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# Atomic layer deposition coating of ZnO shell for GaN–ZnO core–sheath heteronanowires

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## ABSTRACT

We have synthesized GaN-core/ZnO-shell nanowires and investigated effects of the ZnO coating. The X-ray diffraction pattern showed that as-synthesized samples are composed of GaN and ZnO. Transmission electron microscopy indicated that the deposited ZnO shell layer is poly-crystalline. The photoluminescence (PL) spectrum of GaN has been changed by the ZnO coating, where emission bands centered at roughly 1.9 eV, 2.5 eV, and 3.3 eV were newly added to the emissions from core GaN nanowires. We found that overall PL intensity has been significantly increased by coating the ZnO shell layers.

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## 1. Introduction

Hexagonal gallium nitride (GaN), with a wide-band-gap of 3.4 eV at room temperature, is suitable for the fabrication of blue light-emitting diodes and laser diodes. Zinc oxide (ZnO) has meanwhile received a great deal of attention owing to its various useful applications stemming from its large exciton binding energy of 60 meV, availability of large area substrates for homoepitaxy, etc. [1,2]. However, the fabrication of ZnO homojunction devices presents certain challenges due to difficulty in fabrication of high quality ZnO and in p doping on ZnO [3,4]. Accordingly, the fabrication of heterostructures with ZnO active regions has attracted significant interest [4]. Also, GaN is closely lattice matched to ZnO, with a mismatch of only 1.8%, and, accordingly, growth of high quality epitaxial ZnO films on GaN has been reported by several groups [5–7]. We believe that the optoelectronic devices consisting of ZnO/GaN heteronanowires will be realized sooner or later.

Semiconductor nanowires are attractive building blocks for nanoscale electronic, photonic, and sensor devices, because of the intrinsic small size, enhanced surface/volume ratio, enhanced mobility from one-dimensional (1D) confinement effects, and

stimulated emission and lasing from optical excitation of single nanowire cavities, etc. [8,9]. Also, nanowires are becoming important for their assembly into increasingly three-dimensional complex systems in future ultra-large-scaled-integration system. Accordingly, in addition to research work on GaN thin films and related devices, there have been increasing interests on the fabrication and characteristics GaN nanowires and their applications [10].

In coaxial 1D nanostructures, shell layers can afford different shapes, enhanced surface or interface area, and extremely thin films with controllable thickness, thus provide interesting physical and chemical properties unattainable with other 1D nanostructures. In our previous report, introduction of ZnO shell layer and varying the shell thickness significantly changed the structural and optical properties [11]. The changes in the structural and photoluminescence properties of core-shell nanowires with varying the shell thickness were not dependent on the core nanowires but the shell layer.

In this communication, we report on the fabrication of GaN–ZnO core–sheath heteronanowires. We have utilized atomic layer deposition (ALD) for sheathing the core GaN nanowires, as it provides a surface controlled process. The samples before and after the ZnO coating were comparatively studied with respect to their morphological, structural, and PL characteristics. Our research group previously reported on the fabrication of GaN/ZnO core-shell nanowires by means of using the Zn sputtering technique [12].

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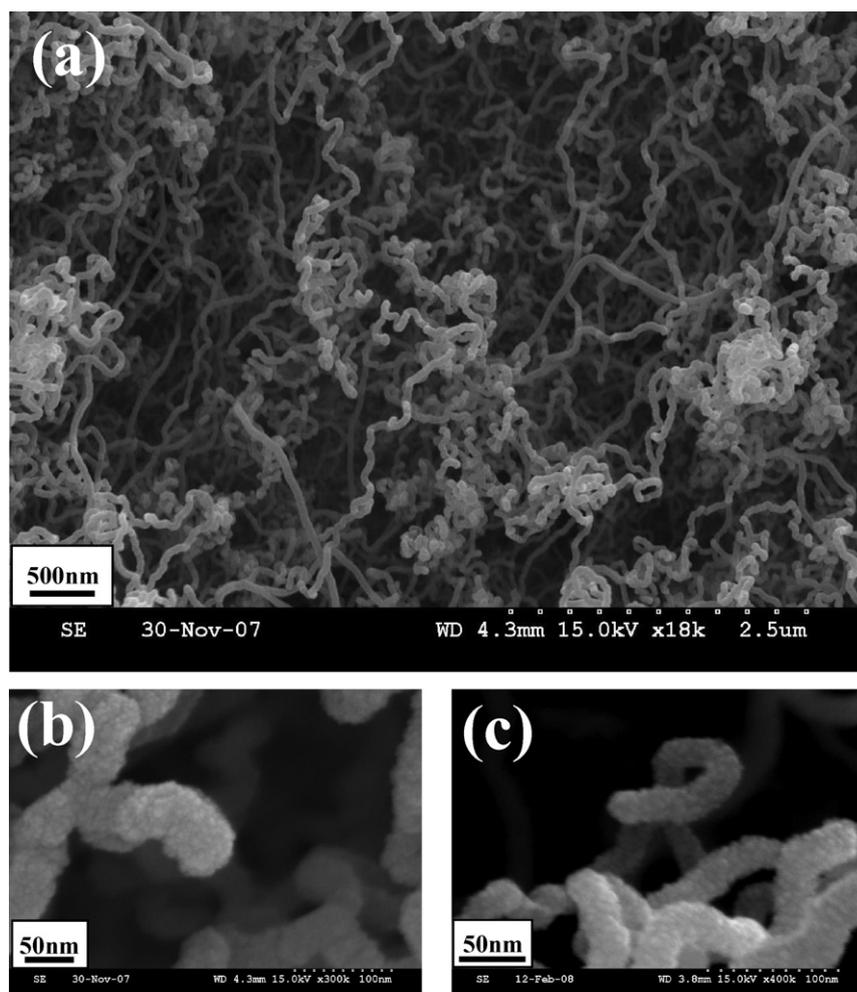


Fig. 1. (a) Typical SEM image of the GaN–ZnO core-sheath nanowires. (b) Enlarged SEM images of (b) ZnO-coated and (c) uncoated GaN nanowire.

However, the sputtering technique was not adequate for uniform coating. Not only the shell thickness was not uniform along the nanowire surfaces, but also some part of nanowires could not be coated at all. Accordingly, the introduction of surface-controlled ALD method is urgently required for future industrial applications. The ALD with a good conformability has an excellent step coverage property and able to attain the thinnest and uniform coating, which is required for future ultra-large-scale-integration scheme.

## 2. Experimental

By evaporating GaN powders, we have fabricated GaN nanowires on silver (Ag: about 10 nm)-coated Si substrates. Both the substrate and GaN powders were placed inside a quartz tube in a horizontal tube furnace. The substrate was kept at a reaction temperature of 1000 °C for 1 h under a constant flow of NH<sub>3</sub> (flow rate: 20 sccm) and Ar (flow rate: 100 sccm).

In the following step, ZnO coating experiments were carried out on the as-synthesized GaN nanowires. The substrate temperature and pressure in the ALD chamber were set to 150 °C and 0.3 Torr, respectively. With the bubbler temperature set at 10 °C, diethylzinc (DEZn) and H<sub>2</sub>O gases were alternately introduced into the chamber [11].

The structural properties were analyzed by X-ray diffraction (XRD) (Philips X'pert MRD diffractometer with CuK $\alpha$  radiation), field emission scanning electron microscopy (FE-SEM) (Hitachi, S-4200), and transmission electron microscopy (TEM) (Philips, CM-

200). The PL spectra were measured at room temperature with a dominant excitation wavelength of 325 nm, using a He–Cd laser (Kimon, 1K, Japan).

## 3. Results and discussion

Fig. 1a shows a typical SEM image of the GaN–ZnO core-sheath nanowires, indicating that the heteronanowires retain their 1D morphology. Fig. 1b presents an enlarged SEM image, revealing that the surface of the heteronanowires exhibits a small degree of roughness. For comparison, we have presented an enlarged SEM image of a core GaN nanowire in Fig. 1c. Since the surface of the core GaN nanowire is not smoother than that of the GaN–ZnO core-sheath nanowires, the surface roughness of the GaN–ZnO core-sheath nanowires appears to be attributable to that of the core GaN nanowires. It is known that growth condition significantly affects the surface smoothness/roughness of GaN surface [13]. We surmise that excess N in the present synthetic condition reduces the Ga effective diffusion length on GaN nanowire surface, inducing the rough surfaces.

Fig. 2 shows the XRD pattern of GaN–ZnO core-sheath nanowires. Diffraction peaks corresponding to a hexagonal wurtzite GaN structure (JCPDS card: No. 02-1078) are observed and the XRD pattern also exhibits reflection peaks of a hexagonal structure of ZnO, with lattice constants of  $a = 3.249 \text{ \AA}$  and  $c = 5.205 \text{ \AA}$  (JCPDS File No. 05-0664), presumably originating from the ZnO

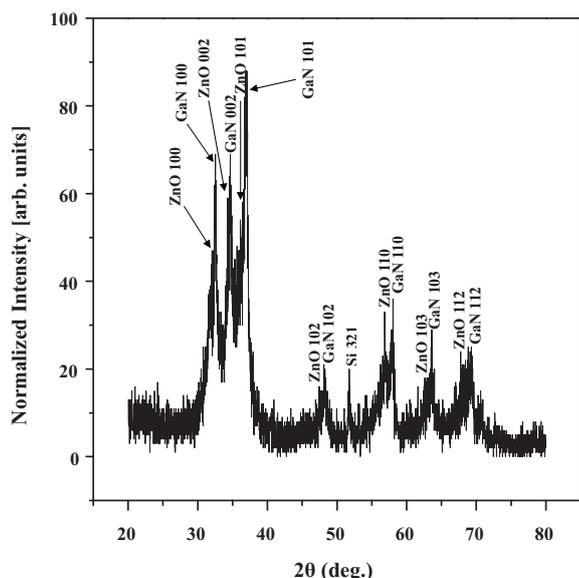


Fig. 2. XRD pattern of ZnO-coated GaN nanowires.

shell layers. Accordingly, the XRD pattern confirms that the as-synthesized samples are composed of GaN and ZnO.

Fig. 3a shows a low magnification TEM image of as-synthesized products, indicating that the structure has a wire-like morphology with a relatively rough surface on the shell layer. There exists a

slight contrast variation between the core and sheath structures, suggesting that the sheath and core of the nanowires may consist of different materials. The enlarged TEM image shown in Fig. 3b reveals that the shell layer of the coaxial nanowire comprises a crystalline phase. The interplanar spacings are about 0.28 nm, being consistent with the (100) plane of hexagonal ZnO. Fig. 3c shows the associated selected area electron diffraction (SAED) pattern. The pattern shows a halo as well as weak diffraction rings, suggesting that the ZnO shell layer contains both amorphous and poly-crystalline phases. The diffusive rings from inside to outside correspond to (100) and (101) planes of hexagonal ZnO, respectively. For comparison, the SAED pattern of core GaN nanowires prior to ZnO coating is presented in Fig. 3d, revealing that the core nanowires corresponds to hexagonal GaN structure. Figs. 3c and d shows that the ZnO shell layer covers the core GaN nanowires, effectively diminishing the reflections from the GaN core.

Fig. 4a shows the PL spectrum of the GaN core nanowires. Peak-deconvolution by means of Gaussian distribution functions shows that the broad band is composed of three peaks centered at 2.2 eV, 2.8 eV, and 3.2 eV. The blue emission band at 2.8 eV in GaN is attributed to crystal defects such as  $V_{Ga}$ -related complexes [14–16]. In particular, the yellow emission band at 2.2 eV is known to be related to defects such as  $V_{Ga}O_N$  complex [16]. Also, the ultraviolet (UV) emission around  $\sim 3.2$  eV is associated with shallow donor–acceptor-pair (DAP) transitions [17] or free-to-bound transitions (e, A transitions) [18]. Fig. 4b shows PL spectrum of the GaN–ZnO core-sheath nanowires, coated in 40 ALD cycles. Apart from the bands centered at 2.2 eV, 2.8 eV, and 3.2 eV, presumably from the GaN core, three new emission bands centered at roughly

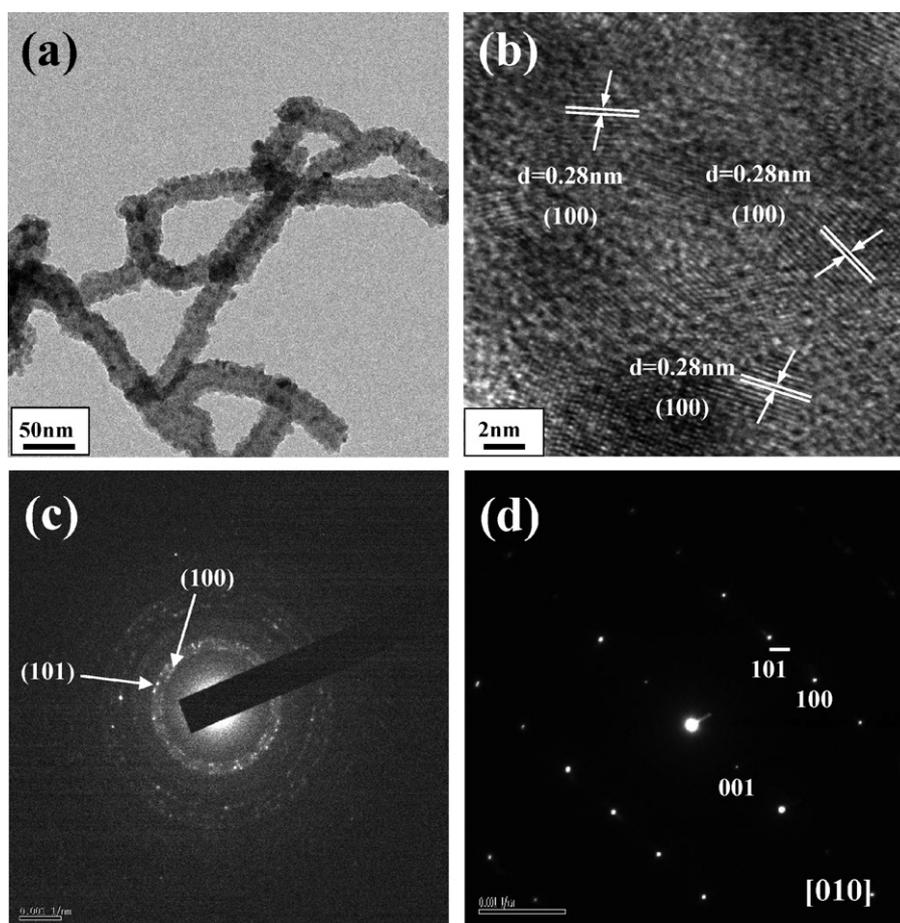


Fig. 3. (a) Low magnification TEM image of ZnO-coated GaN nanowires. (b) Enlarged TEM image, revealing that the shell layer of the coaxial nanowire comprises a crystalline phase. (c) SAED pattern of ZnO-coated GaN nanowires. (d) SAED pattern of core GaN nanowires prior to ZnO coating.

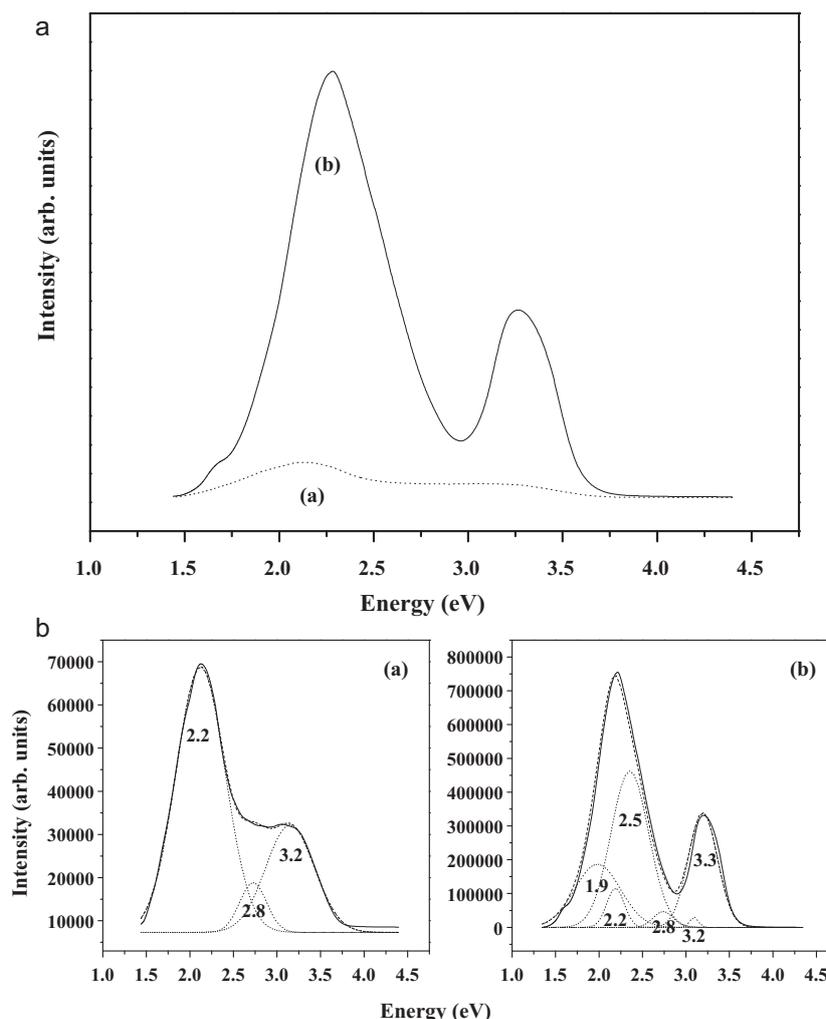


Fig. 4. PL spectra with the multi-peak Gaussian fitting of (a) GaN core nanowires and (b) GaN-ZnO core-sheath nanowires coated with a ZnO thickness of 6.4 nm.

1.9 eV, 2.5 eV, and 3.3 eV could be observed. Since these bands were generated after the ZnO coating, it was surmised that they originate from the ZnO shell layer. Although the nature of green luminescence in undoped ZnO is not yet clearly understood, in the present apparatus without Cu impurities, it appears that the green emission at about 2.5 eV can be attributed to an emission involving defects such as  $V_O$  [19–21],  $V_{Zn}$  [22,23],  $Zn_i$  [24], and  $O_{Zn}$  [25]. On the other hand, red emission band appears to be mainly attributable to defect levels in ZnO [26]. The UV emission at roughly 3.3 eV was observed from ZnO-coated GaN nanowires. In a previous study on ZnO-coated  $SiO_x$  nanowires conducted by the present authors, it was confirmed that the UV originated from the ZnO shell layer [11], as no UV emission arised from  $SiO_x$  core nanowires. Since we have coated ZnO shell layers under similar deposition conditions, it is speculated that the UV luminescence at 3.3 eV in Fig. 4b was generated from the ZnO shell layer, being overlapped with the UV emission from the GaN core nanowires. By comparing Fig. 4b with Fig. 4a, we reveal that not only the peak positions but also the intensities of GaN-related peaks were nearly invariant, in spite of the subsequent ZnO coating. It is noteworthy that the ZnO-related bands were simply added to the GaN-associated bands.

#### 4. Conclusions

In summary, GaN-ZnO core-sheath nanowires were successfully synthesized, and their structural and optical properties were

investigated. The XRD spectrum exhibits diffraction peaks corresponding to hexagonal ZnO and GaN. Lattice-resolved image and SAED pattern show that shell layers are mainly poly-crystalline with a hexagonal ZnO structure. The ZnO coating significantly changes the shape of the normalized PL spectrum, adding bands centered at 1.9 eV, 2.5 eV, and 3.3 eV, to those from GaN core nanowires.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apsusc.2011.06.022.

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