Original articles

Structural and optical properties of composition-graded InGaN nanowires

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Abstract

At the moment, InGaN ternary compounds are of a great interest for the development of devices for sunlight driven water splitting. However, the synthesis of such materials is hindered by the fact that $In_xGa_{1-x}N$ layers are susceptible to phase decomposition at x from 20 to 80%. Nanowires can be a promising solution to this problem. The purpose of our study was to analyze the structural and optical properties of $In_xGa_{1-x}N$ nanowires with a gradient x content being inside the miscibility gap.

$In_xGa_{1-x}N$ nanowires were grown on silicon substrates using plasma-assisted molecular beam epitaxy. The structural properties of nanowires were studied using scanning and transmission electron microscopy. The chemical composition and optical properties of nanowires were analyzed using energy-dispersive microanalysis and photoluminescence spectroscopy.

It was shown for the first time that the composition-graded $In_xGa_{1-x}N$ nanowires with x from 40 to 60% can be grown using plasma-assisted molecular beam epitaxy. The grown samples exhibit photoluminescence at room temperature with a maximum at about 890 nm, which corresponds to an In content of about 62% according to the modified Vegard's rule and the transmission electron microscopy data. The obtained results can be of practical interest for the development of devices for water splitting induced by sunlight or sources of near IR radiation.

Keywords: InGaN, Structural properties, Miscibility gap, Molecular beam epitaxy, Optical properties, Photoluminescence, silicon

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1. Introduction

One of the main trends in the modern semiconductor industry is the development of devices which can be sources of renewable energy. In particular, devices for sunlight driven water splitting. There are a large number of materials that can be used to make water-splitting photoelectrochemical cells, including $In_xGa_{1-x}N$ ternary compounds, which are currently of great interest (1–6). Such an interest is explained by the fact that the band gap of $In_xGa_{1-x}N$ can be varied practically within the whole solar spectrum (from 0.7 eV for InN to 3.4 eV for GaN) and adjusted to the redox potential of water [1,7]. Moreover, $In_xGa_{1-x}N$ ternary compounds have a high chemical stability and a high catalytic activity [1, 2, 8]. However, the synthesis of such materials is hindered by the fact that $In_xGa_{1-x}N$ compounds are susceptible to phase decomposition, when x is from 20 to 80%, which results in low crystalline and optical quality of the grown structures [9, 10]. Nanowires can be a promising solution to this problem, since nanowires based on ternary compounds are less susceptible to phase decomposition and can be grown with a set chemical composition [11–13]. Besides, nanowires of a high crystalline quality can be grown epitaxially on substrates which differ significantly from the grown material in terms of the parameters of the crystal lattice and temperature coefficient, including on silicon [14, 15]. However, there are very few studies focusing on the growth of $In_xGa_{1-x}N$ nanowires with In within the phase decomposition region on silicon by means of molecular beam epitaxy [16–21].

The purpose of our study was to analyze the structural and optical properties of $In_xGa_{1-x}N$ nanowires with a gradient of x content being inside the miscibility gap.

2. Experimental

Samples were grown on a Riber Compact 12 molecular beam epitaxy setup with a nitrogen plasma source. The experiments were conducted on 2/4 2″ silicon substrates with crystallographic orientation (111). The substrates were put in the growth chamber and annealed at the temperature of 950 °C for 20 minutes for thermal cleaning. Then the growth temperature was reduced to 560 °C (the thermocouple temperature) and the nitrogen plasma source was ignited. The nitrogen plasma power was 400 W. The nitrogen flow rate was 0.4 cm³/min, which corresponded to the pressure in the growth chamber of $7.4 \cdot 10^{-6}$ Torr. After the pressure in the chamber was stabilized, Ga, In, and Si control valves were opened simultaneously. The beam equivalent pressures of Ga and In flows were $1 \cdot 10^{-7}$ Torr. The temperature of the silicon source was 1350 °C. The samples were doped with silicon so that they could be further used as an anode of the photoelectrochemical cell. The growth time of the samples was 20 hours and 25 minutes.

The morphology and the structural properties of the samples were studied by means of electron microscopy using a Supra 25 scanning electron microscope (Carl Zeiss) and a JEM-2100FTEM transmission electron microscope (Jeol) with an XFlash 6TI30 energy-dispersive microanalysis system (Bruker). The optical properties of the samples were analyzed on a unique setup "Complex optoelectronic unit of the National Research University Higher School of Economics – St. Petersburg" by means of photoluminescence (PL) spectroscopy at room temperature using a He-Cd laser (325 nm) with a power of 6.5 mW. The PL signal from the samples was registered using an Ms5204i monochromator (Sol instruments) and a silicon photodetector.

3. Results and discussion

Fig. 1a-c demonstrate typical SEM images of the grown InGaN nanowires. According to the SEM data, the nanowires were formed in several stages. During the first stage, nanotubes with the length of 560 nm and diameters of ~ 50 nm (Fig. 1c)

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were formed near the surface of the substrate. Then, nanowires with diameters from 100 to 200 nm were formed. The fact that the diameter of the nanowires was larger than the diameter of the nanotubes indicates a local increase in the III/V ratio. Since in our experiments the growth temperature was close to the temperature of thermal disassociation of InN in a vacuum [22–24], we assume that the formation of nanotubes can be explained by the ascending diffusion of In inside nanostructures, which in turn can result in a local increase in the III/V ratio above the nanotubes [21, 25, 26]. The height of the nanowires was 2–2.5 μm. The average density of the nanowires was $1.1 \cdot 10^9$ cm^{-2} (Fig. 1b).

An analysis of the inner structure and the chemical composition of the samples demonstrated that the concentration of In as compared to Ga in the nanotubes was about 20%. The nanotubes had a Wurtzite crystal structure. At the same time, the concentration of In in the nanowires formed above the nanotubes varied from 40 to 60% (Fig. 2a-d). Besides, at the base and in the middle of the nanowires (Fig. 2a-c) a spontaneously formed core-shell structure was observed with x of 40–50% in the cores of the nanowires and 0–5% in the shells of the nanowires. At the same time, the ratio of In with regard to Ga was 60% at the top of the nanowires. The diameter of the cores increased from 60 to 120 nm along the nanowires, while the diameter of the shells decreased accordingly, which, apparently, is explained by an increased concentration of In in the nanowires.

The samples demonstrated photoluminescence at room temperature in the range from 450 to 1000 nm (Fig. 3). The maximum PL was registered close to 890 nm. As it was previously demonstrated, the concentration of In in InGaN in the range from 0 to 50% can be evaluated with good accuracy using photoluminescence spectra [13, 16, 27, 28] according to the modified Vegard's
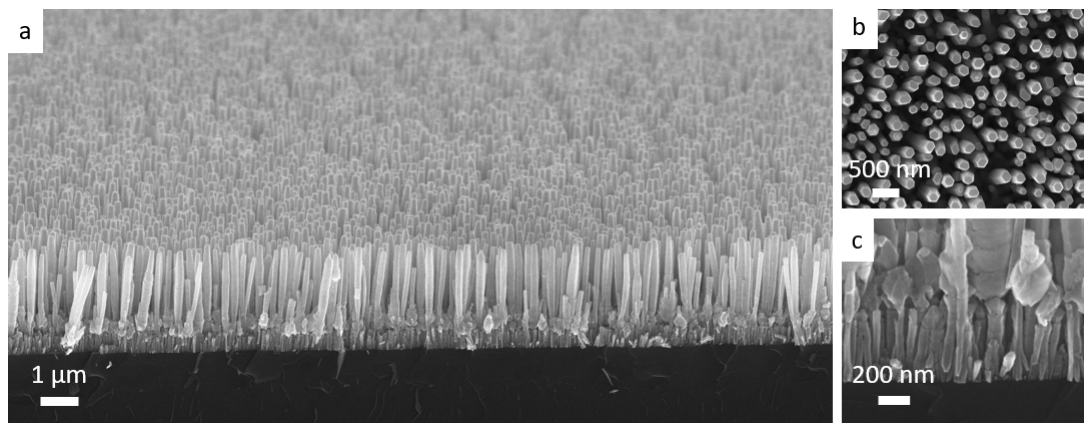

Fig. 1. Typical ISO (a) and plan-view (b) SEM images of the grown nanowires. Typical ISO SEM image of nanotubes (c)
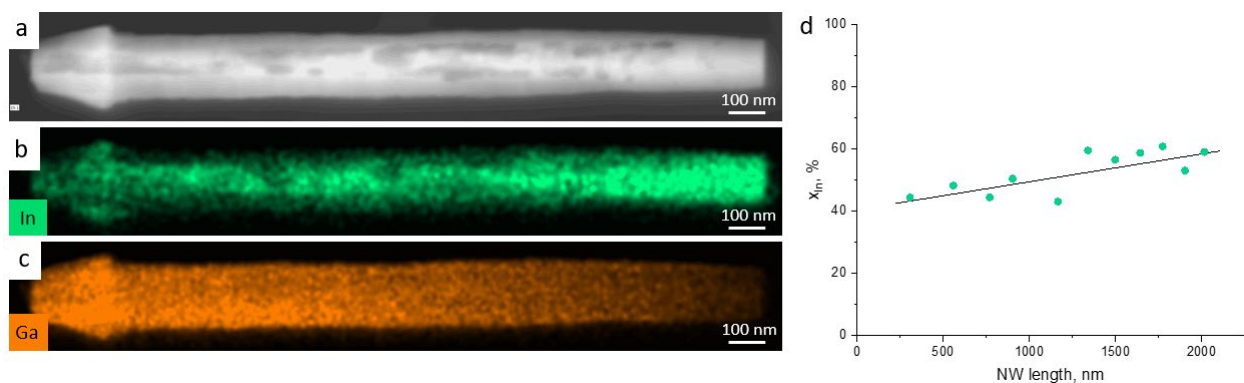

Fig. 2. A typical TEM image of InGaN nanowires (a); the distribution of Ga and In inside the nanowires (b,c); the distribution of In relative to Ga along the nanowires obtained using energy-dispersive microanalysis (d)

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law with the bowing parameter b of 1.43 eV: $E_g = xE_g^{\text{InN}} + (1-x)E_g^{\text{GaN}} - bx(1-x)$, where E_g^{InN} and E_g^{GaN} are band gaps of InN and GaN (0.7 and 3.4 eV respectively), x is the concentration of In in InGaN, and b is the bowing parameter equal 1.43 eV. If we apply this law to the PL spectrum of the grown nanowires (Fig. 3), the maximum PL should correspond to InGaN with the concentration of In of 62%, which agrees well with the chemical composition at the top of the nanowires determined by means of transmission electron microscopy. Therefore, the observed maximum PL is connected with the radiation from the top of the nanowires. At the same time, the PL spectrum demonstrated regions of relatively low intensity in the range from 500 to 700 nm, which apparently can be explained by the radiation from the low-component regions of the nanowires.

4. Conclusions

In our study, we analyzed the structural and optical properties of composition gradient InGaN nanowires. The study demonstrated that at relatively high growth temperatures (the thermocouple temperature of 580 °C) the formation of nanowires can proceed in several stages, including the formation of nanotubes and the growth of nanowires above them. According to the TEM data, the concentration of In increases along the nanowires from 40 to 60%. The obtained nanowires demonstrated maximum photoluminescence close to 890 nm, which corresponds to the concentration of In of about 62% according to the modified Vegard's law with the bowing parameter b of 1.43 eV. The obtained results can be of practical interest for the development of devices for water splitting induced by sunlight or sources of near IR radiation.

Author contributions

V. O. Gridchin – growth of the samples, analysis of the results, text writing, conclusions. R. R. Reznik – growth of the samples. K. P. Kotlyar – analysis of the samples by means of scanning and transmission electron microscopy. D. A. Kirilenko – analysis of the samples by means of transmission electron microscopy. A. S. Dragunova – analysis of the samples by means of photoluminescence spectroscopy. N. V. Kryzhanovskaya – analysis of the samples
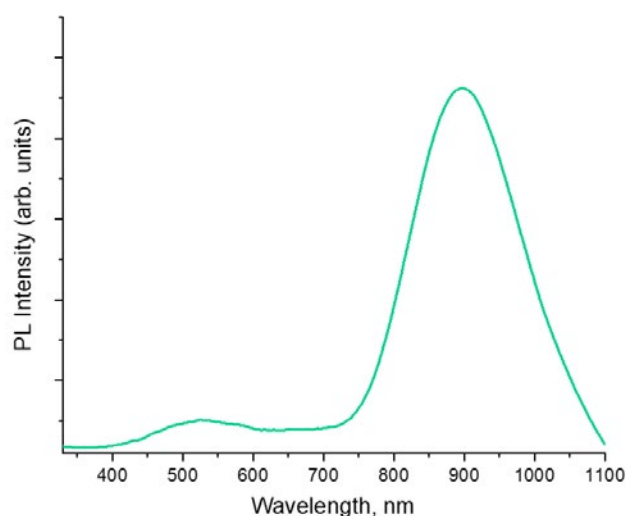

Fig. 3. A typical PL spectrum at room temperature from grown nanowires

by means of photoluminescence spectroscopy. G. E. Cirlin – problem statement, supervision.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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