Light extraction from GaN-based light emitting diode structures with a noninvasive two-dimensional photonic crystal

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A noninvasive fabrication process involving soft nanoimprint lithography is used to pattern a photonic crystal (PhC) in titania film for enhanced light extraction from a GaN light emitting diode (LED). This technique avoids damaging the LED structure by the etching process, while photoluminescence measurements show extracted modes emitted from the quantum wells which agree well with modeling. A light extraction improvement of 1.8 times is measured using this noninvasive PhC. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3067837]

Solid state lighting based on GaN light emitting diodes (LEDs) has rapidly gained interest and contributed to an ever growing number of applications in the broad area of energy efficiency.[1] Such LEDs have shown high brightness with high wall-plug efficiency. Highly efficient blue LEDs have been used for the production of white light sources by using the photoexcitation of red and green phosphors or colloidal quantum dots.[2] Although the internal quantum efficiency of InGaN/GaN LEDs has reached up to 90%, the light emission from InGaN quantum wells (QWs) into air is fundamentally limited by total internal reflection (TIR). In fact, only 12% of the light generated can directly escape from both top and bottom surfaces of the high refractive index (RI) medium of GaN (RI=2.5) into air. In a planar InGaN/GaN-based LED on a sapphire substrate, 66% of the total emitted light is wave guided within the GaN layer, while the remainder is found in the delocalized modes in the sapphire.[3] To circumvent this problem, a number of solutions based on geometrical optics have been developed.[4,5]

Another promising method to extract the guided light from the LED structure uses photonic crystals (PhCs).[3] Among the various possible PhC designs, a two-dimensional (2D) hexagonal lattice has been used successfully to enhance the light extraction. Several groups have applied imprint lithographic techniques to etch the PhC directly onto the top GaN layer of blue LEDs.[2,6] With this method, a silicon wafer is patterned with a hexagonal lattice by holographic lithography, which is then used to mold a resist layer by nanoimprint lithography.[7] The pattern is finally transferred to the GaN by dry etching. In a more elaborate approach, the patterns can be directly imprinted on a resist layer on GaN by electron-beam lithography, followed by a dry etching to transfer the nanostructures.[6] However, these conventional methods are not optimal since they involve an etching step that can damage the active InGaN QWs. The etching process can also create defects and carrier traps on the top GaN layer and reduce the overall efficiency of the LEDs.

Soft nanoimprint lithography (SNIL)[8] offers significant improvements for the high throughput fabrication of surface patterns over large areas while preserving the integrity of the GaN LED device. The technique involves the high fidelity fabrication of multiple polymeric stamps from a single lithographically defined hard master. The flexible stamps are optimal for sol-gel processing[9] since they can easily conform to rough surfaces and allow for solvent diffusion through the matrix, without appreciable swelling. However, current materials available for the preparation of polymeric stamps involve long curing times, multiple step preparation, and oxygen-sensitive chemistry and/or the use of expensive cross-linkable prepolymer mixtures that are prohibitive in high throughput processing.[10,11] To overcome these challenges, we have recently developed a family of versatile materials that can be cross-linked within 2 min under ambient conditions and are capable of replicating sub-50 nm features.

Here we report a nondestructive process for the fabrication of 2D PhC lattices and demonstrate their use for light extraction from GaN LEDs. The process involves the use of a soft cross-linked polymeric stamp based on poly([3-mercaptopropyl] methylsiloxane) (PMMS).[12] First, a titania (TiO_2) sol gel[9] is drop casted onto the substrate and the stamp is pressed to allow the sol gel to conform to the protrusions of the stamp. The titania sol gel is then cured by applying heat (100 °C) under pressure (20 psi) over a period of 10 min to obtain the solid titania pattern on the GaN substrate. Upon hardening, the soft stamp is simply peeled and the patterned titania is calcined at 300 °C for 2 min to maximize its RI (RI=2.1 at λ=460 nm). The nondestructive patterning of the titania allows the GaN to remain intact while closely matching the RI of the PhC for efficient light extraction. In addition, the SNIL process does not dam-

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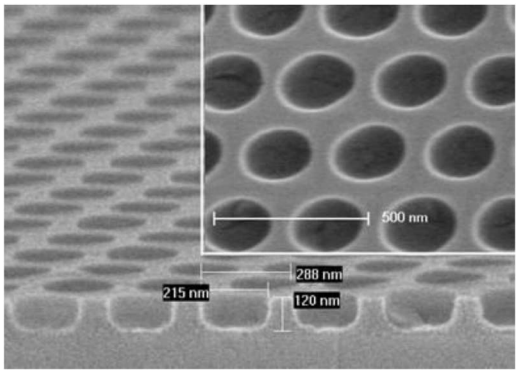

FIG. 1. PhC lattice of titania on a GaN LED substrate (inset: top view).

age the QWs and yields large area patterns using inexpensive, fast curing, and disposable stamps.

The stamps were fabricated using PMMS (6 wt. eq.), ethoxylated (4) bisphenol A dimethacrylate (1 wt. eq.), triallyl cyanurate (4 wt. eq.), and the UV-active (365 nm) radical initiator 2,2-dimethoxy-2-phenylacetophenone (<1% total weight).[12] The liquid precursors are poured onto a patterned silicon master, which was fabricated using interference holographic lithography as previously reported.[2] The 1 cm^2 pattern on the Si master was composed of a matrix of holes of 200 nm depth and 175 nm wide and a periodicity of 290 nm. The GaN LED consists of three InGaN/GaN QWs embedded between a 200 nm *p*-type GaN layer and a 2.5 μm thick layer of *n*-type GaN and GaN buffer. The peak emission wavelength of the LED is λ_{center}=460 nm. The overall GaN structure is grown on a sapphire substrate by metal organic chemical vapor deposition. The resulting PhC structure based on titania on GaN is shown in Fig. 1. The PhC is composed of a hexagonal lattice of holes and is a negative replica of the polymeric stamp. The holes in titania are wider (215 nm) and shallower than the original polymeric posts. These changes are attributed to shrinkage of the titania during the evaporation of the solvent and thermal curing.

Angular scans of the far field photoluminescence[2,6] (PL) measurements were performed on the final device to assess the effect of the titania PhC on the guided mode extraction. The samples are optically pumped by a 325 nm HeCd laser beam incident at 60° to the sample normal and focused to a spot of about 50 μm in diameter on the surface. At this incident angle, our experiment shows no coupling between the laser beam and the PhC. The PL is collected by a detector rotating in the normal plane of the sample. The light emission is measured by angular PL while the spectrum output is collected at all angles from to 0° (vertical direction) to 90°. To show the dispersion relation of the guided modes diffracted by the PhC, the coordinates of the PL angular emission are converted from collection angle and wavelength into in-plane wave vector $k_{\|}$ and frequency, respectively, in units of the PhC period *a*.[6]

The dispersion diagram of the diffracted guided modes shown in Fig. 2 is measured along the ΓM direction of the PhC for TE guided modes. In Fig. 2(a), two kinds of modes are observed: Fabry–Pérot modes (broad curves as the background), present in any planar structure with embedded QWs, and guided modes diffracted by the PhCs (sharp lines) corresponding to an enhancement on the total emitted light due to the titania PhC on the surface. The GaN and sapphire

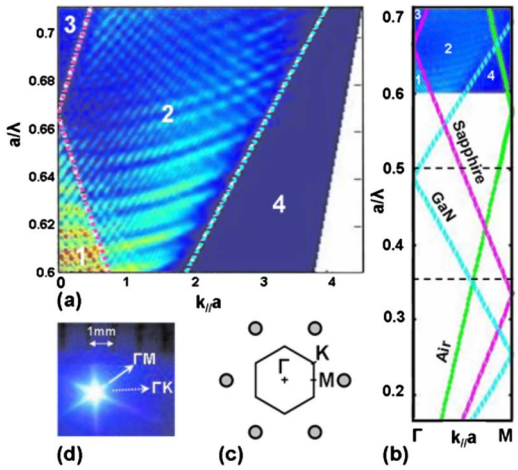

FIG. 2. (Color online) (a) Angular resolved PL measurements at 460 nm center wavelength in TE mode along the ΓM direction. (b) The same measurement on an expanded frequency scale. Green, magenta, and cyan lines correspond to light, sapphire, and GaN lines, respectively, in both figures. (c) First Brillouin zone of a hexagonal lattice. (d) A macroscopic picture of a PhC device excited by an UV laser.

lines are defined by the critical angles of their TIR and are drawn by converting the effective index of refraction into in-plane wave vector $k_{\|}$ ($n_{effective}=k_{\|}/k_0$) and folding the lines into the first Brillouin zone of the PhC [Fig. 2(b)]. These lines clearly define four distinct regions in the angular PL measurement. Region 1 corresponds to modes guided inside the GaN slab (GaN modes), which are well excited by the QWs due to their higher confinement compared to the sapphire modes. The GaN modes fall between the GaN and sapphire lines and are diffracted into air by the PhC. When they cross the sapphire line, going from region 1 to region 2, these modes are not only diffracted into air but also into the sapphire layer [Figs. 2(a) and 2(b)]. This competition results in a reduction in the diffracted intensity of these modes, which is clearly seen in region 2. Regions 3 and 4 are dark regions: the former corresponds to modes originally excited in the sapphire slab (sapphire modes) which are poorly excited by the QWs and the latter corresponds to the region with no guided modes ($n_{effective}>n_{GaN}$). For an optimal application of PhCs as light extractors, it is desirable to reduce as much as possible the extent of the dark regions 3 and 4 as well as the diffraction of modes toward the substrate (region 2). This can be achieved by decreasing the a/λ_{center} ratio.[13] In the present experiments a/λ_{center}=0.65, the diffraction of modes into the sapphire would be reduced if the PhC period was changed to a corresponding a/λ_{center}=0.35–0.5 as shown in Fig. 3(b) by the frequency region defined between the two horizontal dashed lines.

Another requirement for an efficient PhC extractor is that the extraction length must be smaller than the dimension of the device. To quantify the effect of a PhC material with lower index of refraction than the LED material, we developed a numerical model based on three-dimensional (3D) scattering matrix formalism.[13,14] In this model, we considered the entire 3D LED structure with the 2D PhC patterned on the surface. The guided waves are represented as Bloch modes and the real part of their wave vector describes the mode propagation and the electric field profile. The imaginary part of the modal wave vectors contains information about their extraction to air as they propagate inside the LED

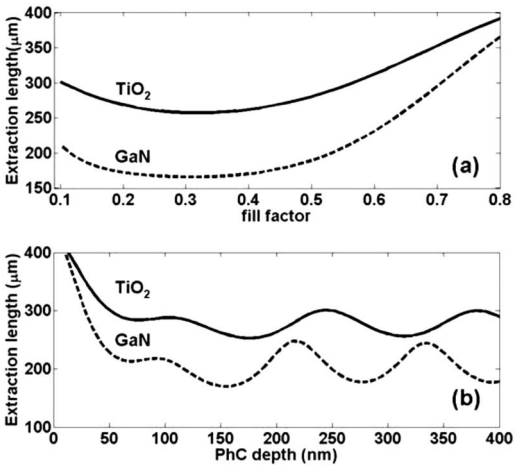

FIG. 3. PhC extraction length $[L=1/2img(k\|)]$ obtained from numerical simulation comparing GaN and titania PhCs for the TE9 mode in the ΓM direction as a function of (a) fill factor (defined as the ratio of the air hole volume over the PhC volume) and (b) the PhC depth.

structure. Since the light absorption is very weak in GaN and sapphire, the PhC diffraction to air is the main cause of the mode extinction. The extraction length, related to the inverse of the imaginary part of the wave vector as shown in Fig. 3, gives important information on how fast a mode is extracted while coupling with the PhC.

In this simulation, the extraction lengths of GaN and titania PhCs were compared for the TE9 mode, one of the numerous modes in the GaN layer. This mode is efficiently extracted by the PhC [Fig. 3(a) for a fill factor of 40%]. The extraction length for titania PhC (~300 μm) and is larger than for a PhC etched into GaN because of the titania film's lower index contrast to air. The oscillations of the extraction length in Fig. 3(b) correspond to vertical resonances of the mode with the PhC when the PhC depth increases. In the present device, the 120 nm deep titania PhC (Fig. 1) gives an extraction length of 280 μm. None of these oscillations are observed experimentally because the PhC dimensions are extremely large compared with the extraction length; hence the modes are completely extracted by the PhCs. However, this factor needs to be considered when designing a real device with finite lateral extension.

The intensity integrated over wavelength in the ΓM and ΓK directions of the PhC under TE and TM polarizations is shown in Fig. 4. A 120 nm thick layer of titania was deposited on top of the LED sample without a PhC to compensate

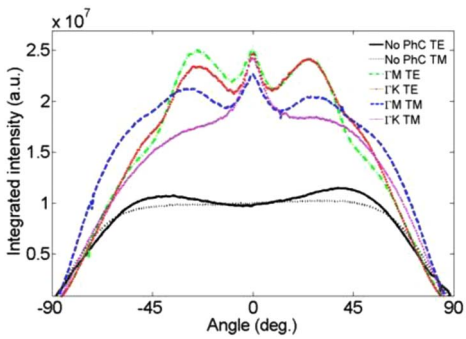

FIG. 4. (Color online) Comparison of the integrated intensity over wavelength for angular PL measurements in the ΓM and ΓK directions of PhC at TE and TM polarizations. All measurements were taken in the same conditions.

for the effect of light absorption of the titania PhC. Experimental results of the LED with PhC show a marked improvement in the light extraction. The increase in light extraction compared to the same LED with a bare 120 nm thick titania film deposited on top ranges from 1.6 to 1.9 times depending on directions and polarizations. The improvement is a function of the emission angle and increases by a factor of 2.2–2.5 at normal incidence and $\theta=25°$. This result matches the improvement factors ranging from 1.5 to 2.3 times as previously obtained by other techniques.[4,5,15]

This analysis shows that the extraction scheme proposed here is efficient for samples with sufficiently large size and low internal absorption. The titania PhC film could be combined with fluorescent species in the titania layer for producing wavelength conversion. In that case, the grating could be designed to also extract the downconverted light as was demonstrated by Diana *et al.*,[2] leading to a high efficiency white light LED.

In conclusion, we have nondestructively integrated a hexagonal PhC film in titania on top of an InGaN/GaN LED structure by combining the holographic lithography with SNIL. The fabrication process has a remarkable pattern replication fidelity and minimal impact on the electronic properties of the material while also being applicable to large-scale production under simplified conditions. PL measurements have shown that the titania film PhC strongly enhances the light extraction in a direction normal to the LED surface and these characteristics may also find application in systems requiring directional lighting.

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[1] M. R. Krames, O. B. Shchekin, R. Mueller-Mach, G. O. Mueller, L. Zhou, G. Harbers, and M. G. Craford, J. Disp. Technol. **3**, 160 (2007).
[2] F. S. Diana, A. David, I. Meinel, R. Sharma, C. Weisbuch, S. Nakamura, and P. M. Petroff, Nano Lett. **6**, 1116 (2006).
[3] H. Benisty, H. De Neve, and C. Weisbuch, IEEE J. Quantum Electron. **34**, 1612 (1998).
[4] T. Fujii, Y. Gao, R. Sharma, E. L. Hu, S. P. DenBaars, and S. Nakamura, Appl. Phys. Lett. **84**, 855 (2004).
[5] Y. C. Shen *et al.*, Appl. Phys. Lett. **82**, 2221 (2003).
[6] A. David, C. Meier, R. Sharma, F. S. Diana, S. P. DenBaars, E. Hu, S. Nakamura, and C. Weisbuch, Appl. Phys. Lett. **87**, 101107 (2005).
[7] S. Y. Chou, P. R. Krauss, and P. J. Renstrom, Science **272**, 85 (1996).
[8] E. Menard, M. A. Meitl, Y. Sun, J. U. Park, D. J. L. Shir, Y. S. Nam, S. Jeon, and J. A. Rogers, Chem. Rev. (Washington, D.C.) **107**, 1117 (2007).
[9] M. J. Hampton, S. S. Williams, Z. Zhou, J. Nunes, H. H. Ko, J. L. Templeton, E. T. Samulski, and J. M. DeSimone, Adv. Mater. (Weinheim, Ger.) **20**, 2667 (2008).
[10] T. T. Truong, R. Lin, S. Jeon, H. H. Lee, J. Maria, A. Gaur, F. Hua, I. Meinel, and J. A. Rogers, Langmuir **23**, 2898 (2007).
[11] J. P. Rolland, E. C. Hagberg, G. M. Denison, K. R. Carter, and J. M. DeSimone, Angew. Chem., Int. Ed. **43**, 5796 (2004).
[12] L. M. Campos, I. Meinel, R. Guino, M. Schierhorn, N. Gupta, G. D. Stucky, and C. J. Hawker, Adv. Mater. (Weinheim, Ger.) **20**, 3728 (2008).
[13] A. David, H. Benisty, and C. Weisbuch, J. Disp. Technol. **3**, 133 (2007).
[14] S. G. Tikhodeev, A. L. Yablonskii, E. A. Muljarov, N. A. Gippius, and T. Ishihara, Phys. Rev. B **66**, 045102 (2002).
[15] J. J. Wierer, M. R. Krames, J. E. Epler, N. F. Gardner, M. G. Craford, J. R. Wendt, J. A. Simmons and M. M. Sigalas, Appl. Phys. Lett. **84**, 3885 (2004).