equal and is about ~400 nm.

3. PL study
The measurements were performed with an excitation wavelength of $\lambda = 507$ nm at the temperature 5 K using a closed cycle He cryostat. The optical experiment was schematically shown in figure 2 with green arrows.

Firstly, we obtained the PL signal from the as-grown GaPN/GaP NW array. Secondly, the NW array was encapsulated into a polydimethylsiloxane (PDMS) matrix using the novel G-coating method (see figure 2 (d)). The NW encapsulation and membrane exfoliation technique was described by Neplokh et al. in [7]. Thick PDMS cap-film with a thickness of (50-150 μm) was necessary for the mechanical stability of the thin NW membrane. Then a part of this membrane was exfoliated from the growth Si substrate.
The PL spectrum obtained from pure GaP NWs, which is shown as an orange line in figure 2 (b) and (e), shows no prominent PL response due to the indirect-gap behavior of the GaP semiconductor.

In contrast, PL spectra of the heterostructured NWs demonstrate a bright PL signal indicating the quasi-direct bandgap-like transitions in the dilute nitride GaP$_{1-x}$N$_x$ alloys [8].

At the PL spectra, obtained from as-grown NWs on substrate and substrate after exfoliation, there are sharp lines, which can be attributed to highly-localized N-level and its phonon replica (see figure 2 (b) and (e)) where NN$_1$ – NN$_2$ – NN$_3$ – NN$_4$ – NN$_5$ is a position of highly-localized N level in nitrogen diluted GaP solid alloys, their nature was detailed described by Thomas [9] and Lasarenko [10]. The existence of sharp lines is evidence of quasi-direct bandgap into GaPN solid solution.

The most intense emission line (labeled NN$_1$) at the above-mentioned PL spectra is associated with the recombination of carriers through a localized state formed by the closest pair of nitrogen atoms. The possible nitrogen pairs are designated NN$_n$, for n = 1 nitrogen atoms are located at the nearest anion positions.

High intensity of NN$_1$ and NN$_2$ lines indicates low average content of embedded N atoms into GaPN parasitic islands and also indicates quasi-direct bandgap. The concentration of impurity nitrogen over the entire volume and surface of the studied sample is about 0.2 – 0.3%. The shape of the PL spectra and maximum PL position at 5K shown in figure 2 (b) indicates that the incorporation of nitrogen

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**Figure 2.** Schematic representation of the (a) MBE GaP nanowire array on Si substrate, (c) substrate after NW exfoliation, (d) encapsulation of NW array into PDMS-membrane and cap-film covering, (f) the released membrane, (b) and (e) low-temperature PL spectra of studied samples.
atoms during the growth occurs both in the NWs and in the parasitic islands, and the average concentration over the parasitic islands is about 0.1 – 0.2% [8, 11-13].

The PL spectrum which was observed from GaPN/GaP NW/PDMS membrane has a complicated shape and is located in the range from 560 to 660 nm with FWHM is 55 nm with a maximum at 580 nm (depicted as magenta triangles in figure 2 (e)). The shortwave tail, which appears at the PL spectra, obtained from membrane samples, it can be attributed to low-temperature luminescence from the polymer matrix. Additional proof of the membrane PL signal is the existence of a shortwave tail at the PL spectrum pure NWs array encapsulated into the PDMS membrane.

The PL signal from encapsulated GaPN/GaP NW into the PDMS matrix (see figure 2 (e)) differs from PL signal from the grown nanowire array (see figure 2 (b)).

Sharp damping of the PL signal from strongly localized levels is observed upon encapsulation of NWs into the polymer membrane. Such an effect most probably relates to the inefficient excitation of the active medium in PDMS due to the appearance of stresses in the NWs into the polymer matrix and the possibility of surface luminescence quenching. Nevertheless, the nature of this behavior remains still unclear.

A comparison of the absolute intensities of the PL spectra suggests that the emission of parasitic islands prevails over the emission from GaPN/GaP nanowire array, since the intensity of the PL signal, not related to strongly localized levels, is in almost in two times lower.

4. Conclusions
The vertically aligned arrays of the self-catalyzed heterostructured GaPN/GaP NWs were grown on Si (111) by PA-MBE. By studying the sample PL response before and after NW exfoliating, we demonstrated that nitrogen is incorporated both into NWs during their VLS growth and into parasitically grown nanoislands. Judging by the characteristic dilute nitride fine structure appearing at helium temperatures PL spectra we estimate the amount of incorporated nitrogen as ~0.2% into the as-grown NW arrays. After the NW encapsulation into the PDMS membrane, the fine structure disappears and broad PL signal in the range from 565 to 660 nm with FWHM of 60 nm is visible both at the 5K. We assume that the smudging of the fine structure spectral line is related to the appearance of the charge states at the NW/PDMS interface. The main source of light emission is parasitic islands, which were grown at the substrate surface.

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