One-step fabrication and photoluminescence of alumina-sheathed GaN nanowires

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Gallium nitride (GaN)/alumina (Al$_2$O$_3$) core-shell structures were successfully synthesized by a simple and one-step thermal evaporation method. We characterized their morphology, microstructures, and optical properties by SEM, TEM, EDX, and photoluminescence (PL). The core-shell structures were comprised of a core of single crystalline, GaN nanowires surrounded by a shell of Al$_2$O$_3$ tubular structures. We proposed a base-growth process as the dominant mechanism for the growth of the core/shell nanowires. We have discussed the possible reason for the preferential formation of the Al$_2$O$_3$ shells on the outside of the core/shell structures. In regard to the core/shell structures, an emission peak of 3.3 eV was observed in the room-temperature PL measurements in addition to the GaN-associated peaks, and was attributed to the Al$_2$O$_3$ shell.

Key words: GaN, Nanowires, Alumina, Photoluminescence, Growth mechanism.

Introduction

Hexagonal gallium nitride (GaN) has a large bandgap, high melting point, saturation drift velocity, breakdown field, and chemical inertness. Accordingly, it is most attractive material for the fabrication of high temperature and high power optoelectronic devices, blue and ultraviolet light-emitting diodes and laser diodes [1, 2]. With various nanostructures exhibiting specific physical and chemical properties [3-28], the GaN nanowires has a higher surface-to-volume ratio, resulting in a higher-sensitivity for a GaN-based gas sensor and the successful application of such nanowires in future field emission displays [29, 30]. In fabricating GaN nanowires [31-33], their finite size confines the electron wave functions and quantizes the energy levels, significantly modifying the transport and optical properties [34].

In recent years, radial heterostructured nanowires have been developed to enhance the functionality of nanowires and to protect against contamination [35]. In general, insulating shells offer a lot of advantages [36-38], including chemical stability, insulating characteristics, and protection from contamination, mechanical and radiation damage. Such shells can be used to prevent strong noise in nanocircuits and they protect against unnecessary charge injection, and partially screen external fields [6, 39]. Also, the coating on GaN nanowires can improve the electron emission uniformity and capability [40].

In particular, an Al$_2$O$_3$ shell has been found to be effective in enhancing physical and chemical properties, for a variety of academic and industrial applications. Owing to the importance of such shells, numerous researchers have fabricated low-dimensional nanomaterials surrounded by an Al$_2$O$_3$ shell. For electronic applications, the passivation by a thin Al$_2$O$_3$ shell has been found to effectively remove dispersion and has improved transport properties in the channel of InAlN/GaN high-electron mobility transistors [41]. Since such a shell can play a role as a gate dielectric in coaxial field effect transistors (FETs) [42], it is crucial to study the characteristics of the Al$_2$O$_3$ shell layer on GaN nanowires. A GaN metal-organic FET (MOSFET) based on an atomic layer deposition (ALD) Al$_2$O$_3$ coating as a gate dielectric has been shown to have excellent dc output as well as transfer characteristics [43]. In Al$_2$O$_3$-coated In$_2$O$_3$ nanostructures, the Al$_2$O$_3$ shell remarkably decreased the effective work function and improved the field emission capabilities [44]. For optical applications, in ZnO/Al$_2$O$_3$ core-shell nanorod arrays, the Al$_2$O$_3$ shell generates a flat-band effect near the ZnO surface, resulting in a stronger overlap of the wave functions of carriers in the ZnO core and further enhancing the near-band-edge (NBE) emission [45]. In addition, the photoluminescence (PL) of the GaQ(3)-Al$_2$O$_3$ core-shell nanowires was not degraded in air and water vapor and was only degraded in oxygen, but to a lesser degree than uncalted nanowires [46]. Therefore, the Al$_2$O$_3$ shell was found to be effective in protecting the PL of nanowires. Peapodlike SiO$_2$/Al$_2$O$_3$ heterostructures showed a stable and strong blue emission [47].

For magnetic applications, the Al$_2$O$_3$ shell in Ni/Al$_2$O$_3$ core-shell nanowires has been used to prevent oxidation and thus to maintain magnetic memory capabilities [48]. The Fe$_3$O$_4$/Al$_2$O$_3$ core-shell microspheres not only have

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an Al₂O₃ shell, giving them a high-trapping capacity for phosphopeptides, but also have a magnetic property that enables easy isolation by positioning of an external magnetic field [49]. In the FeNi₃/Al₂O₃ core-shell nanocomposites, the Al₂O₃ insulating shell improves the soft magnetic properties of the FeNi₃ alloy [50]. Besides, the Fe₂O₃/Al₂O₃ core-shell nanoparticles can be used to obtain the highly specific capture of heme proteins for direct electrochemistry [51]. In ZnO/Al₂O₃ core-shell nanowire dye-sensitized solar cells, the Al₂O₃ shell acts as an insulating barrier to improve cell open-circuit voltage (V_{OC}) [52].

In spite of their importance, GaN/Al₂O₃ core-shell nanowires and their synthesis methods have been only rarely studied. Kang et al. reported on the fabrication of Al₂O₃-coated GaN nanowires by means of employing the ALD method [53]. In the present study, we fabricated Al₂O₃-coated GaN nanowires by heating a mixture of GaN and Al powders.

To the best of our knowledge, this is the first report on the preparation of GaN/Al₂O₃ core-shell nanowires via a one-step fabrication technique. In addition, we suggest a possible growth mechanism. In our attempt to prepare nanowires, we accidentally discovered a novel spontaneous phase separation within the Ga-N-Al-O alloy system. This approach will provide an inexpensive and simple scheme to support applications in future, ultra-large-scale integration devices and nanosystems.

**Experimental**

We synthesized GaN/Al₂O₃ core-shell nanostructures in a 51 mm inner-diameter quartz tube by means of directly heating a mixture of GaN and Al powders (volume ratio = 1 : 1). An alumina boat holding both the substrate and the mixed powders was placed inside a quartz tube in a horizontal tube furnace. The substrate was kept at the preset reaction temperature for 1 h under a constant flow of NH₃ (flow rate: 20 sccm) and Ar (flow rate: 100 sccm). The synthesis temperature was optimized in the preliminary experiments and was set at 900 °C. An Au layer (about 3 nm) on the Si substrate was deposited by ion sputtering (Emitech, K757X).

The as-synthesized product was examined by X-ray diffraction (XRD, Philips X’pert MRD diffractometer), scanning electron microscopy (SEM, Hitachi S-4300 SE), transmission electron microscopy (TEM), selected area diffraction (SAD), and energy-dispersive X-ray spectroscopy (EDX, attached to TEM). PL spectroscopy was conducted at room temperature with the 325 nm line from a He-Cd laser (Kimon, 1K, Japan) at KBSI.

**Results and Discussion**

Fig. 1(a) shows a top-view SEM image of the product at a growth temperature of 900 °C. Based on the diameter distribution graph (in upper-right inset of Fig. 1(a)), we have calculated the average diameters of the 1D nanostructures. The average diameters of the nanowires are about 46.6 nm. Fig. 1b shows an XRD pattern. Apart from the peaks of the cubic Au phase with lattice parameter of a = 4.0786 Å (JCPDS File No. 04-0784), which originated from the substrate, the most recognizable reflection peaks could be indexed to the diffraction peak in regard to the hexagonal GaN phase with a lattice parameter of a = 3.186 Å and c = 5.178 Å (JCPDS File No. 02-1078). In addition, there exist relatively weak diffraction peaks in regard to the orthorhombic Al₂O₃ phase with a lattice parameter of a = 4.844 Å, b = 8.330 Å and c = 8.955 Å (JCPDS File No.88-0107).

Fig. 2(a) shows a low-magnification TEM image of a nanowire, indicating not only that the core structure has a straight-line morphology, but also that the outer solid layer is relatively smooth and continuous along the nanowire. From Fig. 2(a), the diameter of the core structure and the average thickness of each shell layer were measured at 22 nm and 4.5 nm, respectively. On the other hand, the arrowhead in the upper-left corner of the figure indicates that the tip part of the nanowire does not comprise the metallic nanoparticle. Figs. 2(b) and 2(c) show the EDX line profiles of Ga and Al, respectively, across the diameter of a coaxial nanowire, confirming the existence of elemental Ga with a rather uniform intensity profile; there is a valley-like profile for Al. With the XRD data (Fig. 1(b)) revealing the
presence of GaN and Al₂O₃ phases, EDX line profiles and the TEM image are in good agreement with the predicted profiles for the Al₂O₃-shelled GaN nanowires.

For a detailed investigation, the lattice-resolved TEM image and SAD pattern were examined. Fig. 3(a) shows the SAD pattern taken from the square box in Fig. 2(a); this was recorded perpendicular to the rod axis, as it was indexed for the [01̅1] zone axis of crystalline hexagonal GaN. The pattern corresponds to a complicated structure, but a closer examination reveals that it consists of ring spots corresponding to poly-crystalline/single-crystalline hexagonal GaN. The single-crystal diffraction spots were indexed as the hexagonal GaN, including (011) and (111) reflections, etc. The poly-crystalline diffraction rings were indexed as the hexagonal GaN, including (100) and (300) reflections, etc. In addition, the SAD pattern shows the presence of weaker ring patterns, presumably corresponding to the poly-crystalline structures of orthorhombic Al₂O₃ ((122), (044), and (331) reflections). Fig. 3b shows a lattice-resolved TEM image, enlarging an area near the center of the nanowire in Fig. 2(a). In spite of the shell coating, lattice fringes are clearly visible in the GaN core region. The interplanar spacings between the two neighboring fringes are about 0.24 nm and 0.27 nm, agreeing with the interplanar distance of the (011) and (100) planes of the hexagonal GaN lattice. Although some part of the shell layer was found by TEM observation to be crystalline orthorhombic Al₂O₃ (Fig. 3(c)), TEM investigation does not clearly show the lattice fringes of the Al₂O₃. Accordingly, we suppose that the sheath layer must be amorphous and/or polycrystalline.

Based on the above observations, we speculated on the growth mechanism of the core-shell nanowires. Up to the present, a lot of 1D core-shell nanostructures have been synthesized, and there are two well-accepted mechanisms: the vapor-solid-liquid (VLS) and the vapor-solid (VS) mechanisms. From the TEM observation, no Au particles are clearly observed at the ends of the nanowires. Accordingly, it is not possible to regard the main growth mechanism as the Au-catalyzed tip-
growth VLS process. Some previous studies have reported the fabrication of core-shell nanowires via a VS route. In the typical VS-typed process, core nanowires from one source are first generated and, subsequently, the vapors from the other source are directly adsorbed onto the cores. For example, in the growth of SiC/Al\textsubscript{2}O\textsubscript{3} core-shell nanowires, the Si in the SiC core has been found to originate from the Si substrate [54]. The formed Al\textsubscript{2}O\textsubscript{3} cluster will diffuse to the upstream Si substrate and adsorb onto the surface of the SiC nanowires. In the fabrication of SiC/BN core-shell nanowires, the BN shell was found to originate from the BN crucible [55]. The BN layers from the BN crucibles were deposited on the outer surfaces of the SiC nanocable nucleus, forming SiC/Al\textsubscript{2}O\textsubscript{3} core-shell nanowires. However, in the present case, both core and shell structures are thought to originate from the same source, which is a mixture of powders. Accordingly, it is unlikely that the core-shell nanowires were formed via a sequential process in which the GaN stem nanowires formed first and were subsequently coated with Al\textsubscript{2}O\textsubscript{3} shell layers. Also, TEM investigation indicated that the shell thickness did not significantly vary along the wire length for any given nanowire (Fig. 2(a)). If the Al\textsubscript{2}O\textsubscript{3} shell layer was formed via the direct adsorption of gas species during the growth of GaN nanowires, the nanowire diameter should vary from the bottom to the tip. Instead, we surmise that the growth proceeded by the diffusion through the alloy particles to form the core nanowire and the migration of Al\textsubscript{2}O\textsubscript{3} on the surface of the alloy particle to the nanowire interface in a simultaneous growth process. Similarly, Moore et al. proposed a growth model for ZnS/SiO\textsubscript{2} core-shell nanowires, in which the ZnS core was formed by volume diffusion across the catalyst particles while the silica shell was formed by surface diffusion on the catalyst particle [56].

In the present case, we suggest that the alloy particle/clusters reside at the bottom of the nanowires, which is called a base-growth mechanism, and which can be included in the VLS-typed process. Similarly, previous studies on the production of carbon nanotubes [57], MgO nanowires [58], and GeO\textsubscript{2} nanostructures [59] have revealed that such growth could be ascribed to a base growth mechanism, wherein the metal catalyst remains situated at the bottom of the nanostructures.

Herein, we illustrate a possible growth model for GaN/Al\textsubscript{2}O\textsubscript{3} core-shell structures (Fig. 4). In the first step, a mixture of GaN and Al powders was heated and evaporated, forming Au/Ga/Al/N/O liquid droplets on the substrate with the incorporation of Ga, Al, N and O vapor species from the ambient (Fig. 4(a)). There are several oxygen sources in the present experiments, including residual oxygen in the chamber, leakage of the low vacuum system, and native oxide oxygen on the wafer surface. We surmise that the GaN powder will evaporate to be dissociated into Ga and N\textsubscript{2} vapors. In a previous study, GaN nanowires were grown via the following reaction: Ga + NH\textsubscript{3} → GaN + 3/2H\textsubscript{2} [60]. The Al powders can be evaporated to become Al vapors. In this case, the growth temperature should have exceeded the eutectic temperature. The main candidates of compounds should be GaN, AlN, Ga\textsubscript{2}O\textsubscript{3}, and Al\textsubscript{2}O\textsubscript{3}. The free energies of formation (ΔG\textsubscript{f}) at the growth temperature of 900 °C for GaN, AlN, Ga\textsubscript{2}O\textsubscript{3}, and Al\textsubscript{2}O\textsubscript{3}, are about -176, -371, -1269, and -1812 kJ/mol, respectively. From the thermodynamic considerations, the Al\textsubscript{2}O\textsubscript{3} compound will preferentially form in the first place, with the Ga and N atoms remaining in the droplets. The remaining Ga and N atoms will subsequently form the GaN compound. However, it is not clear when and how the Al\textsubscript{2}O\textsubscript{3} outer shell is formed. One possibility is that the Al vapor is barely soluble in the liquid droplet for some unknown reason. The Al vapor can be oxidized in the course of the surface diffusion process, ultimately forming the solid Al\textsubscript{2}O\textsubscript{3} shell. The other possibility is that the relatively low density of the Al\textsubscript{2}O\textsubscript{3} compound plays a crucial role. The densities of GaN and Al\textsubscript{2}O\textsubscript{3} compounds are 6.15 and 3.95 g/cm\textsuperscript{3}, respectively. Accordingly, it is expected that the generated Al\textsubscript{2}O\textsubscript{3} compound will float on the surface of the liquid droplet, with the GaN compound remaining inside the droplet (Fig. 4(b)). Subsequently, the liquid droplet will soon be supersaturated with GaN, and the solid GaN will nucleate underneath the
Al$_2$O$_3$ compound layer (Fig. 4(c)). The incorporation of Ga, N, Al, O gas species onto the bottom of the liquid droplet will continue, and the supersaturated Al$_2$O$_3$ will grow onto the predeposited Al$_2$O$_3$ outer layer. Similarly, the GaN will grow onto the pregenerated GaN nanostructure. Ultimately, GaN/Al$_2$O$_3$ core-shell nanowires will be formed, as depicted in Fig. 4(d).

Figs. 5(a) and 5(b) show the PL emission spectra of the uncoated and Al$_2$O$_3$-sheathed GaN nanowires, respectively. Multi-peak Gaussian fitting analysis reveals that the PL spectrum of the uncoated GaN nanowires mainly consists of five bands, which peak at approximately 1.7, 2.0, 2.5, 2.7, and 3.0 eV (Fig. 3(c)). On the other hand, the PL spectrum of the Al$_2$O$_3$-sheathed GaN nanowires mainly consists of six bands, which peak at approximately 1.7, 2.0, 2.5, 2.7, 3.0, and 3.3 eV (Fig. 3(d)). In order to reveal the origin of bands, we have compared PL spectrum of the Al$_2$O$_3$-sheathed GaN nanowires with that of the pure GaN nanowires. It can be seen that the overall intensity has been significantly reduced by adding a shell layer (Figs. 5(a) and 5(b)). Since GaN is a highly luminous material, the Al$_2$O$_3$ shell layer has significantly reduced the amount of emission from the GaN core by means of the shielding effect. The blue emission (2.7 eV) in GaN is ascribed to crystal defects such as V$_{Ga}$-related complexes [61-63], whereas the violet emission (3.0 eV) is ascribed to various defects in GaN, including dislocations and vacancies [64]. Both yellow (2.0 eV) and green (2.5 eV) emissions in GaN are known to be related to structural defects [65-67]. In particular, the red emission band (1.7 eV) of GaN originates from a donor-acceptor pair (DAP) transition process involving the deep acceptor V$_{Ga}$O$_N$ [68,69]. Also, it is noteworthy that a new peak around 3.2 eV has been added by the Al$_2$O$_3$-coating. It has been known that F$^-$ (oxygen vacancies with one electron) centers in Al$_2$O$_3$ cause UV bands centered around 3.2 eV [70, 71]. Previously, near-band-edge emission in ZnO nanorod arrays was considerably enhanced by the presence of Al$_2$O$_3$ shells [72].

### Conclusion

By means of a one-step evaporation technique, novel GaN/amorphous Al$_2$O$_3$ core-shell 1D structures were synthesized by the simple heating of a mixture of GaN and Al powders. The produced nanostructures typically consisted of a core of single crystalline GaN nanowires and a shell of Al$_2$O$_3$ tubular structures. Owing to the absence of Au-related nanoparticles at the tip, we propose as the dominant mechanism for the growth of the core/shell nanowires a base-growth mechanism. Also, we discussed a possible growth mechanism, explaining the preferential formation of the Al$_2$O$_3$ shells on the outside of the core-shell nanowires. In terms of Gaussian convolution analysis, room-temperature PL measurements of the core/shell nanowires exhibit six emission bands. Among these, the bands at 1.7, 2.0, 2.5, 2.7, and 3.0 eV are attributed to the GaN core, whereas the band at 3.3 eV is attributed to the Al$_2$O$_3$ shell. The Al$_2$O$_3$ sheaths will provide perfect electrical isolation of the GaN cores, proposing the application of the prepared nanowires in nano-electronic devices.

### Acknowledgments

This research as supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0009946).

### References
