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GaN microrods growth by combined PA-MBE/HVPE method

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The growth of GaN microrods on silicon substrates by the combined PA-MBE/HVPE method was studied. At the first stage, selective-area growth of submicron-sized GaN rods is performed by molecular beam epitaxy with plasma nitrogen activation (PA-MBE). At the second stage, an array of GaN rods is overgrown by hydride vapor-phase epitaxy (HVPE) to increase their size. Controlled HVPE overgrowth of an array of GaN rods is demonstrated, leading to an increase in their average diameter from $\sim$ 200 nm to $\sim$ 500 nm and a decrease in the average aspect ratio from $\sim$ 4 to $\sim$ 2. The effect of epitaxial overgrowth on the morphological, optical and structural properties of GaN rods array was studied by scanning electron microscopy and low-temperature photoluminescence.

Keywords: PA-MBE, HVPE, GaN microrods, epitaxial overgrowth.

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1. Introduction

Gallium nitride microrods, a wide-band semiconductor with high thermal and chemical stability, are promising materials for development of electronic and optoelectronic devices. Thus, the researches currently pay much attention to development of emitting light diodes on their basis [1,2]. For this purpose, a multilayer heterostructure InGaN of „core–shell“ type is formed on the surface of GaN microrods. Another application of single GaN microrods is their use as an active region of optical microcavities supporting modes of the whispering gallery with high Q factor and stability of frequencies [3]. It is also important to note the use of GaN microrods as high-sensitivity gas sensors [4]. When device structures are developed on the basis of GaN, the synthesis of arrays of microrods has certain benefits compared to the growth of thin films. Firstly, it is low density of structural defects and absence of cracks due to small surface area of contact with the substrate [1]. As a result, GaN microrods may be synthesized on substrates with high lattice mismatch and, in particular, on silicon, which makes it possible to implement the monolithic integration with the silicon element base. Secondly, due to high ratio of the surface area to the volume, it is possible to increase the active surface of the light-emitting structure by 10 times compared to planar heterostructures [1]. Thirdly, the benefit is the decrease in spontaneous polarization, since the side surfaces of GaN microrods, having the wurtzite structure and formed primarily in c or $-c$ direction, are formed by non-polar or semi-polar faces [2]. The effectiveness of operation of the devices based on GaN microrods depends on the degree of homogeneity of their morphology, polarity and surface density of arrays. To solve the problem of crystal array homogeneity, selective-area methods are used, i.e. the growth is carried out on the substrates coated with dielectric masks (for example, SiO_x or SiN_x) with holes [5–7] or on the profiled substrates [8]. Selective-area growth of GaN microrods is usually carried out by epitaxial methods, such as metalorganic vapour-phase epitaxy (MOVPE) [1,5,9–11], molecular-beam epitaxy with plasma activation of nitrogen (PA-MBE) [6,8,12] and hydride vapor phase epitaxy (HVPE) [7,13,14]. A separate task is achievement of high aspect ratio, i.e. ratio of length of microrods to their diameter. Thus, to obtain a homogeneous array of rods by MOVPE, having high aspect ratio, in paper [9] used a special growth technique, in which the material flows are activated in pulse mode. In papers [5,10] it was found that the necessary condition for production of GaN microrods was the use of mixture of H_2 and N_2 as a carrier gas. Whereas during the growth in the atmosphere of pure N_2 the growth of rods is not observed. Besides, the growth of GaN microrods with high aspect ratio was demonstrated in paper [11] when using H_2 as a carrier gas with impurity of silane (SiH_4). This technique has become widely popular, but its disadvantage is the formation of SiN layer, which is non-uniform in

thickness, on the surface of microcrystals. In selective-area growth of GaN by PA-MBE method the limiting factor of formation of GaN microrods are the dimensions of holes in the mask. In paper [6] it was found that when the size of holes in the mask is more than ~ 500 nm, structures are formed on the silicon substrates with buffer layers of AlN, which represent merged nanorods without expressed GaN facets. This occurs because of polycentric nucleation of GaN in the holes in the mask, which may already be observed in the growth without buffer layers at hole size of ~ 100 nm. Besides, the disadvantage of the PA-MBE selective-area method is the low growth speed, and parasitic nucleation of GaN nanowires on the mask. However, the density of the latter may be substantially decreased by selecting the substrate temperature and material flows [15]. It is also important to note that in growth by PA-MBE method there is a trend observed towards decrease in the diameter of rods from their base to the top related to the mechanism of crystal growth by this method, namely, with formation of step bunches on the side surfaces of crystals [16]. On the other hand, the features of the growth mechanism with PA-MBE method allow for achieving high aspect ratios without the use of special growth techniques. Despite the elevated interest in the synthesis of GaN microrods with epitaxial methods, a relatively small number of papers is dedicted to HVPE method [7,13,14]. As in MOVPE, it was found that the condition to obtain microrods was the presence of H_2 in the reactor atmosphere. Besides, the high aspect ratio (~ 5) was obtained by one group only [7]. It should be noted that in recent papers [7,17] it was demonstrated that the HVPE method, usually used to grow thick GaN layers, was also the promising method to synthesize micro- and nanostructures. Therefore, the advantage of the HVPE method compared to PA-MBE and MOVPE is the relatively low supersaturation near the substrate despite high values of material flows at the inlet to the reactor and high rate of GaN growth, which is related to high rate of chemical reaction of gases [17,18]. As a result the GaN microrods are formed in quasi-equilibrium conditions, have good crystalline quality and shape close to equilibrium one.

In this paper the arrays of GaN microrods are synthesized on silicon substrates by combined PA-MBE/HVPE method. At the first stage selective-area growth of array of GaN microrods of submicron size is conducted on Si(111) substrates by PA-MBE method. At the second stage the HVPE overgrowth is performed on the obtained array to increase the lateral sizes of GaN crystals and form the faceting of their side surfaces (with facets parallel to c axis). It is important to note that large lateral size and the corresponding faceting of GaN crystals are necessary for their use in certain device applications and, in particular, as optical microcavities. Growth of GaN on crystalline seeds of high crystalline quality having high ratio of length to diameter, and the possibility to achieve high anisotropy of growth in the HVPE method, define the viability of using the combined method to synthesize GaN microrods. It should be noted that such combined method of synthesis was previously used by one group only [19] with the purpose to form a „shell“ of GaN of p-type on the surface of self-induced GaN nanowires, having n-type of doping.

2. Experiment

Growth of GaN rods of submicron size (nanowires) was done by PA-MBE method on Riber Compact 12 setup according to the previously developed method [20]. Si(111) substrates of n-type with SiO_2 (50 nm) mask obtained by thermal oxidation method were used for growth. The holes in the mask were formed by method of microsphere photolithography using plasma-enhanced chemical etching [21]. The distance between the centers of holes and their surface density ($\sim 0.4\,\mu m^{-2}$) were defined by the size of used microspheres ($1.8\,\mu$m). The hole diameter was $\sim 0.4\,\mu$m. Prior to growth, thermal annealing of the substrate was conducted for 15 min at 870 °C. PA-MBE growth was carried out at temperature 820 °C for 22 h at equivalent pressure of gallium flow measured using Bayard–Alpert sensor, $2 \cdot 10^{-7}$ Torr. Nitrogen flow was 0.4 sccm at plasma source capacity of 450 W. Epitaxial refilling by HVPE method was carried out in the horizontal-type reactor at atmospheric pressure. Temperature in the growth zone was 1040 °C at HCl flows (above liquid gallium) and NH_3 equal to 100 and 1000 sccm, accordingly; the growth time was equal to 30 and 50 s. Argon was used as a carrier gas. Therefore, for further research, three specimens were prepared: GaN rods synthesized by PA-MBE method (specimen 1); GaN rods after refilling with HPVE method for 30 s (specimen 2) and 50 s (specimen 3). Morphology of the obtained arrays of GaN crystals was studied using a scanning-electron microscope (SEM) Supra 25 Zeiss. To study the polarity of GaN rods, the method of etching in aqueous solution KOH (1:5) at temperature 70 °C was used. To study the optical properties of the obtained specimens, measurements were carried out by method of low-temperature photoluminescence (PL) using a double monochromator MDR-204-2 (LOMO-Fotonika) with dispersion of 25 Å/mm in a helium cryostat of closed cycle (Janis Research Company). PL spectra were excited by ultraviolet He–Cd-laser ($\lambda = 325$ nm).

3. Results and discussion

Figures 1–3 presents typical SEM-images of arrays of GaN rods formed by PA-MBE method, and also after refilling with HVPE method. From the analysis of SEM-images it follows that under the selected conditions of HVPE growth the selectivity is maintained, i.e. epitaxial refilling of GaN crystals formed at the first stage of growth in the holes of SiO_2mask takes place. Besides, the surface density of GaN rods corresponds to the density of holes in SiO_2 mask. Figure 4 presents the statistic data on measurement of diameter of GaN rods for all studied

specimens. It is seen that the average diameter of GaN rods increases from 200 to 470 nm for 30 s and up to 500 nm for 50 s of HVPE growth, i. e. approximately 2 times. The observed slowdown of the growth speed is related to the formation of spurious crystallites, which are responsible for a significant share of the sputtered material flow.

Average ratio of height of GaN rods to diameter in refilling decreases from ~ 4 to ~ 2.5 and ~ 2, accordingly for 30 s and 50 s of deposition. The mean square deviation of distribution in diameters divided into the average diameter before and after refilling has close values for all specimens, namely: ~ 0.4 for specimen 1, ~ 0.5 for specimens 2 and 3. The share of crystals inclined relative to the normal line to the substrate in process of refilling for 30 s is also maintained. Note that the reason for existence of various growth directions is related to etching of silicon in the holes in the SiO_2 mask (at the stage of mask formation) and formation of pits therein, as it follows from SEM-images of the specimens chip. As a result, the GaN nuclei nucleate, having different orientation c-axis. If the refilling time is 50 s, the share of inclined crystals decreases, which is due to the preferential formation of spurious crystallites of them (30 % of the total number). It was also found that, as expected, when refilling by HVPE method, the shape of GaN rods changes.

Thus, for GaN rods obtained by PA-MBE method, the diameter decreases from the base to the top (side surfaces deviate by $\sim 3^\circ$ relative to c-direction), which is related to the formation of step bunches on the side surfaces of rods originating near the base of crystals [16].

When GaN rods grow in the HVPE reactor, the steps formed previously are refilled, and then the nucleation of new steps is possible on the entire area of the GaN crystals side facets. Thus, a layer-by-layer growth of side facts in GaN rods is implemented, and non-polar vertical GaN planes are formed, which correspond to wurtzite structure. Based on the comparison of morphology and, in particular, faceting of GaN crystals after refilling for 30 and 50 s, the conclusion was made that the condition for appearance of spurious crystallites (crystals with diameter of $1-2\,\mu$m in Figure 3), was probably the formation of several GaN rods from one hole in SiO_2 mask (at the first stage), besides, having a certain type of polarity. Such crystals have the highest speed of growth, however, contain many defects, too, found by specimen etching in KOH. After 30 s of refilling their lateral dimensions are in the interval of $\sim 0.6-1.0\,\mu$m (in Figure 2 it corresponds to crystals with highest diameter and top of pyramidal shape) and separation of their distribution by size from the main distribute is not happening yet. Besides, when refilled by HVPE method, it is possible to change the direction of crystal growth and to form so called tripods, the formation mechanism of which is described in the review [17] (~ 2 % of the total number). Besides, note that no substantial increase in the dimensions of parasitic GaN nanowires formed as a result of PA-MBE growth on the SiO_2 mask is observed for the time of HVPE refilling.

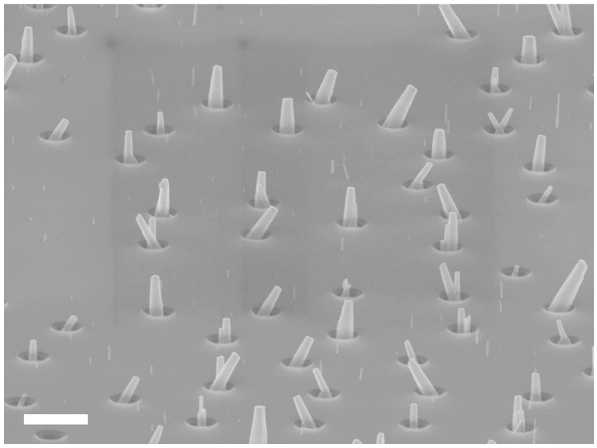

Figure 1. SEM-image of GaN rods selectively formed by PA-MBE method (specimen 1). The measuring scale is equal to $1\,\mu$m.

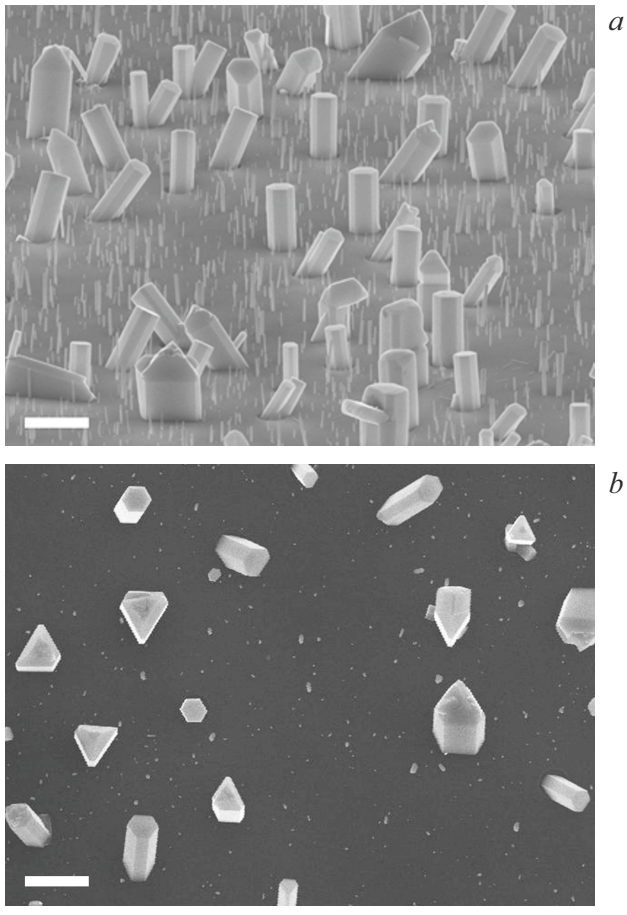

Figure 2. SEM-image of GaN rods after refilling by HVPE method for 30 s (specimen 2): a — isometric view at angle 15° to the substrate plane; b — top view (presence of sections without rods is related to heterogeneous distribution of microspheres on SiO_2 surface when holes are formed in the mask by method of microsphere photolithography). The measuring scale is equal to $1\,\mu$m.

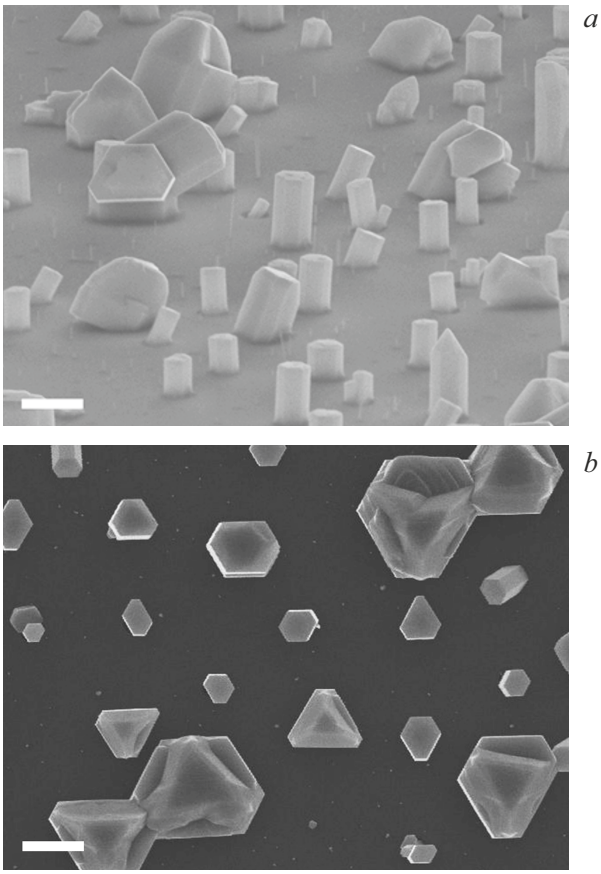

Figure 3. SEM-image of GaN rods after refilling with HVPE method for 50 s (specimen 3): *a* — isometric view at angle 15° to the substrate plane; *b* — top view. The measuring scale is equal to 1 μm.

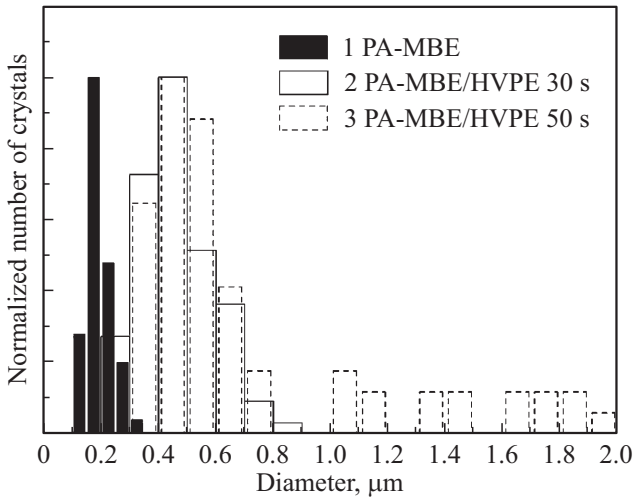

Figure 4. Distribution of diameters of GaN rods before and after refilling by HVPE method (specimens 1, 2 and 3). GaN crystals with diameters of more than $\sim 1\,\mu$m (specimen 3) correspond to spurious crystallites and are not taken into account to estimate the average diameter.

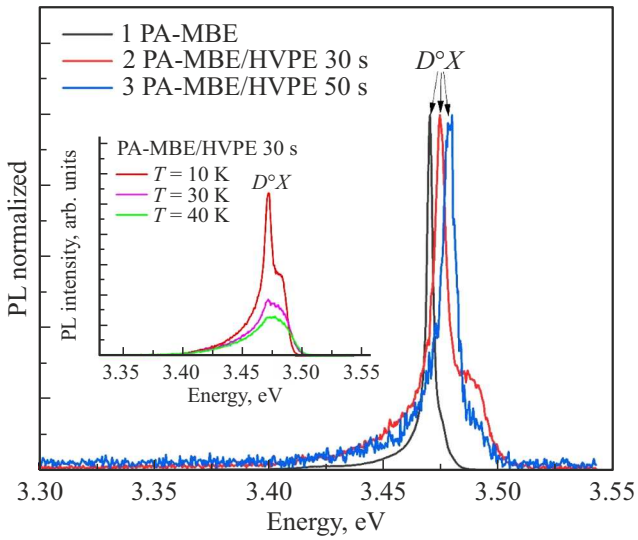

Figure 5. PL spectra of GaN rods before and after refilling with HVPE method (specimens 1, 2 and 3). The insert shows temperature dependence of PL in specimen 2.

Etching of the obtained specimens in KOH showed that GaN rods prior to HVPE refilling (specimen 1) have mostly polarity of N-type ($\sim 80\,\%$), which is indicated by relatively high speed of etching and pyramidal shape of tops after etching [5]. At the same time it was also found that after HVPE refilling (specimens 2 and 3) most crystals have mixed polarity ($\sim 70\,\%$). This manifests itself either in detection of structure „core–shell“, when „HVPE shell“ of rods is etched much faster than its central part formed by PA-MBE method [22], or in the fact that the top of the rod is etched much faster than the part of the crystal underneath (for rods having the top of pyramidal shape as in Figure 2 and Figure 3). The fraction of Ga-polar rods that demonstrated resistance to etching [5] and have a flat top, made $\sim 30\,\%$ (crystals in the form of straight prisms in Figure 2 and Figure 3). To establish the mechanisms of polarity change in refilling by HVPE method, further research is needed.

Figure 5 shows the PL spectra measured at 10 K for three specimens. Insert in Figure 5 demonstrates the temperature dependence of PL for specimen 2. Insert at temperature 10 K shows well the intense peak with maximum of 3.474 eV, which practically fully disappears at temperature of 30 K, and at 40 K it is already absent in the spectrum. Such spectral position and dependence on temperature are specific for PL line in the GaN spectrum, corresponding to the exciton $D^{\circ}X$ bound on the donor. Narrow intense PL lines with maxima 3.47, 3.474 and 3.479 eV for specimens 1, 2 and 3 (Figure 5) also correspond to recombination of excitons bound on the donor. Intense PL spectrum of specimen 1 corresponds to radiation from GaN rods of high crystalline perfection obtained by PA-MBE method [15]. At the same time, for specimens 2 and 3 a small shift of maxima is observed towards the short wave

side, as well as expansion of the main PL line (its half-width ($FWHM$) increases from 4 to 8 meV), and appearance of an additional low intensity PL line of around 3.49 eV.

This may be related to appearance of elastic stresses when refilled by HPVE method both in the interface with „PA-MBE nucleus“, and in the defects that occurred in process of synthesis. Besides, expansion and shift of the main PL line, as well as occurrence of the additional short wave PL line, may be caused by uncontrolled doping. For example, since at refilling temperature the silicon diffusion is possible from SiO_2 substrate and layer into GaN rods [23].

4. Conclusion

Therefore, the paper demonstrated the possibility of controlled selective-area growth of GaN microrods on silicon substrate by combined PA-MBE/HVPE method. It was shown that epitaxial refilling by HVPE method makes it possible to firstly increase several times the lateral size of GaN crystals and, secondly, to form the faceting of their side surfaces. The dependence of morphology, optical properties and structure of GaN rods on the time of refilling with HVPE method was studied. The low-temperature PL method was used to show that GaN rods after refilling maintain good crystalline quality. It was also found that distribution by size and degree of order on the substrate of GaN rods after refilling are determined to a large extent by characteristics of initial arrays of etching GaN crystals. To produce the arrays of GaN microrods suitable for device applications, further optimization of the proposed combined growth method is necessary. In particular, to control polarity and to form ordered arrays, silicon substrates with buffer layers of III-nitrides may be used.

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Conflict of interest

The authors declare that they have no conflict of interest.

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