Tuning a nano-pillar array for enhancing the photoluminescence extraction efficiency of GaN-based light-emitting diodes*

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(Received 18 July 2012; revised manuscript received 12 October 2012)

We demonstrate the fabrication of hexagonal nano-pillar arrays at the surface of GaN-based light-emitting diodes (LEDs) by nanosphere lithography. By varying the oxygen plasma etching time, we could tune the size and shape of the pillar. The nano-pillar has a truncated cone shape. The nano-pillar array serves as a gradual effective refractive index matcher, which reduces the reflection and increases light cone. It is found that the patterned surface absorbs more pumping light. To compare extraction efficiencies of LEDs, it is necessary to normalize the photoluminescence power spectrum with total absorption rate under fixed pumping power, then we could obtain the correct enhancement factor of the photoluminescence extraction efficiency and optimized structure. The highest enhancement factor of the extraction efficiency is 10.6.

Keywords: colloidal lithography, light-emitting diode, extraction efficiency

PACS: 81.05.–t, 85.30.–z, 42.55.Tv **DOI:** 10.1088/1674-1056/22/4/048101

1. Introduction

Gallium nitride (GaN) material, with its direct bandgap, is very important for high performance light-emitting diodes (LEDs) in the wavelength range from ultraviolet to the green light.[1] GaN-based LEDs have received much attention recently in the commercial field for the purpose of illumination and display, due to their advantages over conventional fluorescent lighting sources in the sense of energy saving, longevity, and environmental soundness.[2] These solid-state lighting sources are recognized as the candidate for next generation illumination.[3,4] But to replace traditional lighting sources, more efforts are required to improve the external quantum efficiency (EQE). The EQE is determined by the internal quantum efficiency (IQE) and light extraction efficiency (LEE), i.e., $\eta_{\mathrm{EQE}} = \eta_{\mathrm{IQE}}\eta_{\mathrm{LEE}}$.[5] The IQE of GaN-based LED has been greatly improved due to advances in crystal growth in recent years, such as epitaxial-lateral-overgrowth (ELOG).[6,7] But the LEE of the chip still remains low because of the large refractive index contrast between GaN ($n = 2.5$) and air ($n = 1$), and a smooth interface which results in Fresnel loss and total internal reflection (TIR). The critical angle for the light escape cone is about 23°. Assuming that the output power from the side wall and back side is neglected, only about 4% of the light generated in the multiple quantum well (MQW) can escape into the surrounding space.[8] Various methods have been proposed to increase the extraction efficiency, such as surface patterning techniques,[9–15] inclined side-wall etching,[16,17] and patterned sapphire substrate (PSS).[18,19] Among these approaches, surface patterning is one of the most efficient methods to provide a large enhancement factor of the LEE, due to the increased scattering rate at the roughened surface. The surface patterning techniques include laser holography (LH),[20] laser interference lithography (LIL),[21] nanosphere lithography (NSL),[22] nanoimprint lithography (NIL),[21] and so on. The NSL method is a promising candidate because of low-cost and high-throughput. In this paper, we demonstrate a method to prepare a conical nano-pillar array hexagonally at the surface of GaN-based LEDs by polystyrene (PS) nanosphere lithography. The shape of the nano-pillar can be controlled by tailoring nano-spheres with oxygen plasma etching. It is found that the shape and size of the nano-pillar affect the enhancement factor of photoluminescence (PL) extraction efficiency. Moreover, we utilize an integrating sphere to measure the total absorption rate of the LED. It shows that after patterning the sample, the absorption rate at pumping wavelength nearly doubles. After normalizing the photoluminescence (PL) spectrum by the absorption rate, the light extraction enhancement factor is larger than 10.

2. Experiment

The sample is grown on a 2-inch sapphire substrate by metal–organic chemical vapor deposition (MOCVD), and the epi-layers are listed from substrate to surface: 3.5-μm undoped GaN buffer layer, 2.3-μm Si-doped n-GaN layer, 20-nm 10% In-doped GaN layer for current diffusion, 3-period InGaN/GaN multiple quantum well (MQW) active layer, and

*Project supported by the the National Natural Science Foundation of China (Grant Nos. 10774195, U0834001, 10974263, 11174374, and 10725420), the Key Program of Ministry of Education, China (Grant No. 309024), the New Century Excellent Talents in University, and the National Basic Research Program of China (Grant No. 2010CB923200).

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200-nm Mg-doped p-GaN layer.

The flow chart can be seen from the schematic diagram in Fig. 1(a). Firstly, a single layer of PS spheres on the GaN surface is prepared based on the method developed by Kempa *et al*.[23] In our experiment, the diameter of the PS sphere is 450 nm, therefore the corresponding period of nano-pillars array also equals 450 nm. Figure 1(b) shows the scanning electron microscopic (SEM) image of the PS monolayer. Figure 1(c) shows the picture of a 2-inch wafer coated with a monolayer of PS spheres. The size of each sample is a quarter wafer. Secondly, oxygen plasma etching is used to tailor the diameters of nanospheres.

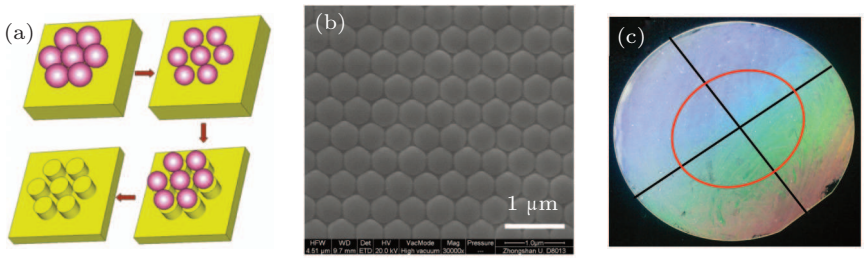


Fig. 1. (color online) (a) Flow chart of patterning the surface of p-GaN material. (b) SEM image of monolayer of PS spheres with a diameter of 450 nm on a p-GaN substrate; the scale bar is 1000 nm. (c) Photo of a 2-inch wafer coated with a monolayer of PS spheres, each sample is one quarter of the wafer, and the red arc in each quarter indicates that the PL spectrum will be measured along this arc.

It should be noted that before oxygen plasma etching, the sample should be heated which makes spheres stick to their positions during the oxygen plasma etching. To vary the shape and size of the nano-pillar, various oxygen plasma etching times are used in the experiment. Then, the p-GaN layer with tailored monolayer is etched by an inductively coupled plasma (ICP) etching machine via the gas flow of nitrogen with Cl_2/BCl_3 for 25 s; the etching rate is 7 nm/s. Therefore, the etching depth is around 175 nm just above the active layer, which is also the height of the nano-pillar. The oxygen etching and ICP etching data are listed in Table 1. For convenience, the samples are numbered from 1 to 7. In more specific terms, samples 1 and 2 are the LEDs without any pattern and covered with a monolayer of PS spheres respectively; sample 3 is etched with ICP but without oxygen plasmon etching; sample 4 to sample 7 are etched with oxygen plasma for 9 s, 13 s, 15 s, and 17 s respectively, then they are etched with ICP. Finally, patterned samples are immersed in methylbenzene to lift off the residual polystyrene.

Table 1. Specifications of samples 1∼7 and the corresponding absorption rates at 405 nm.

Sample number	1[a]	2[b]	3	4	5	6	7
Oxygen etching time/s	0	0	0	9	13	15	17
ICP etching time/s	0	0	25	25	25	25	25
Absorption rate/%	25	22	27	34	37	45	40

[a]LED wafer without any pattern.

[b]LED wafer with a monolayer of spheres on the surface.

Figure 2 shows the SEM images of nano-pillars at the surface of the LED. Figures 2(a)–2(e) exhibit the images of nano-pillar arrays corresponding to samples 3–7 in Table 1 respectively. It can be found that the pillars are hexagonally arranged which is determined by the mask of the hexagonal array of spheres. We can see that with the oxygen plasma etching time increasing, the top and bottom diameters of the nano-pillar decrease. Figure 2(f) shows an SEM image of sample 4 (Fig. 2(b)) observed at a tilted angle of 45°. It is found that the shape of the nano-pillar is conical, which is caused by the fact that PS spheres are not resistant to ICP etching. The pillar in sample 3 is nearly vertical. However, from sample 4 to sample 7, the pillars are truncated cones. The diameters of upper and base circles in sample 4 are 289 nm and 411 nm. The diameters of the upper circles in samples 5 to 7 are 206, 165, and 134 nm respectively, and the diameters of the base circles in samples 5 to 7 are 357, 313, and 282 nm respectively. It is found that the differences in diameter between the upper and base circles in samples 5 to 7 are nearly the same (around 148 nm), in other words, they have the same aperture. To some extent, this truncated cone shape is conducive to the light extraction,[24] due to the effective refractive index gradually changing from the active layer to free space, thereby giving a gradual refractive index matching.

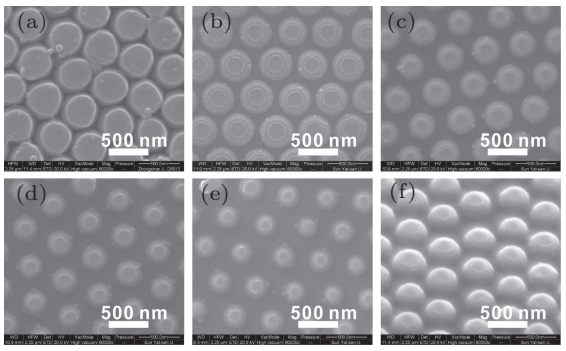


Fig. 2. SEM pictures ((a)–(e)) corresponding to the surface structures of the samples 3–7, respectively; panel (f) shows 45° tilted image of panel (b).

3. Results and discussion

We measure PL power spectra of patterned LEDs with pumping wavelength of 405 nm from the back side with an incident angle of 45°, and the luminescence power is collected from the patterned side. The diameter of the pumping laser spot is about 4 mm, which is much larger than the size of a single LED cell. The size of each sample is a quarter of the wafer, and each PL spectrum is the statistical result which is an average of 5-PL spectra measured at 5 spots along an arc which is shown in Fig. 1(c) by the red circle. We find that the deviations of the average photoluminescence intensities at peak wavelengths of the different samples before being patterned with nanostructure is about 2.36%. This shows that the average photoluminescence intensities are almost the same, except that there is a peak wavelength deviation caused by the inhomogeneity of the LED wafer which is about 2 nm. Before we discuss the PL power spectra of the patterned samples, we should mention that with pumping laser power fixed, the absorptions of the samples are different because the surfaces of samples are patterned with various structures. Based on this reason, we measure the absorption of all samples by an integrating sphere. The light beam generated by a Xenon lamp is incident on the samples in the integrating sphere at an angle of 45°, and the output light passes through the spectrometer, then the light is detected. We only consider the light absorption at the pumping wavelength of 405 nm in PL experiment. The absorption rates are shown in Table 1. The highest absorption rate is 45% after patterning, which is nearly twice that of the conventional sample. The increase in absorption is caused by the coupling of the grating and the reduction of the reflection is due to the gradual refractive index matching, therefore more pumping light can be absorbed by the MQW layer. To compare extraction quantum efficiency of LEDs, it is necessary to normalize the PL power spectra with total absorption rate under fixed pumping power, however, to our knowledge, no report considers this effect. Here we define

$$\mathrm{PL_{nor}} = \frac{\mathrm{PL_{exper}}}{A_{\mathrm{pat}}/A_{\mathrm{con}}}, \tag{1}$$

where $\mathrm{PL_{nor}}$ is the normalized PL intensity, $\mathrm{PL_{exper}}$ is the measured PL power in experiment, and $A_{\mathrm{pat}}/A_{\mathrm{con}}$ is the ratio of the total absorption rate of the patterned sample to that of the conventional sample measured by an integrated sphere. This is quite different from the previous work where just the PL spectra are measured to obtain the enhancement factor of the extraction efficiency. Usually, the patterned sample has high PL extraction efficiency, and it could also have high absorption efficiency at the pumping wavelength. Therefore, if it is not normalized, the extraction efficiency will be over-estimated. The normalized PL spectra can more accurately indicate the extraction efficiency. The normalized PL spectra are shown in Fig. 3(a). There exist random red/blue shifts of the peak wavelengths in samples 1 to 7, which is related to the inhomogeneity of the sample. Figure 3(b) illustrates the normalized and un-normalized peak values of PL spectra of 7 samples. It is found that just a monolayer of spheres on the surface of LEDs (red and blue lines) can also enhance extraction efficiency, and the existence of the GaN nano-pillar array further enhances the extraction efficiency. Moreover, the enhancement factor of the LEE mainly follows a trend of achieving a maximum and coming down again. The largest extraction enhancement factor of 10.6 is obtained in sample 5 with 13-s oxygen etching time. This is to say, when the oxygen plasma etching time is 13 s, the nano-truncated cone array presents an optimum structure for light extraction in our case. If we do not normalize the PL power with the absorption power, we find that the largest extraction enhancement factor of 16.4 appears in sample 6 etched with oxygen for 15 s. This will give us a wrong indication. This means that under fixed pump power, we need to normalize the luminescence power with the absorption power, then one could obtain the real extraction enhancement factor.

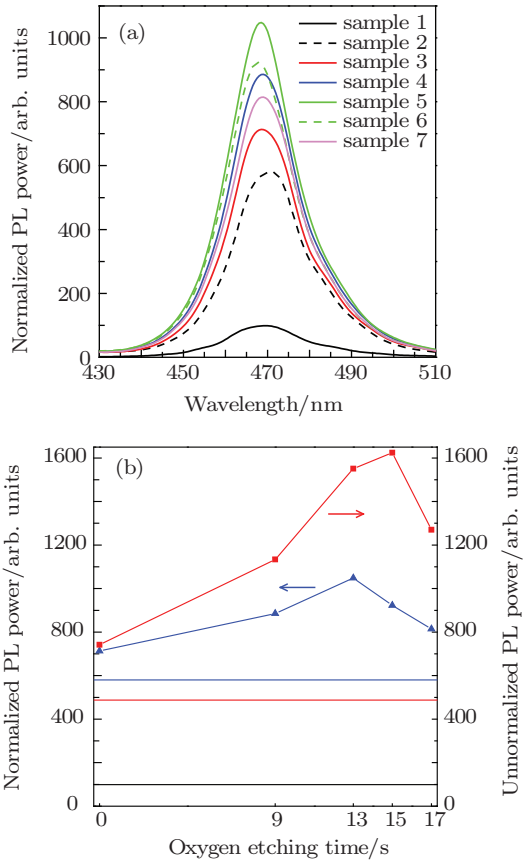


Fig. 3. (color online) (a) Normalized PL power spectra of LEDs. (b) Normalized and unnormalized PL power peak values of all LEDs, the red and blue curves indicate the normalized and un-normalized PL powers, the red and blue straight lines indicate normalized and un-normalized PL powers of the LED with a monolayer of spheres on the surface, while the black straight line is the LED PL power without any surface pattern.

As is well known, the patterned structure on an LED surface will improve the LEE. The enhancement mechanism can be explained in different ways according to the ratio between the pattern period and emitting wavelength, as well as the shape of the patterned unit. In our case, we think that there

are two mechanisms which result in the enhanced extraction efficiency. The first is that the truncated cones serve as a gradual effective refractive index matcher from the surface of the sample to the active layer, which strongly increases the light cone and reduces the reflection. However, in an ideal gradual effective index matching, the extraction efficiency could reach nearly 100%; in our case it is still far from reaching the perfect gradual refractive index matching. In an idea gradual effective index matching, the diameter of the upper cone should be nearly zero, and the diameter of the cone at the bottom should nearly equal the period, which makes a better gradual effective refractive index matching.[25] In other words, the effective refractive index can be gradually changed from 1 at the top of the conical pillar to 2.5 (the refractive index of GaN) at the bottom of the conical pillar. As we can see, in our case, the diameters of the conical cone at the bottom and top do not fulfill this condition, therefore, the maximum extraction should be achieved when the reflections at the top and bottom of the pillars, and their interference, make the minimum reflection. This might be the reason that the extraction efficiency follows a trend of achieving a maximum and coming down again. The second is the periodic structure, which serves as a two-dimensional grating. When the light from GaN material is outside the light cone, the longitudinal propagation constant is too large for light to be coupled outside, and thus a waveguide mode comes into being in the active layer. But with the presence of the grating structure, according to the conservation of the momentum in the longitudinal plane, the longitudinal propagation constant k_x under the grating can be expressed as

$$k_x = k_0 + \upsilon \frac{2\pi}{n_{\text{eff}}\Lambda}, \tag{2}$$

where k_0 is the wave vector of the light in vacuum, $\upsilon = 0, \pm 1, \pm 2, \ldots$, Λ is the period of grating, and n_{eff} is the effective refractive index of the grating. Even though $k_x > k_0$, with the positive values of ν and suitable value of Λ, one could obtain a momentum conversation[1], then light could be coupled out.

4. Conclusion

In the present paper, we demonstrated the fabrication of hexagonal nano-pillar array at the surface of GaN-based LED by NSL. By varying the oxygen plasma etching time, we could tune the size and shape of the nano-pillar. It is found that the nano-pillar has a truncated cone shape. To compare with PL extraction efficiency of LEDs, it is necessary to normalize the PL power spectra with total absorption rate under fixed pumping power, then we could obtain the correct enhancement factor of the PL extraction efficiency and the optimized structure. The highest enhancement factor of PL extraction efficiency is 10.6, which is caused by two factors: one is the truncated cones array that serves as a gradual effective refractive index matcher, reducing the reflection and increasing light cone; the other is the periodic grating that converts more light from the waveguide modes into the propagating modes. This NSL method might provide a route to low-cost and highly efficient GaN-based LEDs.

References

[1] Horng R H, Tsai Y L, Wu T M, Wuu D S and Chao C H 2009 *IEEE J. Sel. Top. Quantum Electron.* **15** 1327

[2] Lee Y C, Ni C H and Chen C Y 2010 *Opt. Express* **18** A489

[3] Schubert E F and Kim J K 2005 *Science* **308** 1274

[4] Steigerwald D A, Bhat J C, Collins D, Fletcher R M, Holcomb M O, Ludowise M J, Martin P S and Rudaz S L 2002 *IEEE J. Sel. Top. Quantum Electron.* **8** 310

[5] Schubert E F 2006 *Light-Emitting Diodes* 2nd edn. (Cambridge: Cambridge University Press)

[6] Huang C Y, Ku H M, Liao C Z and Chao S 2010 *Opt. Express* **18** 10674

[7] Lai W C, Yang Y Y, Peng L C, Yang S W, Lin Y R and Sheu J K 2010 *Appl. Phys. Lett.* **97** 081103

[8] Fujii T, Gao Y, Sharma R, Hu E L, DenBaars S P and Nakamura S 2004 *Appl. Phys. Lett.* **84** 855

[9] Kim T S, Kim S M, Jang Y H and Jung G Y 2007 *Appl. Phys. Lett.* **91** 171114

[10] Byeon K J, Hong E J, Park H, Yang K Y, Baek J H, Jhin J, Hong C H, Kim H G and Lee H 2009 *Semicond. Sci. Technol.* **24** 105004

[11] Park H, Byeon K J, Yang K Y, Cho J Y and Lee H 2010 *Nanotechnology* **21** 355304

[12] Sim J I, Lee B G, Yang J W, Yoon H D and Kim T G 2011 *Jpn. J. Appl. Phys.* **50** 102101

[13] An H M, Sim J I, Shin K S, Sung Y M and Kim T G 2012 *IEEE J. Quantum Electron.* **48** 891

[14] Liu S H, Feng Y C, Niu H B and Li Y 2006 *Chin. Phys. B* **15** 702

[15] Li Y, Zheng R S, Feng Y C, Liu S H and Niu H B 2006 *Chin. Phys.* **15** 1009

[16] Baik K H, Min B K, Kim J Y, Kim H K, Sone C, Park Y and Kim H 2010 *J. Appl. Phys.* **108** 063105

[17] Lin C C and Lee C T 2010 *IEEE Photon. Technol. Lett.* **22** 1132

[18] Kao C C, Su Y K, Lin C L and Chen J J 2010 *Appl. Phys. Lett.* **97** 023111

[19] Huang H W, Huang J K, Kuo S Y, Lee K Y and Kuo H C 2010 *Appl. Phys. Lett.* **96** 263115

[20] Kim D H, Cho C O, Roh Y G, Jeon H, Park Y S, Cho J, Im J S, Sone C, Park Y, Choi W J and Park Q H 2005 *Appl. Phys. Lett.* **87** 203508

[21] Kim S H, Lee K D, Kim J Y, Kwon M K and Park S J 2007 *Nanotechnology* **18** 055306

[22] Ke M Y, Wang C Y, Chen L Y, Chen H H, Chiang H L, Cheng Y W, Hsieh M Y, Chen C P and Huang J J 2009 *IEEE J. Sel. Top. Quantum Electron.* **15** 1242

[23] Kempa K, Kimball B, Rybczynski J, Huang Z P, Wu P F, Steeves D, Sennett M, Giersig M, Rao D, Carnahan D L, Wang D Z, Lao J Y, Li W Z and Ren Z F 2003 *Nano Lett.* **3** 13

[24] Song Y M and Lee Y T 2009 *Proceedings of 9th International Conference on Numerical Simulation of Optoelectronic Devices* p. 103

[25] Li Y, Zhang J and Yang B 2010 *Nano Today* **5** 117