OPTOELECTRICAL CHARACTERIZATION OF WELL ORIENTED N-TYPE ZnO NANOROD ARRAYS ON P-TYPE GaN TEMPLATES

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Abstract

A heterojunction formed between a single n-type ZnO nanorod and p-type GaN template was successfully prepared by low cost chemical bath deposition technique. Periodic circular patterns were fabricated by focused ion beam etching through poly(methyl methacrylate) mask to control the size, position, and periodicity of the ZnO nanorods. A possible growth mechanism is introduced to explain the growth process of the nanorods. Optical and electrical properties of the heterojunctions were investigated by low temperature photoluminescence spectroscopy and by the measurement of current-voltage (I-V) characteristics. The I-V characteristics were measured by directly contacting single ZnO nanorods with the conductive atomic force microscopy tip. The diode-like rectifying behavior was observed with a turn-on voltage of *2.3 V* and the reverse breakdown voltage was *5 V*.

Keywords: ZnO nanorods, focused ion beam, ZnO/GaN heterojunctions, photoluminescence spectroscopy, conductive atomic force microscopy

1. INTRODUCTION

The problem with reproducibility in preparation of stable p-type in ZnO [1] emphasizes the importance of heterojunctions realized on p-type GaN. The combination of ZnO and GaN was first motivated by the desire to find a suitable substrate for heteroepitaxy [2]. As a result of the same wurtzite crystal structure with similar lattice parameters in both materials, heteroepitaxial layers of ZnO on GaN showed better structural quality as compared with other substrates, such as sapphire. Nevertheless, even very close lattice constants do not enable to prepare heterojunctions with acceptable device quality. The situation is quite different for the growth of high quality nanosized heterojunctions of ZnO, since the strain in nanostructures can be efficiently relieved by elastic relaxation of the free lateral surfaces rather than by plastic relaxation. The nanosized heterojunctions are expected to have a good interface contact, because the nanosize contact area and the small lattice mismatch between GaN and ZnO lead to epitaxial growth without extended defects. The nanosized heterojunctions are commonly fabricated by epitaxial growth of vertically oriented one-dimensional ZnO nanostructures, such as nanorods or nanowires. One of the crucial problems in such heterojunctions is to create electrical contact on the ZnO nanorods. Conventionally, a three-step approach is used [3-6]: first, the space between individual ZnO nanorods is filled with an insulating material; second, oxygen plasma is used to remove the insulating layer from the top of the ZnO nanorods; and finally, a contact is deposited. Moreover, in a majority of studies, the GaN substrate is covered with a ZnO seed layer to lower the nucleation barrier. All three fabrication steps strongly affect both electrical and optical properties of ZnO nanorods and current transport in such heterojunctions.

In this work we demonstrate an efficient method to fabricate single ZnO nanorod/GaN heterojunctions. The optical and electrical properties of these heterojunctions are studied by photoluminescence spectroscopy and by the measurement of current-voltage (I-V) characteristics.

2. EXPERIMENTAL METHODS

The p-n junction consist of n-type ZnO nanorods which are grown directly on p-type GaN:Mg epitaxial layer. The *2μm* thick Mg doped GaN layer with the hole concentration of $5x10^{17}$ cm^{-3} was grown on saphire/n-type

GaN template (HVPE; Kyma, Inc.). The n-type ZnO nanorods were grown by chemical bath deposition in aqueous solution consisting of zinc nitrate hexahydrate and hexamethylenetetramine [7,8]. The growth was carried out at *95°C* for *2h* in *5* and *50 mM* equimolar solutions. Prior the growth, the GaN film was cleaned for *5 min* in acetone at room temperature in an ultrasonic bath and rinsed with high purity DI water. Than it was etched for *20 min* in concentrated ammonium hydroxide solution *(28%)* at *50°C* and finally rinsed with high purity DI water and dried in Ar. The cleaning procedure was important to assure uniform nucleation of the ZnO nanorods. To precisely control the position and size of the ZnO nanorods, a GaN film with lithographic pattern was used. First, a *200nm* polymethylmethacrylate (PMMA) film was deposited by spin-coating on the GaN template. Then, a Ga^+ focused ion beam (FIB) was used to fabricate circular hole arrays in the PMMA layer (the acceleration voltage and the probe current were *30 keV* and *57 pA,* respectively). The patterned PMMA layer served directly as a mask, as it is resistant to the growth solution.

The morphological analysis of the ZnO nanorods was carried out by scanning electron microscopy (SEM). The photoluminescence (PL) spectra were measured with a set-up comprising a HeCd laser *(325 nm)* as an excitation source, a grating monochromator Jobin Yvon THR 1000, a closed cycle He optical cryostat, and photomultiplier detection system (S1 operated at *77K*). The DC electrical properties of single n-type ZnO nanorod/p-type GaN heterojunctions were studied by the measurement of their I-V characteristics using conductive atomic force microscopy (AFM) (Nano Wizard 4, JPK Instruments). Single ZnO nanorods were contacted directly by conductive AFM tip; the p-type GaN template was contacted by conductive silver paste.

3. RESULTS AND DISCUSSION

Figure 1 (a) shows that the chemically etched non-patterned GaN substrate is uniformly covered with randomly nucleated ZnO nanorods. The ZnO nanorods are well oriented with hexagonal rod shapes suggesting that they grow epitaxially along the c-axis. Nevertheless, the random nucleation of the ZnO nanorods results in high variation of their diameter and length; the diameter varies from *100* to *500 nm* and the length is up to *7 μm.*

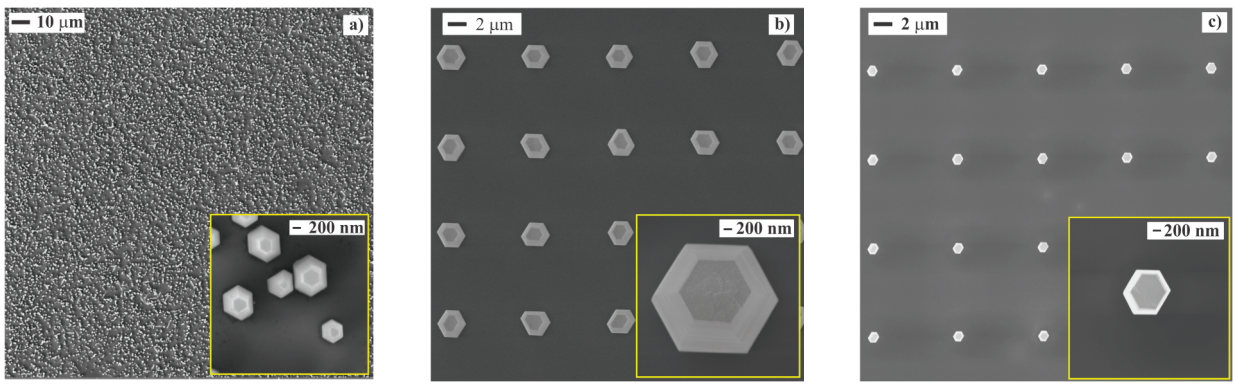

Figure 1 SEM images of the ZnO nanorods grown by chemical bath deposition on p-GaN:Mg epitaxial layer: (a) non-patterned with *50 mM* concentration of precursors, (b) patterned with *50 mM* concentration of precursors, (c) patterned with *5 mM* concentration of precursors. The growth time and temperature were identical for all samples

To precisely control the position and size of the ZnO nanorods, the GaN template with a PMMA layer was patterned by FIB. **Figure 2 (a, b)** show dimensions of the circular hole pattern. The diameter of the hole at the interface with the GaN epitaxial layer was *~250 nm*. As presented in **Figure 1 (b, c)**, the ZnO nanorod arrays exhibited vertical alignment and uniform distribution in their diameter and length. The length and diameter of the ZnO nanorods can be easily controlled by the precursor concentration. The diameter decreases from *3 to 1 μm* when the precursor concentration decreases from *50 to 5 mM.* At the same time the nanorod length

decreases from *10.8 to 3.2 μm.* The diameter of nanorods was larger than the diameter of the pattern hole. While in the first growth step the lateral growth is limited by the hole dimension, in the second step, there is no limitation for the growth and the final rod shape is given by different growth rates of polar and nonpolar planes (**Figure 2c**). We also observed that nanorods diameter decreased in c-axis. Such behavior can be explained by time-varying supersaturation effect [9], in the stationary bath reactor the growth units are consumed during the growth.

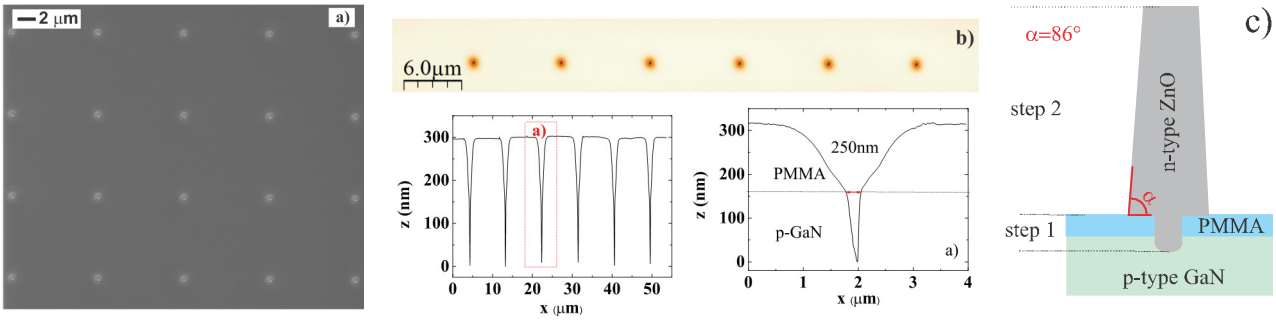

Figure 2 SEM (a) and AFM profile (b) of patterned hole prepared by FIB, c) schematically illustration two step growing process of the ZnO nanorods

Photoluminescence (PL) spectra of the ZnO nanorods and of the p-type GaN:Mg epitaxial layer are shown in **Figure 3**. The room temperature PL spectra of Mg doped GaN show a strong PL band at *2.8 eV,* which is attributed to band-Mg-doped acceptor recombination and a low-intensity near-band-edge (NBE) emission band at *3.41 eV* [10]. The *4.2K* near band edge spectrum consists of the acceptor bound exciton line at *3.45 eV* (ABE), of the line at *3.27 eV* associated with the donor-acceptor pair transition (DAP), and of the ultraviolet luminescence band at *3.2 eV* (UVL) [10-13]. The room temperature PL spectra from the ZnO nanorodsconsists of the NBE emission with the maximum at *3.24 eV* and of a broad composite band comprising three sub-bands peaked at *2.2 eV* (YL band attributed to $Zn(OH)_2$ groups attached to the surface of ZnO NRs), *2.05 eV* (OL band caused by transitions between a shallow donor and Li_{Zn} acceptor), and *1.8 eV* (RL band associated with zinc interstitials) [14-16]. At *4.2 K* the dominant exciton line at *3.36 eV* is attributed to donor bound exciton transition. The lines at *3.33 eV* and *3.22 eV* labeled as A and DAP are associated with bound exciton to structural defect transition and shallow donor-shallow acceptor transition, respectively. In the deep level region we observed only RL and OL, which are located at the same position as at room temperature; the YL is quenched at *4.2 K* [14-16].

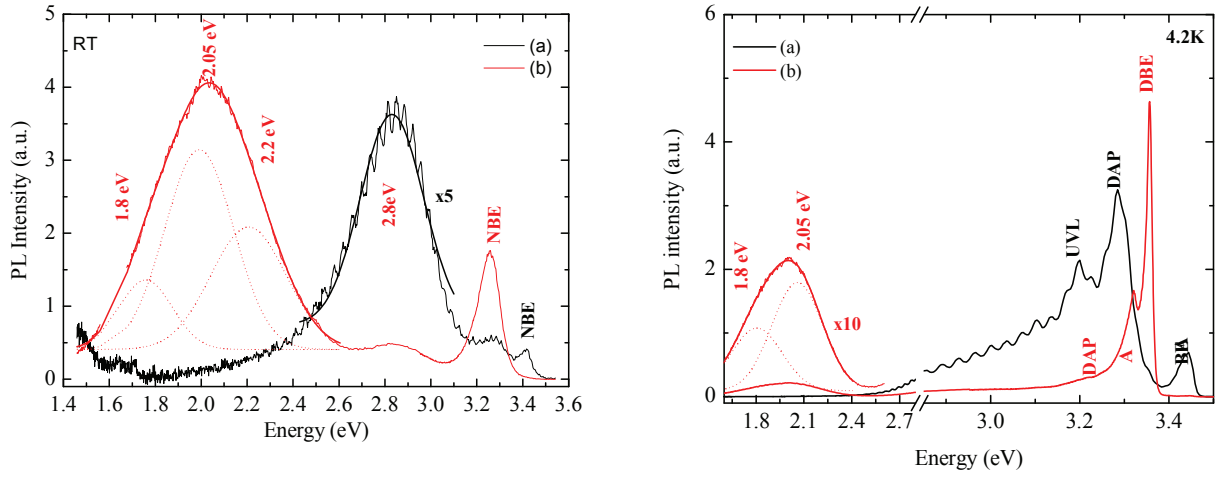

Figure 3 Room temperature and *4.2K* PL spectra of the (a) p-type GaN:Mg film; and (b) n-type ZnO nanorods

The room temperature I-V characteristics of single ZnO nanorod/GaN heterojunctions are presented in **Figure 4**. The AFM tip was placed on the top of ZnO NRs in contact mode. The forward current is approximately one order magnitude higher than the reverse current at *3 V*. The turn-on voltage of this junction is *~2.3 V*. Lower turn-on voltage obviously is explained by lower quality of the p-n junction. For the p-n heterojunction the I-V relationship can be expressed by empirical diode equation $I=I_0(exp(qV/\eta kT)-1)$ [17]. We extract ideality factor from linear part of the forward I-V characteristics (inset in **Figure 4**) by using equation $\eta=q/kT*d(V)/d(lnI)$. The high value of the ideality factor for our devices $(\eta=5.9)$ can be attributed to the defects at interface, or by multi-current transport mechanism in the heterojunction [18].

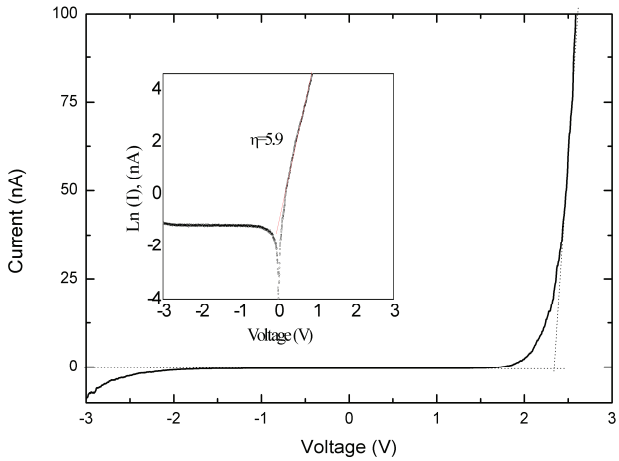

Figure 4 Room temperature I-V characteristics of the single ZnO nanorod/GaN heterojunction. The inset shows the semi-logarithmic I-V characteristics

4. CONCLUSION

We demonstrated size and position controlled selective growth of well oriented ZnO nanorods on GaN substrate by combining low temperature chemical bath deposition and focused ion beam etching. The high optical quality of the ZnO nanorods was confirmed by the low temperature photoluminescence spectroscopy; a strong bound exciton emission peak *(3.36eV)* and low defect-related peak in the visible region was obtained at *4.2K*. The DC electrical properties of the single ZnO nanorods/GaN heterojunction were studied at room temperature. Single nanorods were contacted directly by conductive atomic force microscopy tip. The heterojunction shows rectifying I-V characteristics with the turn-on voltage of *2.3 V* and the ideality factor of *5.9*. Such behaviour can be explained by presence defect at ZnO/GaN interface, or by multi-current transport mechanism.

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