Structure and Optical Properties of ZnO Nanowires Fabricated by Pulsed Laser Deposition on GaN/Si(111) Films with the Use of Au and NiO Catalysts

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Abstract—The growth of ZnO nanowires on a Si(111) substrate with a GaN buffer layer by pulsed laser deposition at a high argon pressure and with the use of Au and NiO catalysts has been investigated. Application of the low-temperature NiO catalyst makes it possible to reduce the optimal growth temperature from 900°C (in the case of the Au catalyst) to $T = 570^\circ\text{C}$ and grow ZnO nanowires 20 nm in diameter, which are highly-oriented in the direction of the c lattice axis and completely free of dislocations.

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A promising direction in nanotechnology is the development of methods of self-assembled growth of semiconductor nanowires. The combination of high optical, mechanical, and piezoelectric properties of ZnO determines good prospects of this material in design of new nanoelectronic devices.

Hybrid structures based on ZnO nanowires and films that are highly-oriented along the c axis are promising as basic elements of UV ZnO nanolasers with optical, electrical, and electron-beam pumping, UV photodetectors, nanotransistors, electron emitters, piezoelectric nanocomposites with a dielectric or polymer filling, piezoelectric transducers and acoustic receivers, high-efficiency solar energy converters, nanosensors of chemical and biological materials, and elements of devices for nanomechanics and nanospintronics.

Despite significant efforts, p -ZnO structures with high mobility have not yet been obtained. Therefore, it was proposed in [1] to use n -ZnO/ p -GaN for heterojunctions to fabricate light-emitting ZnO-based film structures. The first light-emitting heterostructure of the n -ZnO nanowire/epitaxial p -GaN film type was investigated in [2]. However, the low electroluminescence intensity in the UV region and high-intensity green luminescence indicated poor structural quality of the nanostructures obtained.

We investigated the growth of ZnO nanowires on an n -GaN epitaxial film formed on a (111)Si substrate by organometallic vapor deposition. ZnO nanowires were fabricated by pulsed laser deposition [3–6] in an evacu-

ated quartz cell using an external resistive heater. Radiation of a KrF laser ($\lambda = 248$ nm) was focused on the surface of a rotating ZnO ceramic target. The energy density in a pulse on the target surface was 2 J cm^{-2} . The laser pulse repetition rate was 3–10 Hz. Synthesis of ZnO nanowires was performed applying from 12 to 24 thousand laser pulses. The substrate temperature was varied in the range $850\text{--}950^\circ\text{C}$. The quartz cell was previously evacuated to a pressure of 5 Pa. Then high-purity (99.998%) argon was leaked into the chamber. The argon flow was 0.2 l min^{-1} at a pressure of 75–200 mbar. Si(111) substrates with previously deposited epitaxial GaN films were oriented parallel to the laser torch at a distance of 20–35 mm from the target surface. A thin gold layer ($h = 2\text{--}3$ nm), used as a catalyst, was deposited on the substrate by rf magnetron sputtering.

As our experiments showed, at temperatures from 900 to 1100°C , an Au film with a thickness of 3–5 nm is divided into isolated nanoislands due to the self-organization. With an increase in the film thickness, the average and maximum sizes of the nanoislands increase, as well as the spread of their diameters. An increase in temperature from $900\text{--}1100^\circ\text{C}$ increases the average and maximum sizes of nanoislands and decreases their density. The most uniform distribution of nanoislands with approximately equal diameters was observed for a (3–5)-nm-thick gold film, previously heated to 900°C in an argon atmosphere.

Fig. 1. HRTEM image (400 kV) of the growth defects in ZnO nanowires on a Si(111) substrate with a GaN film (Au catalyst, growth temperature 900°C).

Fig. 2. HRTEM image (400 kV) of the top part of an isolated ZnO nanowire on NiO/GaN/Si(111).

Fig. 3. Secondary-electron image of the surface of ZnO nanowires 20 nm in diameter, grown on a Si(111) substrate with an epitaxial GaN layer (catalyst NiO). The observation angles are (a) 0° and (b) 45°.

The surface morphology of the nanowires was investigated on a CamScan CS44 scanning electron microscope and a Comebax-micro electron microscope microanalyzer. According to the measurements, when gold was used as a catalyst, the nanowires were 65 nm in diameter and 1–2 μm in height for the growth at 900°C in argon. In the initial growth stages, drops of the catalyst (gold) are observed on the nanowire tips. An epitaxial ZnO film, formed in the initial growth stage, was observed between the GaN film and ZnO nanowire. Investigation by high-resolution transmission electron microscopy (HRTEM) showed that the high growth temperature (900°C) (characteristic of the use of a thin gold film as a catalyst) facilitates the formation of misfit dislocations in ZnO nanowires in directions perpendicular to the c axis in the early growth stage (Fig. 1).

The microphotoluminescence spectra of the lattice of ZnO nanowires grown on a Si(111) substrate with a GaN buffer film using gold as a catalyst showed a high photoluminescence intensity at room temperature in the UV range and a very weak peak in the visible range, which is indicative of low concentration of oxygen vacancies in the nanowires grown. The width of the emission peak of the edge exciton D^0X was 1.7 meV ($T = 2$ K); it coincides with the corresponding value for high-quality epitaxial ZnO films obtained by us by multistep pulsed laser deposition [7].

The structure of the films was investigated on a Philips X'Pert high-resolution X-ray diffractometer. The analysis showed that the X-ray diffraction patterns obtained by 2θ – ω scanning of the ZnO nanowire lattice contain only 002 and 004 reflections of ZnO nanowires; this fact indicates that the c axis of ZnO nanowires is oriented perpendicularly to the substrate and coincides with the preferred growth direction. The half-width of the ZnO 0002 reflection in the θ – 2θ scanning mode was 33 arcsec, and the half-width of the rocking curve of the 0002 reflection was $\Omega = 1564$ arcsec. For comparison, the half-width of the ZnO 0002 reflection in the θ – 2θ scanning mode is 131 arcsec for the high-quality epitaxial ZnO film, obtained by us using pulsed laser deposition at a low oxygen pressure [7].

To decrease the optimal growth temperature of ZnO nanowires, we investigated their growth on a GaN/Si(111) substrate using a thin (3–4 nm) NiO film as a catalyst. The NiO film was formed by pulsed laser deposition. The use of a low-temperature NiO catalyst (at the same pressures and flow velocities of argon and target–substrate distances) makes it possible to reduce the growth temperature to 570°C. The minimum radius of a growing nanowire decreases (at a constant gas flow), approximately inversely proportionally to the growth temperature [8]. HRTEM analysis showed that ZnO nanowires in the ZnO/NiO/GaN/Si(111) structure are completely free of dislocations and have a perfect internal structure (Fig. 2). The nanowires grown at the

substrate temperature $T = 570^\circ\text{C}$ have a diameter of 20 nm and a surface density of 10^9 cm^{-2} (Fig. 3).

In this study, we have implemented growth of ZnO nanowires, highly-oriented along the c crystallographic axis, on GaN films by pulsed laser deposition at a high argon pressure, using Au and NiO catalysts. In contrast to the nanowires grown at a high temperature, the low-temperature ZnO nanowires grown on an ultrathin NiO catalyst film have a diameter up to 20 nm, are almost completely free of dislocations, and possess a perfect internal structure.

The high structural and optical properties of the obtained ZnO nanowire/GaN film hybrid heterostructures on a silicon substrate make them promising for application in new devices of nanoelectronics and nanophotonics.

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