Titanium oxide nanotube arrays for high light extraction efficiency of GaN-based vertical light-emitting diodes†

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TiO2 nanotube (NT) arrays were fabricated on the surface of n-GaN through a liquid-phase conversion process using ZnO nanorods (NRs) as a template for high-efficiency InGaN/GaN multiple quantum well (MQW) vertical light-emitting diodes (VLEDs). The optical output power of the VLEDs with TiO2 NTs was remarkably enhanced by 23% and 189% at an injection current of 350 mA compared to those of VLEDs with ZnO NRs and planar VLEDs, respectively. The large enhancement in optical output is attributed to a synergistic effect of efficient light injection from the n-GaN layer of the VLED to TiO2 NTs because of the well-matched refractive indices and superior light extraction into air at the end of the TiO2 NTs. Light propagation along various configurations of TiO2 NTs on the VLEDs was investigated using finite-difference time domain simulations and the results indicated that the wall thickness of the TiO2 NTs should be maintained close to 20 nm for superior light extraction from the VLEDs.

1. Introduction

Light-emitting diodes (LEDs) have become popular and have rapidly superseded traditional lighting sources, such as fluorescent and incandescent lamps, due to their benefits such as high energy efficiency, sustainability, and eco-friendliness.1–7 Thin-film vertical LEDs (VLEDs) in particular have attracted a considerable amount of attention as light sources that can be used in high-power illumination applications because of their excellent heat dissipation capability and uniform current injection properties.8,9 Although GaN-based LEDs have a remarkably high internal quantum efficiency (∼80%),10 the light extraction efficiency (LEE) of VLEDs is primarily limited by the total internal reflection (TIR) effect of light, which is caused by the abrupt change in refractive indices at the interface between GaN (n = 2.5) and air (n = 1). Many approaches have been proposed for reducing the TIR effect,11 such as surface texturing,12–15 antireflection coatings,16–18 and photonic crystal structures.19,20 To date, ZnO nanorods (NRs) grown using the hydrothermal method have been actively investigated because they can reduce the TIR and are favorable to be integrated on the surface of LEDs without deteriorating the electrical properties.21–25 Although the refractive index of ZnO (n = 2.0) NRs can partially mitigate the abrupt change in refractive indices between GaN and air, TIR loss and Fresnel loss still occur at ZnO/GaN and ZnO/air interfaces due to a sudden change in refractive indices, thereby limiting the enhancement of optical output in VLEDs with ZnO nanostructures.22 Therefore, it is necessary to seek an alternative material and structure for effective light injection from GaN to surface nanostructures by matching the refractive indices and for exceptional light emission from surface nanostructures such that it can further enhance the optical output of VLEDs.

TiO2 has been extensively studied as a key material for a wide range of applications in solar cells, photocatalysts, gas sensors, Li-ion batteries, and self-cleaning coatings because of its novel functional features, such as wide energy bandgap (Eg ~ 3 eV), non-toxicity, environmental friendliness, biocompatibility, and corrosion resistance.26–30 For many of these applications, TiO2 in a nanotube (NT) configuration is employed to significantly increase the density of surface nanostructures to achieve a maximum effect arising from the innate abilities of TiO2. In addition, optically interesting inferences of TiO2 are a high refractive index (n = 2.5 for the anatase phase to 2.9 for the rutile phase) and a very low absorption coefficient.
coefficient in the visible range. These optical properties can allow very interesting photonic configurations to be designed, such as negative-refractive-index photonic crystal structures and resonant waveguide grating structures. \(^{32,33}\) Therefore, integrating anatase-phase TiO\(_2\) NTs onto the surface of GaN-based VLEDs is an attractive strategy for improving the LEE because of the effective injection of light from the GaN layer to TiO\(_2\)-based surface structures by matching the refractive indices and outstanding emission of light through the TiO\(_2\) NTs by tuning the structural geometry.

Herein, we demonstrate the fabrication of vertically aligned TiO\(_2\) NTs to improve the light extraction of GaN-based VLEDs. For this purpose, TiO\(_2\) NTs were synthesized on a ZnO NR template via a liquid-phase conversion process.\(^{34}\) VLEDs with TiO\(_2\) NTs provide an enhancement in light output power of 23% and 189% compared to those of VLEDs with ZnO NRs and planar VLEDs, respectively. This improvement is attributed to the effective suppression of the TIR effect by refractive index matching and the thickness-controlled wall of TiO\(_2\) NTs. We explain the enhancement in optical output by calculating the light propagation in TiO\(_2\) NTs on VLEDs using three-dimensional finite-difference time domain (FDTD) simulations.

2. Experimental

2.1. Fabrication of GaN-based blue VLEDs

GaN-based LED wafers with a dominant emission peak at 440 nm were grown on c-plane sapphire substrates via metal organic chemical vapor deposition (MOCVD). After a 25 nm thick GaN buffer layer was grown at 550 °C, a 5 µm thick undoped GaN layer and a Si-doped n-GaN layer were grown at 1010 °C. Then, five pairs of InGaN/GaN multiple quantum well (MQW) layers were grown, followed by a p-type GaN layer. The p-GaN and MQW layers were partially etched using an inducively coupled plasma (ICP) etching process until the n-GaN layer was exposed, and Cr/Au-based n-pad electrodes were deposited using electron beam evaporation. Next, 1 mm × 1 mm VLEDs were fabricated by depositing a Ag-based p-pad electrode on the p-GaN layer by electron beam evaporation. A SiAl substrate was bonded on the p-pads, and then the laser lift-off (LLO) process was performed to separate the sapphire wafer. The Ti/Au metal layers were deposited by electron beam evaporation as n-pad electrodes after the u-GaN layer was completely etched. A patterned SiO\(_2\) mask was used to prevent the growth of ZnO NRs or TiO\(_2\) NTs on the mesa sidewalls of the VLEDs. Details of the fabrication method have been described elsewhere.\(^{35}\)

2.2. Fabrication of TiO\(_2\) NTs

Fig. 1 presents a schematic diagram of the steps for fabricating the vertically aligned TiO\(_2\) NTs on the VLEDs. The sol–gel ZnO seed used in this study was synthesized according to procedures reported in the literature.\(^{36,37}\) Zinc acetate dihydrate \((\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O})\) was first dissolved in a mixture of 2-methoxyethanol \((\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH})\) and monoethanolamine \((\text{MEA}, \text{NH}_3\text{CH}_2\text{CH}_2\text{OH})\) at room temperature. The solution was stirred vigorously at 60 °C for 30 min under ambient conditions to yield a homogeneous solution and then stored in an ice bath for 12 h to achieve a stable ZnO solution. The ZnO seed layers were deposited on the VLEDs by spin coating of the ZnO solution followed by sintering at 150 °C for 90 min. The VLEDs with the ZnO seed layers were dipped into an aqueous solution that contained 30 mM zinc nitrate hydrate \((\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O})\), 30 mM hexamethylenetetramine \((\text{HMTA}, \text{C}_6\text{H}_12\text{N}_4)\), and 5 mM polyethyleneimine \((\text{PEI})\) at 95 °C for 3 h to grow crystalline ZnO NRs on the VLEDs. Then, the ZnO NRs on the VLEDs were immersed in an aqueous solution that contained 40 mM ammonium hexafluorotitanate \(((\text{NH}_4)_2\text{TiF}_6)\) and 100 mM boric acid \((\text{H}_3\text{BO}_3)\) at room temperature for reaction times in the range of 10 to 180 min. The wall thickness of the TiO\(_2\) NTs on the ZnO NR templates was
increased as the process time of the liquid-phase conversion increased. To remove the top end of TiO\(_2\), the resulting TiO\(_2\) NTs with closed top ends were partially etched by reactive ion etching (RIE) using Cl\(_2\) as the plasma etching gas. After the physical etching process, the remaining ZnO NR templates covered by the TiO\(_2\) NTs were removed by treating with 500 mM boric acid at room temperature for 1 h (see Fig. S1 in the ESI†). The TiO\(_2\) NTs with opened top ends on the VLEDs were annealed at 450 °C for 2 h in an air furnace to convert the amorphous phase to the anatase phase. Consequently, anatase-phase TiO\(_2\) NTs with open top ends were formed on the VLEDs.

3. Results and discussion

Fig. 2a and b show bird’s-eye view scanning electron microscopy (SEM) images of the ZnO NRs and TiO\(_2\) NTs on the n-GaN layer of VLEDs, respectively. The density of ZnO NRs and TiO\(_2\) NTs on the VLED is 1.7 × 10\(^6\) cm\(^{-2}\). The average diameter and height of the ZnO NRs are approximately 160 nm and 3.0 µm, respectively. Fig. 2c–e show the top-view SEM images of the ZnO NRs, TiO\(_2\) NTs with closed top ends, and TiO\(_2\) NTs with open top ends with an average diameter of 180 nm on the n-GaN layer of VLEDs, respectively. During the liquid-phase conversion reaction, ZnO was converted to TiO\(_2\) in the solution with acids originating from the hydrolysis of hexafluorotitanate.\(^{34,38}\) Therefore, the wall thickness of the TiO\(_2\) NTs increased from 25 to 80 nm as the liquid-phase conversion reaction time increased because TiO\(_2\) NTs on the VLEDs developed as the ZnO NR templates were gradually etched away.

To investigate the structural properties of the TiO\(_2\) NTs fabricated by combining a liquid-phase conversion and a ZnO NR template-assisted method, we performed transmission electron microscopy (TEM) and X-ray diffraction (XRD) analyses. Elemental information on Ti, O, and Zn of the TiO\(_2\) NTs was obtained by scanning TEM (STEM) and energy-dispersive X-ray (EDX) spectroscopy. As shown in the STEM-EDX elemental maps (Fig. 3a), the presence of Ti and O without Zn confirms that the liquid-phase conversion method can be used to grow TiO\(_2\) NT layers on the ZnO NR template. However, these findings do not clearly indicate whether the TiO\(_2\) NTs are composed of anatase-phase crystals; therefore, we performed TEM analyses on the TiO\(_2\) NTs. Fig. 3b and c present a low-magnification bright-field TEM (BF TEM) image and the selected area electron diffraction (SAED) pattern of a TiO\(_2\) NT. The SAED pattern shows clear ring patterns, indicating that the TiO\(_2\) NT is polycrystalline, as shown in Fig. 3c. Furthermore, the diffraction pattern of TiO\(_2\) polycrystals demonstrates that the TiO\(_2\) NT structure is an anatase phase because the ring patterns correspond to the (101), (103), (004), (200), (105), (211), and (213) lattice planes, which agree well with the interplanar spacings of anatase-phase TiO\(_2\). The crystallographic properties of the TiO\(_2\) NTs are also confirmed by the high-resolution TEM (HRTEM) image presented in Fig. 3d. The HRTEM images were taken at [010] from the boxed area in Fig. 3b. The lattice spacings of 3.46 Å, 2.39 Å, and 2.34 Å correspond to the (101), (103), and (004) interplanar spacings of anatase-phase TiO\(_2\), respectively. The corresponding fast Fourier transform (FFT) pattern, shown in the inset of Fig. 3d, reveals that the selected region in the wall of the NT, as indicated by a dotted yellow rectangular area in the expanded image in Fig. 3b, is monocrystalline with an anatase structure. We performed synchrotron radiation XRD measurements using the 5D GIST beamline of the Pohang Light Source (PLS) in Korea. The X-ray energy was fixed at 10 keV (1.24 Å) using a double-bounce Si (111) monochromator. The XRD profiles of the ZnO NRs and TiO\(_2\) NTs along the substrate normal direction are presented in Fig. 3e. These two XRD profiles of surface nanostructures show a predominant diffraction peak of sapphire (0006) at 33.27°. Peaks appear at 27.56° and 56.89° in the diffraction pattern of the ZnO NR template, and they correspond to the (0002) and (0004) planes of the wurtzite structure of ZnO, respectively. The well-defined (0002) and (0004) Bragg reflections indicate that the ZnO NRs are monocrystalline with the <0002> orientation aligned to the substrate normal direction. The peak positions of the TiO\(_2\) NTs in the XRD pattern are shown in Fig. 3c, and the peaks were well matched with the standard XRD data file for an anatase-phase TiO\(_2\) with lattice constants of \(a = b = 3.78\) Å and \(c = 9.49\) Å. The XRD peaks corresponding to the anatase-phase TiO\(_2\) crystal planes of (101), (103), (004), (200), (105), (211), (213), (220), and (215) indicate that anatase-phase TiO\(_2\) NTs can be efficiently formed on the ZnO NR template using the liquid-phase conversion process. Furthermore, if the monocrystalline ZnO remained inside the polycrystalline TiO\(_2\) NTs, the XRD profile of TiO\(_2\) NTs shown in Fig. 3e should show the XRD peaks of ZnO at 27.56°.
and 56.89°. However, these peaks were not observed in the XRD data and the result indicates that wet-etching can completely remove ZnO inside the TiO2 NTs with a height of 3 µm.

To investigate the effect of the TiO2 NT configuration on the optical properties of the VLEDs, three-dimensional FDTD simulations were conducted. Fig. 4a–c present the results of FDTD simulations for planar VLED, ZnO NR VLED, and TiO2 NR VLED, respectively. The model structure of the VLED is surrounded by a perfectly matched layer (PML).39 A monochromatic blue light source with an emission wavelength of 440 nm is located in the GaN layer. In the ZnO NR VLED, flat-end ZnO NRs with a diameter of 180 nm and a height of 3.0 µm stand on the GaN layer, as determined by the SEM images shown in Fig. 2a. Although an electric field with a high intensity efficiently guides through the ZnO NR structure, coupling of this guided light into air is limited due to the Fresnel reflection at the flat end of the ZnO NRs. Therefore, Fig. 4b clearly shows that the intensity of the electric field within the ZnO NRs is strong because of the constructive interference of light waves reflected at the two different interfaces, the ZnO/GaN interface and the ZnO/air interface, due to a sudden change of refractive index at each interface (see Fig. S2 (ESI†) for detailed information). Fig. 4c, however, shows that the electric field intensity inside of the TiO2 NR is relatively weak due to the elimination of reflection at the TiO2/GaN interface by refractive index matching. The weak electric field intensity at the end of TiO2 NRs could be attributed to the increase in the Fresnel reflection due to the large difference in the refractive indices between TiO2 and air, although...
the light generated from the active region of the VLED efficiently injects into the TiO₂ NRs compared to ZnO NRs because of the well-matched refractive indices between TiO₂ and GaN. However, TiO₂ in a NT configuration could more efficiently emit the guided light toward air. As shown in Fig. 4d, the intensity distributions of the cross-sectional electrical field within TiO₂ NTs with different wall thicknesses from 10 to 80 nm were simulated, and the largest enhancement was realized by a wall thickness of 20 nm. For the TiO₂ NTs with a wall thickness of 20 nm, the injected light from the GaN layer is effectively guided through the hollow core region of the NTs, whereas the intensity of the electric field within the wall region of the NTs is weaker than that in the hollow core region. This result indicates that the light within the wall region of TiO₂ NTs can be efficiently emitted into air, because the coupling of light in the fundamental mode of NT with air increases with decreasing wall thickness.⁴⁰ Hence, Fig. 4d depicts that the electric field intensity outside TiO₂ NT is higher with decreasing wall thickness. Note that the simulated optical output of TiO₂ NTs decreased as the wall thickness increased above 20 nm. This tendency is attributed to the increase of bound waves within the wall region of TiO₂ NTs because the light propagating along the wall region can be reflected back at the topmost surface of the TiO₂ NTs. Although the light is more weakly trapped within the wall region of the TiO₂ NTs with decreasing wall thickness, light injection from GaN to the TiO₂ NT layer is also diminished due to the reduction of the effective contact area between the TiO₂ NT and GaN layers. Thus, a relatively lower intensity of the electric field is observed above the top end of TiO₂ NTs with a wall thickness of 10 nm compared to those with a wall thickness of 20 nm. Therefore, these simulation results show that the wall thickness of the TiO₂ NTs should be maintained close to 20 nm to maximize the LEE of TiO₂ NT VLEDs (see Fig. S3–S5 (ESI†) for detailed information).

The current–voltage (I–V) characteristics of the planar VLEDs, ZnO NR VLEDs, and TiO₂ NT VLEDs with various wall thicknesses are presented in Fig. 5a. The forward voltages of these VLEDs show almost the same value of 3.5 V at 350 mA. The I–V characteristic curves of VLEDs with various surface structures are almost identical, indicating that the electrical properties of the VLEDs were not degraded by the solution-based processes for growing the ZnO NRs and TiO₂ NTs. Fig. 5b presents the electroluminescence (EL) spectra of the VLEDs recorded at an injection current of 350 mA. As shown in Fig. 5b, the EL intensity of the TiO₂ NT VLEDs increases as the wall thickness of the TiO₂ NTs approaches 25 nm. These results are consistent with the simulation results, as shown in Fig. 4b. Fig. 5c shows the light output power–current characteristics of the TiO₂ NT VLEDs. The light output power of the TiO₂ NT VLEDs with a wall thickness of 25 nm is higher by a factor of 1.23 and 2.89 compared to the ZnO NR VLEDs and planar VLEDs, respectively, at an injection current of 350 mA. This large enhancement in the light output power of TiO₂ NT VLEDs can be attributed to the efficient propagation of light from the GaN layer to the TiO₂ NT layer and superior mitigation of back reflection of light at the interface of TiO₂ NTs and air. These results indicate that TiO₂ NTs grown on GaN-based VLEDs are more effective light-extracting nanostructures than ZnO NRs for high-efficiency VLEDs.
4. Conclusions

In summary, we demonstrate that the surface nanostructure of TiO$_2$ NTs on the n-GaN layer greatly enhances the optical output of VLEDs. The liquid-phase reaction was employed to convert the ZnO NR templates into TiO$_2$ NTs. The high-resolution TEM and XRD analyses reveal that the TiO$_2$ NTs are in a polycrystalline configuration with the anatase phase. The electrical properties of the VLEDs with TiO$_2$ NTs are not degraded by the formation of surface nanostructures. The TiO$_2$ NTs grown on the VLEDs efficiently enhance the light output power by 23% and 189%, compared to the ZnO NR VLEDs and planar VLEDs, respectively, at an injection current of 350 mA. The large enhancement in the optical output power is attributed to the superior suppression of the TIR between the GaN layer and air by employing refractive index matched and geometric configuration controlled TiO$_2$ NTs. This work provides architectural design guidelines for novel TiO$_2$ NT structured surfaces by employing refractive index matched and geometric configuration controlled TiO$_2$ NTs. The high-resolution TEM and XRD analyses reveal that the TiO$_2$ NTs are in a polycrystalline configuration with the anatase phase. The electrical properties of the VLEDs with TiO$_2$ NTs are not degraded by the formation of surface nanostructures. The TiO$_2$ NTs efficiently enhance the light output power by 23% and 189%, compared to the ZnO NR VLEDs and planar VLEDs, respectively, at an injection current of 350 mA. The large enhancement in the optical output power is attributed to the superior suppression of the TIR between the GaN layer and air by employing refractive index matched and geometric configuration controlled TiO$_2$ NTs. This work provides architectural design guidelines for novel TiO$_2$ NT structured surfaces to improve the optical performance of various optoelectronic devices, such as semiconductor LEDs, organic LEDs, and solar cells.

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Notes and references

1 S. Nakamura, Rev. Mod. Phys., 2015, 87, 1139.