

Enhanced light emission of nano-patterned GaN via block copolymer thin films

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Abstract—We demonstrate that the nanoscopic block copolymer patterns on GaN can enhance light extraction efficiency of GaN-based light emitting diodes. Nanoporous patterns were fabricated on a bare GaN substrate via self-assembly of poly(styrene-*b*-methyl methacrylate) block copolymers from which PMMA microdomains were selectively removed later on. A bare GaN surface was treated with a photo-crosslinkable thin layer of poly(styrene-*r*-methyl methacrylate) random copolymers to tune the cylindrical microdomain orientations. The nanoporous block copolymer thin film was controlled to be thicker than its typical repeat period in bulk by incorporating PMMA homopolymer into block copolymer. Consequently, the light extraction efficiency in photoluminescence spectra could be tuned with the thickness of nanopatterned thin film on GaN.

Key words: GaN, Light Emitting Diodes, Block Copolymers, Nanoporous Templates

INTRODUCTION

GaN-based light-emitting diodes (LEDs) have many applications such as liquid-crystal display back lighting, traffic signals, car headlamps and full-color display [1,2]. Furthermore, GaN-based LEDs have been considered to replace the traditional incandescent tungsten-filament lamps in the near future due to their long lifetime and low power consumption [3]. Besides, the microelectronics of GaN has dramatically advanced in high frequency and high power area. AlGaIn/GaN high electron mobility transistors (HEMTs) have outperformed the conventional Si- and GaAs-based transistors [3]. Owing to this intensive research and much progress for the improvement of crystal quality, the internal quantum efficiency now has little room for further improvement [4]. Instead, many researchers have begun to improve the extraction efficiency by KOH-based photo-electrochemical (PEC) etching [5], photonic crystal patterns [6], and surface anodizations [7]. These techniques have succeeded in improving the extraction efficiency, but have drawbacks in reproducibility and higher costs. Clearly, there is a plenty of room for further improvement of extraction efficiency.

Producing nanoscopic features using self-assembly of block copolymers has been extensively studied due to their various potential applications, such as microelectronics, high-density storage media, large area surface catalyst, separation membrane, etc. [8-18]. In this work, we demonstrate a new approach to enhance the light emission of a GaN via nanotexturing of its surface by using the self-assembly of cylinder-forming poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) block copolymers. By controlling the orientation

of cylindrical microdomains and subsequently removing the PMMA blocks, well-defined nanoporous patterns can be produced on the GaN substrates. These patterns may be used as a lithographic mask for pattern transfer, such as reactive ion etching or chemical vapor deposition [8-11], to impose a texture on the bare GaN surface. However, it was also found that the nanoporous pattern itself enhances the extraction efficiency of LEDs without further processing. The block copolymer films with oriented microdomains can act as an excellent antireflective coating, because the refractive index and the film thickness can be easily controlled. Their typical repeat period, far less than the wavelength of visible light, avoids the interaction with visible wavelength and makes the film transparent. Due to the existence of removable microdomains, the refractive index of the surface can be finely adjusted. Also, the thickness of porous films can be readily controlled according to the specific wavelength of emitted light. Thus, the application of the block copolymer thin film on an LED substrate would improve the light extraction efficiency, and this method can be extended to enhance the light harvesting efficiency of photovoltaic materials.

EXPERIMENTAL SECTION

Cylinder-forming PS-*b*-PMMA diblock copolymers ($M_n \sim 60,100$, $f_{PS} = 0.70$, PDI = 1.06) were spun-cast on the GaN substrate to fabricate densely packed nanoporous structures. Prior to film casting, GaN substrates were cut into $1 \times 1 \text{ cm}^2$ pieces, and cleaned repeatedly in acetone and isopropyl alcohol at least three times. Azide-containing PS-*r*-PMMA random copolymer was spun-cast from 0.4 wt% toluene solution onto the cleaned GaN substrates at 3,000 rpm, resulting in 6-8 nm thick layers as the neutral mattress. The film was then crosslinked by UV irradiation ($\lambda_{max} \sim 254 \text{ nm}$) under vacuum for 10 min. Thin films of PS-*b*-PMMA and mixtures with PMMA homopolymer ($M_n \sim 21,200$, PDI = 1.04) (PMMA $\sim 5 \text{ wt\%}$)

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were prepared by spin-casting toluene solutions onto GaN substrates coated with the crosslinked random copolymer layers. The film thickness was varied from about 34 nm to 402 nm by adjusting the solution concentration and spin speed. The polymer solutions were filtered through 0.2 μm Teflon[®] membrane filter before spin-casting. After film depositions, the samples were annealed in a vacuum oven at 170 °C for 12 hours and subsequently cooled to room temperature. UV light ($\lambda_{\text{max}} \sim 254$ nm) was irradiated to the samples for 10 min under vacuum. Degraded PMMA domains were removed from the template by rinsing with acetic acid/ethanol (9 : 1 by weight) mixture. The top and cross-sectional morphologies of the nanoporous films were observed by an atomic force microscope (AFM), Digital Instruments Dimension 3100 and a field emission scanning electron microscope (FE-SEM), JEOL JSM-6700F. The photoluminescence (PL) intensities of the patterned and bare GaN substrates were measured at room temperature, with an ozone-free xenon arc-lamp (150 W) with an excitation wavelength of 325 nm. Thickness of the neutral matrix layer and PS-*b*-PMMA block copolymer film was measured by ellipsometry.

RESULTS AND DISCUSSION

From the application viewpoint, block copolymer thin films are of particular interest due to the possibility of obtaining two-dimensional regular nanoscopic materials. In this case, controlling the orientation and the lateral order of the microdomain in the thin films has been the essential issue. Many efforts have been made to achieve this by various strategies, such as electric field, graphoeptaxy, chemically patterned surface, solvent evaporation, controlled interfacial interaction, etc. [12–16]. Among these efforts, the most useful approach may be the surface modification using random copolymers, which neutralizes the interaction between block copolymers and substrates. The earlier method was to anchor a hydroxyl-terminated PS-*r*-PMMA random copolymer onto silicon oxide (SiO_2) substrates [13]. By thermal annealing for ~ 3 days at 160 °C, the covalent bonding between the hydroxyl group in PS-*r*-PMMA and oxide layer was formed, and hence these brush layers neutralized the interfacial interaction. As a consequence, the perpendicular orientation of microdomains of PS-*b*-PMMA block copolymers, forming PMMA cylinders, could be achieved. However, this approach has a critical limit, as the oxide layer is always required to form a neutral brush

layer.

Recently, a general approach to modify the surface via crosslinking strategy has been developed [14]. It was demonstrated that an incorporation of crosslinkable units, such as benzocyclobutene (BCB) or azide groups, into the backbone of PS-*r*-PMMA random copolymers can crosslink films on various substrates, e.g., Au, Al, Si_3N_4 , etc., and the interfacial interactions were successfully controlled on these substrates. Moreover, the crosslinking strategy is much more efficient, as the processing time was only a few minutes compared to a few days for anchoring PS-*r*-PMMA random copolymers. Therefore, the crosslinking of random copolymer is the only choice to modify the bare GaN surface without an oxide secondary layer and to produce the nanoscopic patterns. Here we used an azide-containing PS-*r*-PMMA random copolymer, which can be crosslinked simply by UV irradiation [14].

The general procedure to fabricate the nanoscopic patterns of PS-*b*-PMMA block copolymers is illustrated in Fig. 1. A key issue is to examine whether the interfacial interaction of the bare GaN substrate can be simply neutralized via crosslinking of PS-*r*-PMMA random copolymers. The ultra-thin layers of PS-*r*-PMMA random copolymers, 6–8 nm in thickness, were spin coated onto the GaN substrate, and then exposed to UV light for ~ 10 minutes, with a total dose of approximately 1–5 J/cm², to crosslink the layer as described elsewhere [14]. After crosslinking, thin films of PS-*b*-PMMA block copolymers were prepared onto these substrates. The films were annealed at 170 °C for at least 12 hours, and the equilibrium morphologies of PS-*b*-PMMA thin films were obtained. Fig. 2a represents phase contrast AFM images of PS-*b*-PMMA films prepared

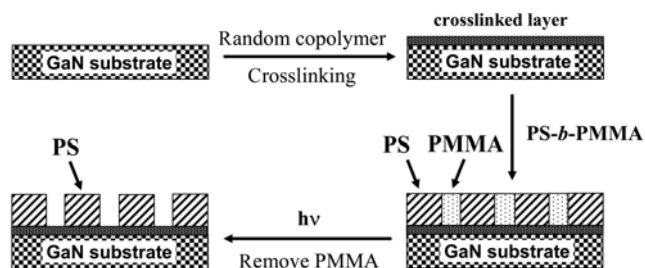


Fig. 1. Schematic illustration for the fabrication of nanoporous patterns on GaN substrate using cylinder-forming PS-*b*-PMMA block copolymers.

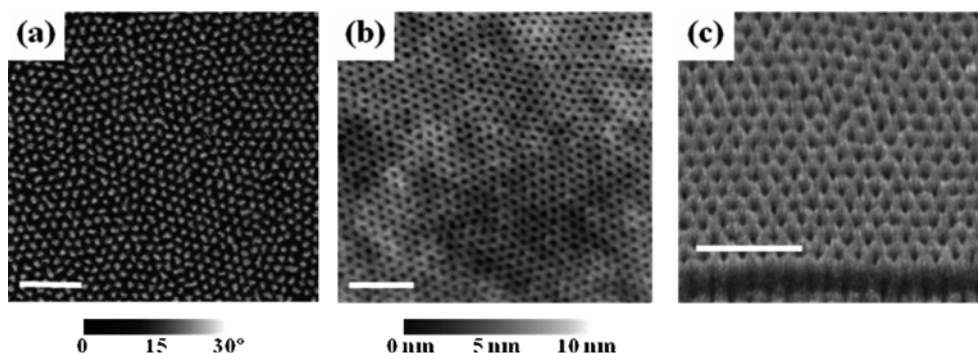


Fig. 2. Structure of nanopatterned block copolymer ($M_n \sim 60$ k) thin film on GaN substrate: (a) Tapping mode AFM phase image before removing PMMA microdomains, (b) AFM height, and (c) FE-SEM images (45° tilted) of nanoporous film on GaN substrate after removing PMMA microdomains. Scale bars are 200 nm.

on the GaN substrates after thermal annealing, where the surface was modified by photo-crosslinking of PS-*r*-PMMA random copolymer. Overall, hexagonally-packed arrays can be observed, which indicates that the microdomains of PMMA cylinders are oriented perpendicularly to the substrates. Therefore, it can be concluded that the crosslinking strategy using azide-containing random copolymers successfully neutralizes the interfacial interaction between PS-*b*-PMMA block copolymers and GaN substrates. Also, the ordering behaviors are similar to those on the SiO₂ substrates that are modified with hydroxyl-terminated random copolymers. A good lateral ordering of hexagonally packed arrays can be seen in Fig. 2a.

To generate nanoporous films, the next step, after controlling the nanoscopic patterns, is the generation of porous structures by removing the microdomain selectively. For this purpose, PMMA is a great choice of microdomains, as PMMA can be readily removed by UV irradiation, followed by washing away with acetic acid and water. Figs. 2b and 2c represent an example of a nanoporous template produced on the surface-modified GaN substrate. From AFM height images in Fig. 2a, the hexagonally packed arrays are shown as dark spots, implying that they are porous structures. The porous structures can be clearly seen from the side view (45° tilted) of the SEM images in Fig. 2c.

The reflectance of a surface depends on the refractive index and the thickness of a top surface film between a substrate and air [19]. The surface film should have lower refractive index than substrate to make the surface antireflective, and porous structures have been usually applied in order to make the refractive index of the film lower than its non-porous one. The block copolymer films with oriented microdomains are suitable for generating an antireflective surface. The refractive index of porous film can be simply estimated from the equation, $n^2 = n_{\text{polymer}}^2 \times (1 - f_{\text{pore}}) + n_{\text{air}}^2 \times f_{\text{pore}}$, where n_{polymer} , n_{air} , and f_{pore} are the refractive indices of polymer and air, and the pore volume fraction of block copolymer film, respectively. Since the refractive indices of PS and air are 1.59 and 1.0, respectively, and the pore volume fraction of PS-*b*-PMMA films is 0.3, the refractive index of porous film on GaN is 1.44. The refractive index of porous film can be readily adjustable by volume fraction of PMMA block, which is degradable by UV irradiation. Also, the inherent nanoscopic structure of block copolymer detours the interaction with visible light, and the removable microdomains offer a chance to control the refractive index of the surface coating. Furthermore, the nanoporous characteristics can make a surface roughened, which will certainly enhance the antireflection of light. Since the microdomains are aligned normal to the substrate, any potential interaction with lateral grain boundary could be avoided.

It is also necessary to control the thickness of nanoporous film to tune the transmittance of surface coating. It has been reported that a block copolymer template, thicker than its repeat period in bulk, cannot be generated only with PS-*b*-PMMA itself [20]. To overcome this issue, Jeong and coworkers demonstrated that the addition of PMMA homopolymer to PS-*b*-PMMA enables one to generate much thicker film than its repeat period with high-aspect ratio cylindrical microdomains being normal to the substrate. We varied the thickness of the nanoporous thin films by adding a small amount of PMMA homopolymer to PS-*b*-PMMA block copolymers as well, and measured the light extraction efficiency of GaN substrates. Fig. 3 shows the PL spectra of bare and patterned GaN sub-

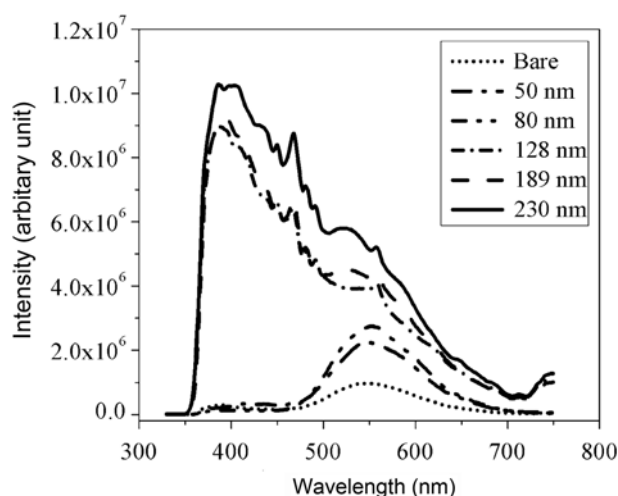


Fig. 3. PL spectra of bare GaN and nanoporous patterned GaN with varied film thickness.

strates measured at room temperature. The PL peaks can be seen at ~400 nm and ~550 nm for both samples. For the patterned GaN substrates, the PL intensity at the wavelength of ~550 nm was enhanced by ca. 6 times, compared to the bare GaN substrate, due to the textured structures on the GaN surface as the thickness of block copolymer film increased. However, we also observed a sudden increase in the PL intensity at shorter wavelength region, ~400 nm, when the thickness of the film was thicker than 128 nm. We do not have a clear answer for the sudden increase in PL intensity at a wavelength of ~400 nm. We just conjecture that this is probably due to destructive interference, as the wavelength and the thickness of patterned layer are matched. This result suggests that the nanoporous patterns can be used to enhance the PL intensity at the blue light emission and, at the same time, to suppress the undesired wavelength.

CONCLUSION

In summary, it was demonstrated that nanopatterned block copolymer thin film can be directly used to enhance the extraction efficiency of GaN. The interfacial interaction of GaN substrates can be successfully controlled via crosslinking of random copolymers. Photo-crosslinkable, azide-containing PS-*r*-PMMA random copolymer was used to modify the bare GaN surface. Consequently, nanoporous templates of PS-*b*-PMMA block copolymers, with various film thicknesses, could be successfully prepared. It is suggested that this method can be extended to improve the efficiency of photovoltaic devices as well as other LED materials.

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