Light-Emitting Diodes with Hierarchical and Multifunctional Surface Structures for High Light Extraction and an Antifouling Effect

Young-Chul Leem, Jung Su Park, Joon Heon Kim, NoSoung Myoung, Sang-Youp Yim, Sehee Jeong, Wantae Lim, Sung-Tae Kim, and Seong-Ju Park*

Recent technical demands in the lighting industry require innovative performance features from lighting sources, such as high brightness, high energy efficiency, environmental friendliness, high reliability, and sustainability. Light-emitting diodes (LEDs), in particular group III-nitride-based LEDs, have rapidly replaced conventional lighting sources, such as incandescent bulbs and fluorescent lamps, because they can meet these industrial requirements. The evolution of LEDs has been mainly driven by the significant developments of sophisticated growth techniques and bandgap engineering. The advent of these developments enabled LEDs to obtain high internal quantum efficiency (≈80%) with excellent reliability and sustainability. The other factors enabling the remarkable progress of LEDs have been achieved through modifications of the chip and surface configurations that can enhance the light extraction efficiency (LEE) in LEDs. Although the electrical and optical properties of LEDs have evolved dramatically because of the above-mentioned developments, there is a desire to achieve further enhancements of the optical output and to introduce additional functions into LEDs so that they can serve as next-generation light sources for diverse illumination applications.

Natural systems have inspired various applications in the field of optics, electronics, chemistry, and biomimetics because nature already includes highly developed configurations as survival strategies against various environmental conditions. Imitating a natural configuration that has a superior optical property is a possible strategy to improve the performance of LEDs. Interestingly, many of these structures found in nature exhibit highly ordered hierarchically structured surfaces from the micro- to nanometer scales, and they are often multifunctional. For example, the structures found in the compound eyes of moths to minimize the reflection of light over a broad range of angles are highly similar to the superhydrophobic structures of mosquito eyes and lotus leaves. Therefore, the adoption of these versatile surface structures in LEDs can be expected to yield not only high optical efficiencies but also additional surface properties, such as the self-cleaning effect due to superhydrophobicity, which is desirable for applications in diverse illumination conditions.

To date, several approaches to fabricate hierarchically structured surfaces on LEDs have been reported to increase the LEE by the synergistic effect of microstructures and nanostructures: microstructures provide multiple scattering at the LED/air interface, whereas nanostructures result in a smooth transition of the refractive indices at the surface of the LEDs. However, in all these studies, the nanostructures are randomly located on the microstructures due to the lack of methods for fabricating well-ordered nanostructures on nonplanar or curved surfaces. Furthermore, the specific functionalities created by bioinspired structured surfaces strongly depend on the pattern fidelity, although most of these surfaces maintain their functionality even with some imperfections and defects. Therefore, the fabrication of well-ordered multiscale structures that efficiently imitate the configuration of nature with superior optical properties is highly appropriate for the development of high-performance LED devices.

In general, an encapsulation of a rough-surface LED can increase the LEE, but it can also cause problems, such as discoloration at high light flux densities, extension of the optical source size, and low thermal conductivity of the encapsulating layer. These problems have been linked with lower quantum efficiencies, higher junction temperatures, and a decrease in the brightness of such LEDs. Therefore, unencapsulated LEDs are desirable for next-generation LED applications.

When well-ordered hierarchical structures inspired by nature are recreated on the surface of unencapsulated LEDs, they can further enhance the optical output and add new functionality, such as an antifouling effect. In practical use, lighting equipment with LEDs is often exposed to pollution, which leads to a partial blocking of the light emitted to the environment.
communications

air and a reduction of the optical output. This problem can be overcome via the integration of hierarchical structures with superhydrophobic properties on the surface of LEDs to obtain water contact angles higher than 150° and thus achieve self-cleaning behavior.[26–28] However, superhydrophobicity alone is not sufficient to prevent contamination of the LED surfaces because it can repel water but not oil.[29,30] Therefore, the surfaces of LEDs should be made to repel not only water but also nonpolar liquids with low surface tensions, such as oils and organic solvents. Such highly oleophobic surfaces, which can highly repel any contacting oils, are expected to widen the range of illumination applications using LEDs. Adoption of these novel surfaces in LED applications can lead to a competitive advantage resulting from the self-cleaning phenomenon for electronic billboards, street lamps, exterior illumination, and finger-print resistant surfaces for touch panels and cell phones.[31,32] Furthermore, it is expected that the LEDs with superhydrophobicity and high oleophobicity will pioneer new applications in medicine, such as optogenetic neuromodulation and photodynamic therapy, which demand spatially and temporally precise light illumination to target neuronal tissue or tumor tissue without pollution of the light sources in the blood, fluid, and lipids in the human body.[33–37]

Here, we demonstrate the fabrication of a novel hierarchically structured surface with well-ordered features to achieve an extremely high LEE in GaN-based vertical-structure LEDs (VLEDs) with superhydrophobicity and high oleophobicity for the antifouling effect. VLEDs fabricated by laser lift-off (LLO) and wafer bonding processes are promising candidates for high-power LEDs because they have several advantages, such as an excellent capability for heat dissipation and uniform current spreading.[38,39] silica nanospheres serving as an etching mask were deposited on the microdome-structured surface of VLEDs[40] via self-assembled dip-coating methods[41] and nanopatterning transfer methods. VLEDs with hierarchically structured surfaces showed a 3.16-fold higher LEE compared to that of planar VLEDs. Here, we also explain the light extraction process in VLEDs with hierarchically structured surfaces by using an electromagnetic simulation. Moreover, superhydrophobic and highly oleophobic properties with contact angles of 153° for water and 143° for corn oil were observed on the hierarchically structured surfaces of VLEDs. The Cassie–Baxter model was employed to explain the highly oleophobic wetting property.[42]

Figure 1 is a schematic of the fabrication steps for the hierarchical structures on the nitrogen (N)-face GaN-based VLEDs. The technique uses a transfer of close-packed 2D colloidal crystals, which were formed on the planar sapphire substrate by dip-coating, to the GaN microdome surface of the VLEDs via a thermal-release tape. The sapphire substrate was pretreated in oxygen plasma at room temperature for 5 min to modify the surface energy of the sapphire substrate to repel with the 2D colloidal layer. A dip-coating method was used to deposit hexagonally close-packed (HCP) 2D colloidal crystals of silica nanospheres with a diameter of 100 nm using an ethanol solution containing 15 wt% silica nanospheres. The film of silica nanospheres has a blue iridescence due to the constructive interference of visible light by the ordered colloidal crystals. Then, the HCP 2D colloidal crystals were transferred from the sapphire substrate to the microdome structures on the N-face GaN of the VLEDs through a thermal-release tape. The VLEDs with microdome structures covered with the thermal-release tape were baked at 110 °C to release the tape for the transfer of the HCP 2D colloidal layer from the tape to the microdome structures. Next, inductively coupled plasma (ICP) etching was performed to transfer the pattern of HCP 2D colloidal crystals to the surface of the microdomes. After the ICP etching process, the residual silica nanospheres were removed by a buffered oxide etchant (BOE). To produce a highly oleophobic solid surface, a combination of novel surface structures inspired by nature and chemical modification is typically required to lower the surface energy of the solid.[43] The surface energy of LED surfaces with hierarchical structures was further reduced by exposing them to 5% 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDTS) vapor in toluene inside an oven at 90 °C for 3 h. Then, the chemically modified hierarchically structured surfaces were dried for 12 h in an ambient environment. Hierarchically structured surfaces consisting of periodic microdome arrays and conical subwave-length nipple arrays formed on the VLEDs. The detailed fabrication procedures are described in the Experimental Section and Supporting Information.

Figure 2a,a’ shows the top view (bird’s eye view) scanning electron microscopy (SEM) images of the hierarchical structures fabricated on the VLEDs. Each microdome in the array of microdomes with a HCP structure has a diameter and height of 3 and 1.5 µm, respectively. As shown in the magnified SEM image of Figure 2a,a’, the HCP array of nanoscale nipples is formed on the microdomes, and the diameter and height of the nanonipples are 100 and 300 nm, respectively. Different etching rates of the silica nanospheres and GaN microdomes enabled the formation of the nanonipple array. Figure 2b shows bird’s eye view SEM images of the silica nanosphere-coated microdome structure as a function of etching time. The conical GaN nanoscale nipple array is developed as the silica nanospheres are gradually etched away on the N-face GaN layer with increasing ICP etching time.

The current–voltage (I–V) characteristics of the VLEDs with planar, microdome, and hierarchically structured surfaces (Figure 3a) show that the forward voltages of 3.39–3.40 V are nearly equal and that the series resistances of 1.9–2.0 Ω are highly similar. Furthermore, the reverse leakage currents of the three VLEDs are less than 10⁻⁵ mA at −10 V (inset of Figure 3a). These results indicate that the ICP etching process does not affect the electrical properties of the VLEDs with various optical structures. The electroluminescence (EL) spectra of VLEDs with planar, microdome, and hierarchical structured surfaces (Figure 3b) were measured at an injection current of 350 mA. The EL intensities of VLEDs with the three different optical structures increased with an increasing level of hierarchy in the top-most optical structures of the VLEDs without showing any peak shift of the EL spectra. These findings indicate that the formation of optical structures on the GaN microdomes increases the LEE of VLEDs without degrading the optical recombination process in the active regions. The light output power-current characteristics of VLEDs with a pristine microdome and hierarchically structured microdome are 2.70- and 3.16-fold higher,
respectively, than those of the planar VLEDs at an injection current of 350 mA (Figure 3c).

To investigate the mechanism responsible for the enhancement of the optical output power of VLEDs, cross-sectional confocal scanning electroluminescence microscopy (CSEM) analysis of the light emission was performed on VLEDs with the pristine microdome and hierarchical structured surfaces (Figure 3d,e). As shown in the confocal CSEM mapping images, the EL intensity of the hierarchically structured VLED was significantly higher than that of the microdome structured VLED. Figure 3d shows that the gap region between the microdomes appears bright because photons have a higher likelihood of escaping through the gap region due to the decrease in the total internal reflection (TIR) effect at the microdome structured GaN/air interface. In contrast, Figure 3e shows that the central portions of the hierarchically structured microdomes are brighter than the peripheries and gap region between the hierarchical structures. This emission enhancement can be attributed to the further reduction of the TIR effect at the GaN/air interface for the hierarchically structured microdomes. Because the distance between the nipples on the microdome structures is shorter than the emission wavelength, the nipple array at the interface can be considered a medium with a graded refractive index according to the effective medium theories. Thus, the smooth change in refractive indices at the GaN/air interface can remarkably increase the transmittance of the light from the GaN to air, resulting in an enhancement of light extraction at the surface of the hierarchical structures.

To reveal the details of the light propagation through the hierarchically structured surfaces, 3D finite-difference time domain (FDTD) simulations were performed (see the Experimental Section). Figure 4a–c shows geometries of simplified VLEDs with planar, microdome, and hierarchically structured surfaces. In the VLEDs with hierarchically structured surfaces, the HCP nanoscale nipple array with nipple diameters of 100 nm and heights of 300 nm stands on a microscale hemisphere with a diameter of 3 µm. The yellow planes correspond to cross-sectional planes in the x–z planes that slice through the center of the microdome structure. As presented in Figure 4a–c, the intensity distribution of the cross-sectional electrical field within each VLED was simulated at a wavelength of 438 nm, which corresponds to the emission peak in the EL spectra at an injection current of 350 mA.
For the microdome structured surface (Figure 4b'), high-intensity light is efficiently emitted from the microdome structure, which provides multiple collisions of light at the microdome structured GaN/air interface for high LEE compared with the planar VLED (Figure 4a'). Moreover, a strong electric field is observed above the apex of the convex surface, indicating that the microdome structure could efficiently transmit the light from the MQWs of the VLEDs toward the air; however, when the light within the escape cone is incident at the interface between the GaN and air, the light experiences Fresnel reflection due to the high contrast between the refractive indices of the GaN ($n = 2.5$) and air ($n = 1$). Therefore, the peak intensity of the electric field is observed in the core region of the microdome structure.

Compared to Figure 4b', Figure 4c' clearly illustrates that a relatively lower intensity of the electric field is observed at the core of the hierarchical structure compared with the microdome structure. This phenomenon was also observed in the CSEM mapping images. Because the CSEM recognizes only light emanating from the focal plane of the detector, the bright core within the hierarchical structure signifies the extracted light intensity, whereas the dark core within the microdome structures implies that the electric field is more strongly confined in these structures compared to the hierarchical structure, as shown in Figure 3d,e. Consequently, the intensity of the electric field above the apex of the hierarchical structure is higher than that above the microdome structure because the light injected at these surfaces escapes due to the optical coupling caused by the array of nanonipples on the microdome structures.

Figure 4a”–c” shows the far-field emission patterns of planar, microdome, and hierarchically structured VLEDs. Only a small portion of the light at angles less than the critical angle ($\theta_{\text{critical}} = 23.5^\circ$) is emitted from the planar VLED. Thus, most of the light produced in the MQWs propagates inside the planar VLED because of the TIR effect. However, the light emission broadens and intensifies with increasing levels of hierarchy in the optical structures on the surface of the VLEDs. The enhanced light extraction achieved by the hierarchical structures on the VLEDs means that the synergistic effect of microdome structures and nanonipples is highly
effective for light extraction through the minimization of the internal reflection of light.

To examine the wetting properties of VLEDs with the novel hierarchically structured surfaces, contact angles were measured for various liquids, including low-surface-tension liquids. Figure 5a–c shows photographs of water and corn oil droplets on VLEDs with the planar, microdome, and hierarchical structures. Figure 5d shows the contact angles of various liquids on the three different VLED surfaces as a function of the liquid surface tension. On the planar surface, liquids with high surface tensions, such as water (γLA = 72 mN m⁻¹), exhibit contact angles larger than 90°, mainly due to the chemical surface treatment by PFDTS, but liquids with low surface tensions, such as n-hexadecane (γLA = 27.5 mN m⁻¹), still show small contact angles. However, on the surface of VLEDs with microdome structures, all the tested liquids show increased contact angles larger than 90°. In particular, the contact angle of n-hexadecane, which has the lowest surface tension among the tested liquids, is increased by 38° compared to the case of the planar surface, which means that the inherently oleophilic (θ₀ < 90°) wetting behavior of the planar surface switches to an oleophobic (θ > 90°) behavior because of the microdome structures on the surface. This transition of wetting behavior can be attributed to the composite structure of the solid–air–liquid interface of the microdome structure.

A liquid droplet on a rough surface can typically be described by either the Wenzel model or Cassie–Baxter model. For the case of the homogeneous wetting regime, in which the liquid completely covers the rough surface, the apparent contact angle θ can be related to the Young contact angle θ₀ in the Wenzel model

\[ \cos \theta = r \cos \theta_0 \]  

where the roughness factor \( r \), defined as the ratio of the solid–liquid area to its projection onto a flat plane, is always greater than one. In this regime, an oleophobic surface (\( \theta_0 > 90° \)) becomes more oleophobic with increasing surface roughness, whereas an oleophilic surface (\( \theta_0 < 90° \)) becomes more oleophilic with increasing surface roughness. This model is not consistent with our experimental results because the apparent contact angles of corn oil and n-hexadecane on the microdome or hierarchically structured surfaces become greater than 90° even though their low Young contact angles are less than 90° on the planar surface. Therefore, our system likely falls within the heterogeneous wetting regime, in which air can be trapped in the region between microdome structures under the liquid. The contact angle in this regime is described by the Cassie–Baxter model

\[ \cos \theta = (1 - f_{LA}) \cos \theta_0 - f_{LA} \]  

where \( f_{LA} \) is the fractional geometrical area of the liquid–air interface under the liquid droplet. In this case, the trapped air pocket can significantly increase the apparent contact angle of liquid droplets with a low Young contact angle on the planar surface as well as that of liquid droplets with a high Young contact angle. The estimated values of \( f_{LA} \) for corn oil and n-hexadecane from the measured contact angles and geometric conditions are 56% and 50%, respectively, indicating that the droplets of liquids are floating over air pockets trapped between the microdome structures. The contact angle is even more enhanced in the case of VLEDs with the hierarchically

---

**Figure 3.** Electrical and EL characteristics of hierarchically structured VLEDs and a comparison with those of planar VLEDs. a) I–V characteristics of VLEDs with different structured surfaces. The I–V characteristics were obtained by scanning the external bias to an injection current of 1 A. The inset shows the semilogarithmic scale I–V characteristics of the VLEDs. b) Room-temperature EL spectra of VLEDs at an injection current of 350 mA. c) Optical output power of VLEDs as a function of injection current from 0 to 500 mA. Cross-sectional CSEM images of d) a microdome-structured VLED and e) a hierarchically structured VLED. The insets show the respective top-view CSEM images.
structured surface, as shown in Figure 5e. This novel surface structure provides superhydrophobic ($\theta_{\text{water}} = 153^\circ$) and highly oleophobic ($\theta_{\text{corn oil}} = 143^\circ$, $\theta_{\text{n-hexadecane}} = 141^\circ$) properties. These contact angles are even larger than those on the microdome surface. The empirically calculated values of $f_{LA}$ were more than 83% for all liquids according to the Cassie–Baxter model. Thus, the hierarchically structured microdomes repel any liquids on the surface more efficiently compared to the planar and pristine microdome structures because more air pockets are trapped in the gaps between the microdomes, as well as the nanonipples, and because the geometrical area of the air–liquid interface is increased considerably.
In conclusion, we demonstrated that well-ordered nanostructures can be fabricated to form hierarchical structures on VLEDs with curved microdome surfaces by combining self-assembled dip-coating and nanopatterning transfer processes. These novel hierarchical structures, which imitate configurations found in nature, displayed multiple benefits, such as superior optical and antifouling properties. The VLEDs with hierarchically structured surfaces show a 3.12-fold increase in the power of the emitted light compared to the planar VLEDs at an injection current of 350 mA. In addition, the hierarchical surface on VLEDs demonstrates superhydrophobicity and high oleophobicity, with contact angles of 153° for water and 143° for corn oil, due to the high fraction of air pockets at the interface between the liquid droplet and hierarchical surface structures. Therefore, these versatile hierarchically structured surfaces can greatly improve the optical performance and provide novel surface properties for practical applications of various optoelectronic devices, such as semiconductor LEDs, organic LEDs, and solar cells, in areas where not only high device performance but also considerably reduced contamination by the environment are required for devices that are efficient and have long operational lifespans.

**Experimental Section**

**Fabrication of Vertical Light Emitting Diodes:** Blue VLEDs with a dominant emission peak at 438 nm were grown on c-plane sapphire substrates by metalorganic chemical vapor deposition (MOCVD). After the growth of a 25 nm thick GaN buffer layer at 550 °C, a 5 μm thick undoped GaN and a Si-doped n-GaN layer were grown at 1010 °C. Then, five pairs of InGaN/GaN MQWs were grown, followed by a p-type GaN layer, to fabricate the VLEDs. The p-GaN and MQW layers were partially etched by an ICP etching process until the n-GaN layer was exposed, and Cr/Au-based n-pad electrodes were deposited by electron beam evaporation. Next, VLEDs with a size of 1 × 1 mm² 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 as a platform, and then, a laser lift-off (LLO) process was performed to separate the sapphire wafer from the devices. The Ti/Au metal layers were deposited by electron beam evaporation as p-pad electrodes after the u-GaN layer was fully etched. Then, the N-face n-GaN was etched by ICP etching using a hexagonally patterned photore sist mask to fabricate the microdome structures. Details of the fabrication method have been described elsewhere.[56]

**Fabrication of 2D Colloidal Crystals:** The 2D-colloidal crystals were deposited by a dip-coating method using a 15 wt% silica colloidal (100 nm in diameter) suspension (ethanol solvent). A sapphire substrate pretreated by oxygen plasma was dipped into the colloidal suspension and subsequently withdrawn at a speed of 8 mm min⁻¹. During the withdrawal of the substrate from the colloidal suspension, an ethanol influx transported the silica nanoparticles toward an edge of the colloidal suspension, and they self-assembled into ordered HCP 2D-colloidal crystals due to the lateral capillary force.

**Measurement by Cross-Sectional Confocal Scanning Electro-luminescence Microscopy (CSEM):** Cross-sectional CSEM was accomplished through the modification of a commercial confocal scanning microscope (WITec GmbH). The light scattered from the samples passes through the microscope objectives (×100, NA 0.9) and is delivered to the detector (photomultiplier tubes, PMT) via a multimode fiber optic (diameter = 50 μm) for EL mapping. An injection current of 300 μA from a current source (Keithley 2450) was applied to the VLEDs during the experiments to avoid damaging the PMT by high illumination. The spatial EL distribution of 20 × 20 μm² (x–y scan) regions was characterized in the vertical direction with 14 nm steps controlled by a piezoelectric (PZT) nanopositioning stage.

**3D Finite-Difference-Time-Domain (FDTD) Simulation:** A FDTD simulation was performed to investigate the light propagation through the hierarchical surface structures of the VLEDs. A point dipole source polarized along the x–y plane was located in the center of the MQWs because the transverse electric (TE) polarization was predominantly observed in InGaN/GaN MQW blue LEDs.[51–53] The point dipole source emits monochromatic light with a wavelength of 438 nm. The simplified VLED structures for the FDTD simulation were composed of a 300 nm thick Ag mirror, a 200 nm thick p-GaN layer, a 100 nm thick InGaN/GaN MQW layer, and a 4 μm thick n-GaN layer. The model structure of the VLED was surrounded by a perfectly matched layer (PML).[54]

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgments**

This research was supported by Samsung Electronics Co. Ltd., by the Industrial Strategic technology development program (Project No. 10048898) funded by the Ministry of Trade, Industry and Energy (MI, Korea), by the APRI Research Program through a grant provided by the Gwangju Institute of Science and Technology, and the Industrial Strategic Technology Development Program (Project No. 10041879) funded by the Ministry of Trade, Industry and Energy (MOTIE/KEIT, Korea).

---
