Bio-Inspired Flexible Fluoropolymer Film for All-Mode Light Extraction Enhancement

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ABSTRACT: Enhancing the light extraction efficiency is a prevalent but vital challenge for most solid-state lighting technologies, especially for deep ultraviolet light-emitting diodes (DUV-LEDs). In this paper, inspired by the microstructure of the butterfly’s eye, we propose and fabricate a flexible fluoropolymer film (FFP film) to tackle this issue for all-mode, full-wavelength light extraction enhancement for most solid-state lighting technologies compatibly. The experimental results demonstrate that compared with one mounted with a smooth FFP film, the light output power of DUV-LED is enhanced up to 26.7% by mounting the FFP film with 325 nm radius nanocones at a driving current of 200 mA. Importantly, thanks to the super-flexible feature of the FFP film, it can both cover the top surface and sidewalls of the DUV-LED chip, leading to the improvement of transverse electric and transverse magnetic mode light extraction by 20.5 and 21.8%, respectively. Finite element analysis (FEA) simulations of the electric field distribution of DUV-LEDs with the FFP film reveal the underlying physics. The present strategy is proposed from the view of the packaging level, which is cost-effective, able to be manufactured at a large scale, and compatible with the solid-state lighting technologies.

KEYWORDS: deep ultraviolet light emitting diode, nanostructures, flexible fluoropolymer, light extraction efficiency, TE/TM mode

1. INTRODUCTION

Over the past two decades, the conventional incandescent and fluorescent lighting industry has been revolutionized to pursue a more energy-efficient, longer-lived, and environmentally friendlier solid-state lighting, complying with the increasingly stringent and promising, which, depending on quantum efficiency (IQE). Currently, the IQE in the active regions has nearly approached its upper limit for OLEDs (100%)19,20 and blue LEDs (90%),21 while for deep-UV LEDs (DUV-LEDs, <310 nm), the efficiency is quite low. The EQE of the prevailing DUV-LEDs is less than 10% and until recently the record has just been updated to 20%.22 It should be attributed to the difficulties of a growing high Al-content AlGaN quantum well active region and achieving high material quality as well as an efficient conducting and transparent p-type layer in DUV-LEDs.16 As a result, further improvement strategy on the EQE of solid-state lighting packaging/devices falls to the enhancement of LEE greatly, especially for the DUV-LEDs. The LEE is defined as the fraction of emitted light that can be extracted from the active region to the outside air. However, two long-standing challenges remain formidable to enhance LEE.23 First, because of the large difference in the refractive index of nitride semiconductors (n ≈ 2.4) and the air (n = 1), most of the emitted light is trapped inside the chips.

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Supporting Information
because of the occurrence of total internal reflection (TIR) at the boundaries. Second, different from GaN-based blue LEDs, AlGaN-based DUV LEDs imperatively incorporate high Al content. Because of crystal field splitting and spin–orbit effects, the topmost valence band of GaN is the heavy-hole band but it is the crystal-field-splitting band for high Al content AlGaN. As a result, the predominant emission in blue LEDs is transverse electric (TE)-polarized ($E_\perp c$), and in AlGaN-based DUV-LEDs is transverse magnetic (TM)-polarized ($E_\parallel c$). The TM-emission is polarized along the direction normal to the surface and propagated mainly to the lateral facet, leading to extremely low LEE (and EQE) in DUV-LEDs.

To tackle the challenges for LEE enhancement, people proposed to fabricate textures on the chip top-front surfaces, such as photonic crystals, colloidal microspheres, micro-dome structures, patterned sapphire substrate (PSS), and graded refractive index materials, to break down the TIR and extract more light outside. Substrate sidewall roughening by the laser dicing process has also been proven to be effective in helping photons escape out both in blue LEDs and AlGaN-based DUV-LEDs. The enhancements of LEE at different ratios are observed, but the underlying problems are dodged such as the nonuniformity, high cost, material degradation, and reliability on roughening the semiconductor chips. These efforts have only been paid to tackle the aforementioned first challenge. Because the TE- and TM-mode light mainly propagates in the vertical and lateral directions, respectively, the surface roughening in the top-front surface for blue LEDs and in the sidewall surface for DUV-LEDs are adopted, respectively. This does not mean that one-side roughening is enough or there is an upper limit for LEE enhancement. In our recent paper, the top-front surface roughening for DUV-LEDs can also obviously benefit the LEE enhancement for the TE-mode light. Therefore, it is necessary to roughen the top surface and sidewall simultaneously, but the existing manufacturing processes are expensive and not compatible at the moment. The former is mainly achieved by plasma etching, while the latter is obtained by laser dicing. Therefore, we wonder if an alternative solution is compatible with the existing manufacturing process and suitable for different types of solid-state lighting technologies, and helps to enhance the LEE for both TE-and TM-mode light in the meantime.

Particularly, the biomimetic nanostructure with a two-dimensional subwavelength structure can exhibit unique optical properties in suppressing the Fresnel reflections at an interface, yielding high transmittance over a broad spectral range and wide angles of incidence. Therefore, we developed a flexible fluoropolymer film (FFP film) with nanocones to enhance both the TE- and TM-mode light extraction in this study. Because of the flexibility, the FFP film can be packaged on both the top-front surface and the sidewall of the chips, which simultaneously overcome the two challenges to enhance the LEE for the most solid-state lighting packages and devices. Moreover, due to the stable $-\text{CF}_3$ end group, the FFP film shows high transparency (>95%) and good stability for almost the whole wavelength from DUV to red spectra, which makes it applicable for most solid-state lighting technologies, especially for the DUV-LEDs, as shown in Figure

Figure 1. (a) Picture of a blue morpho butterfly specimen and the SEM image of its eye microstructure. The submicron-scale nanocones are arranged neatly on uneven surfaces like a flexible film; (b) top-view SEM images of the FFP film with radii of 325, 340, 350, and 360 nm, respectively. It is observed that the FFP film can maintain a large area of consistency like a butterfly-eye microstructure; (c) cross-sectional SEM image and $5 \times 5 \mu m$ AFM image of the FFP film (R325), and the single nanocone profile.
S1 (Supporting Information). The nanopatterned template is developed to fabricate the nanocone FFP film, which is efficient, cost-effective, and compatible with industrial manufacturing for uniform and large-area nanocone fabrication. The experimental results reveal that the optimized FFP films can significantly improve the TE/TM-modes of DUV-LEDs and enhance the enhancement of LEE compared with the smooth fluoropolymer film. The electric field distribution mode of DUV-LEDs is also simulated based on the finite element analysis (FEA) to shed light on the underlying physical mechanism.

2. EXPERIMENT

2.1. Fabrication Process of the FFP Film. The detailed experimental description of the nanopatterned template was reported in our previous work.12 After cleaning the nanopatterned template using plasma, the fluoropolymer (S-type, Grade name: CTX-809SP2, produced by CYTOP) is spin-coated on the nanopatterned template with a size of 50 × 50 mm², and then baked under a temperature of 120 °C for 1 h, obtaining the FFP film. Subsequently, as the bonding ability of the pure fluoropolymer is very poor and can be easily peeled off, the FFP film is mechanically stripped and cut into small cubes with a size of 3.5 × 3.5 mm², preparing to be mounted on the DUV-LEDs. Finally, the FFP film is mounted both on the top and the sidewalls of the DUV-LED chip by a GO-based fluoropolymer36 to form a sandwich structure under 120 °C in a vacuum chamber for 1.0 h.

2.2. Simulation and Measurements. Exploring the feasibility to improve the LEE with the FFP film, the simulated electric and magnetic field distribution of DUV-LEDs with a smooth fluoropolymer and the FFP film are investigated, respectively, by using FEA in an interactive 3D entity-modeling environment. The measured results of UV transmittance of four FFP films are performed by a UV-1800 dual beam UV-visible spectrophotometer manufactured by Shanghai Macylab Instrument Inc, and the light output power of the DUV-LEDs is measured by using an ATA-1000 Photoelectric Analysis System manufactured by Everline Corporation with a 30 cm-diameter integrating sphere. A near-field intensity distribution is supported by Gold Medal Analytical & Testing Group. Moreover, the light intensity spatial distribution of these DUV-LEDs are measured by using a self-constructed test system with an angle resolution bracket, Glan–Taylor prism, and spectrometer as shown in the Results and Discussion section.

3. RESULTS AND DISCUSSION

The microstructure of the blue morpho butterfly’s eye observed by an environmental scanning electron microscope (SEM, Quanta 250, FEI company) is shown in Figure 1a. It is observed that the sub-micrometer scale nanostructure consists of a periodic and close packed ~300 nm diameter nanocone array, which is beneficial for the photoreception of the butterfly. To fabricate a similar nanostructure of the butterfly’s eye based on the flexible substrate, we first obtain the nanopatterned template. A detailed description of the fabrication process can be referred in the Experiment Section. By controlling the time of wet etching, four 2 in. sapphire nanopatterned templates are fabricated with uniform nanoholes with radii of 325, 340, 350, and 360 nm, respectively, and the period is about 1 μm. The top-view SEM image of the nanopatterned template with a radius of 325 nm is shown in Figure 2a, and the corresponding depth of the nanohole is measured as ~190 nm by the sectional view SEM image in Figure 2a, which is obtained by precisely cutting the nanopatterned template using the focused ion beam. Meanwhile, it is observed from the atomic force microscope (AFM) in Figure 2a that the morphology of nanopatterned template is uniform and adjustable, by using the nano-photolithography and wet-etched technique. Experimental discussions will be
Figure 3. (a) Light output power of bare DUV-LED and the ones mounted with smooth and nanocone FFP film structures as a function of driving current, and the inset presents the image of a lighted DUV-LED with the nanocone FFP film; (b) EL spectra of DUV-LEDs at a current of 200 mA, and the inset shows a detailed view at the wavelength between 250 and 300 nm; near-field intensity distribution in 3D and 2D views of DUV-LED with smooth (c) and R325-FFP film (d), and the color distribution represents light output power intensity; the normalized intensity comparison as a function of the X distance (e) and Y distance (f).

referred later. Then, we spin-coat the fluoropolymer solution onto the nanopatterned template, and the FFP film with uniform nanocones is obtained after baking and stripping, as shown in Figure 2b. Because of the super-flexibility of the fluoropolymer substrate, we use the FFP film to cover the top and sidewall surfaces of the DUV-LED chip, and the final packaging prototype is displayed in Figure 2b. Corresponding to the four templates with different nanohole sizes, four FFP films with different nanocone sizes are shown in Figure 1b, respectively. Similar to the microstructures of the blue morpho butterfly’s eye, the morphology of the FFP film is largely well-arranged, and the nanocone shows the patterns as convex triangle cones because of the anisotropic etching of the sapphire crystal (nano-patterned template). The radii of the nanocone of the four FFP films are 325, 340, 350, and 360 nm, respectively. To achieve the higher transmittance, the ratio of the height and the incidence light wavelength is found to be 0.4 or higher, because the light transmittance is related with both the geometry nanostructures and the wavelength of incidence light.37–39 And the corresponding heights are about 190, 225, 230, and 240 nm, which satisfy foregoing the requirement of high transmittance in the deep ultraviolet spectrum. The thickness of the FFP film depends on the spin coating speed and time, and approximately 4 μm FFP films are fabricated under the conditions of 1000 rpm and 100 s, according to the sectional view SEM image in Figure 1c. Such a thin film possesses extraordinary flexibility, which can be easily mounted onto the top and side surfaces of the DUV-LEDs in a later demonstration.

Transmittance of the FFP film is a key factor when referring to the light extraction enhancement property. However, the FFP film is extremely thin and hardly to realize self-standing feature, so a substrate is required to investigate its transmittance. Therefore, we mounted the FFP film on a double-polished sapphire substrate (DPSS), which is similar to the DUV-LED surface. The transmittance of the DPSS with and w/o the R325 FFP film was measured, respectively. Then, the EF can be calculated as the ratio of transmittance with and w/o the FFP film on DPSS, which should also be regarded as the effective transmittance for the FFP film as shown in Figure 2c. The transmittance of DPSS with the FFP film is improved for the whole spectra from 200 to 800 nm, which is favorable for enhancing the LED light extraction. Simulation is also conducted to support the experimental results. In the simulation, the transmittance was numerically calculated by using a three-dimensional finite difference time domain method. The calculation takes into account the frequency dependence of the refractive index and absorption loss of the interface. A 3D model was established based on the experimentally prepared periodic structural unit sizes, and the boundary was set to the Floquet period type. The refractive indices of the air and FFP film were set to 1 and 1.35, respectively. The simulation results shown in Figure 2c exhibit slight deviations from the experimental curves. It shows in the inset of Figure 2c that the transmittance EF investigated by simulation is also comparable with the experimental result at the designate wavelength of 275 nm, which demonstrate that the FFP film is favorable for light extraction of DUV-LED. This interesting phenomenon should be ascribed to the nanoscale surface of the biomimetic FFP film that effectively decreases the reflectance in a broadband spectrum which can be regarded as diffraction grating. The relatively high transmittance in the deep UV-light spectrum implies that deep UV-light can easily escape from the fabricated FFP film, which may have better performance for the DUV-LEDs. It is attributed to the combined result of the gradual two-dimensional sub-wavelength structure and the continuously tapered morphology on the patterned surface with a superior gradient refractive index profile at the interface.40 With the FFP film, light is, therefore, manipulated in all azimuthal directions over the entire emission wavelength range. Under this circumstance, light interactions cannot be described well.
Figure 4. (a) Light intensity spatial distribution measurement system with angle resolution bracket, Glan–Taylor prism, and spectrometer, and the inset presents orientation and size relation of TE/TM mode light; (b) measured far-field emission pattern of DUV-LEDs with a FFP film of R325 nm and smooth films at a current of 200 mA, and the inset presents a schematic illustration of light transmission in DUV-LEDs with proposed structures; (c) full spatial TE/TM mode light intensity distributions of DUV-LEDs with FFP films and smooth films.

by the Fresnel relations as diffraction and scattering become prominent for the FFP film with nanoscale periodic structures. As a result, there is an extra resonant pathway existing that could facilitate broadband light transmittance owing to the smooth transition of the refractive index at the interfaces. Compared to such characteristics achieved by conventional interference-based multiple coatings which rely on destructive interference from multiple reflections, the FFP film with a graded refractive index profile exhibited inherently extraordinary broadband antireflectivity.

The light output power and the relative electroluminescent (EL) light intensity of bare DUV-LED and the ones with the FFP film measured under the driving current ranging from 50 to 400 mA are shown in Figure 3a,b. Among the four kinds of nanocone FFP film, the FFP film with radius of 325 nm shows the largest light output power and intensity. Meanwhile, the DUV-LED mounted with the smooth FFP film and bare DUV-LED displays the lowest light output power and intensity because of similar conditions of internal total reflection and high transmittance of the FFP film in the DUV spectrum. As we mainly focused on the effect of the FFP film with nanocones in this work, a comparison has been carried out between DUV LEDs mounted with a smooth and nonacone FFP film. Under the driving current of 200 mA, the proposed R325 nanocone FFP film structure could significantly enhance the light output power of DUV-LED by 26.7%, and up to 30.0% at the current of 400 mA, compared with the one with the smooth FFP film. An image of a lighted DUV-LED with a nanocone FFP film is shown in the inset of Figure 3a. Besides, the peak discrepancy among the 6 samples in Figure 3b is 1 nm at most which is attributed to the nonuniformity of the LED samples from an identical epitaxy wafer rather than the effect of the FFP film. Moreover, a detailed light intensity analysis is obtained by using a near-field intensity distribution test in the 3D and 2D mode (Figure 3c,d), and the color distribution represents a light output power intensity. Meanwhile, the normalized intensity along a X distance and Y distance in the 2D mode is presented in Figure 3e,f, respectively. The periodicity along the Y direction in Figure 3f comes from the electrode. It can be seen from Figure 3c–f that the light intensity of DUV-LED with the FFP film is relatively higher benefiting from the light extraction enhancement.

To further understand the light extraction enhancement of the FFP film on the top surface and sidewalls of the chip, respectively, the light intensity spatial distribution test of DUV-LEDs with the FFP film is performed. First, the DUV-LED chip is fixed on an angle resolution bracket, as shown in the Figure 4a. The angle resolution bracket rotation angle \( \theta \) corresponds to the angle of light propagation respective to the c-axis of the DUV-LED, and then the emitted light is transmitting through a Glan–Taylor prism (polarization angle parameter \( \varphi \)) and then collected by an optical fiber spectrometer. The spectral curve and optical power can be obtained by such a setup, and corresponding to each group \((\theta, \varphi)\). Each of the measured values is based on the spatial relationship between \( \theta \) and \( \varphi \). The optical power values are decomposed into the TE/TM mode. As shown in the inset, the surface ABCD is the chip plane, the surface ADEF is the polarizer plane. The power corresponding to \((\theta, \varphi)\) measured by the fiber optic spectrometer is \( P \), so the electric field mode oscillating along the transmissive axis AG is expressed in eq 1

\[
|E_{AG}| = a_0 \sqrt{P}
\]

and eq 2

\[
|E_{AH}| = a_0 \sqrt{P} \cos \varphi^2 \cos \theta^2 + \sin \varphi^2
\]
\[ |E_{\text{GHI}}| = a_0 \sqrt{\mathbf{E}} \cos \varphi \sin \theta \]  

where \( a_0 \) is a constant, the TE and TM electric field modes corresponding to this spatial position can be calculated by eqs 2 and 3, respectively. And then the angle \( \varphi \) is integrated separately to obtain the TE/TM polarized intensity distribution of the DUV-LED chip in space.\(^{31}\)

The far-field distributions of the DUV-LEDs with the FFP film or not are tested at a current of 200 mA. As shown in Figure 4b, the spatial light intensity of DUV-LED with a R325 nanocone FFP film is stronger than that of the one mounted with a smooth FFP film at all viewing angles, which indicates that the nanocone FFP film indeed improve the light extraction efficiency of DUV-LED. The light extraction EF is calculated to be 1.27 by integrating the spatial light intensity of the two DUV-LEDs. The spatial distributions of the TE/TM polarized light intensity of two DUV-LEDs are tested, and the spatial distributions of the polarized light intensity in the TE mode and TM mode are shown in Figure 4c. It can be seen that the introduction of the nanocone FFP film has a very significant enhancement effect on both the TE mode and TM mode by about 20.5 and 21.8%, respectively. Such a large enhancement indicates the effectiveness of the nanocone FFP film structure, and the reason can be attributed to the enhancement of TE and TM mode light simultaneously.

In addition, the simulated TE/TM-mode near-field electric field distributions of DUV-LEDs with the smooth fluoropolymer and the FFP film (\( R = 325 \) nm) are analyzed via a three-dimensional FEA method respectively, as shown in Figure 5, and the color scale bar represents the normalized electric field intensity. Four cases with zero incidence, small angle incidence, total reflection angle incidence, and large angle incidence, are displayed. At a wavelength of 275 nm, for both TE and TM mode, the angle of total reflection of the smooth interface is calculated as 48°, thus the electric field of the smooth interface showed strong TIR and most emission is trapped within the film when the angle of incidence (\( \theta_s \)) is larger than 48°. The electric field distribution of the smooth interface is in accordance with the feature of the evanescent wave. In contrast, for the interface with a FFP film with \( \theta_s > 48° \), there still exists a strong electric field distribution in ambient air though some light is reflected back into the film, as shown in Figure 5a,c. For a detailed analysis, the 3D intensity distributions at an incident angle of 70° are shown in Figure 5b,d, respectively, in which the red arrow represents the electric field direction and intensity. It is clearly shown that the TE/TM electric field of the smooth interface in the ambient air is zero but there existed an electric field distribution in ambient air for the interface with the FFP film due to the nanostructure. The FFP film can effectively increase the out-coupling probability of the emitted light according to the intensity field distribution with propagation at the FFP film/air interface, which is chiefly attributed to the gradual transition in the refractive index of the nanocone arrays on the surface of the DUV-LED chip for both TE- and TM-mode light as shown in Figure 4c. These factors enable the emitted light towards the surface normal with higher out-coupling efficiency.

4. CONCLUSIONS

In this paper, inspired by the microstructure of the butterfly’s eye, we propose and fabricate a FFP film for all-mode, full-wavelength light extraction enhancement for most solid-state lighting technologies compatibly, especially for the deep ultraviolet light-emitting diodes (DUV-LEDs). This is the
first time that a large area uniform nanostructure on the sidewall of the light-emitting device was achieved. The experimental results demonstrate that compared with a smooth FFP film mounted structure, the light output power of DUV-LED is enhanced up to 26.7% by mounting the FFP film with a radius of 325 nm at the driving current of 200 mA. Importantly, thanks to the flexible feature of the FFP film, it can both cover the top surface and side walls of the DUV-LED chip, leading to the obvious improvement of the TE and TM mode by 20.5 and 21.8%, respectively. FEA simulations of the electric field distribution of DUV-LEDs with the smooth or nanocone FFP films validate the mechanism. The present strategy is proposed from the view of the packaging level, which is cost-effective, able to be manufactured at a large scale, and compatible with most solid-state lighting technologies, and it can benefit all-mode full-wavelength light extraction enhancement with promising applications.

**ASSOCIATED CONTENT**

2 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b02942.

Transmittance test and molecular structural formula of S-type fluoropolymer (PDF)

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**Notes**

The authors declare no competing financial interest.

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