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Enhancement of Light Extraction Efficiency via Inductively Coupled Plasma Etching of Block Copolymer Templates on GaN/Al_2O_3

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We report that nanostructured patterns can be achieved on GaN/Al_2O_3 by a nanofabrication method that employs the inductively coupled plasma (ICP) etching of block copolymer templates. We first prepared the nanoporous patterns of a poly(ethylene oxide-*b*-methyl methacrylate-*b*-styrene) (PEO-*b*-PMMA-*b*-PS) triblock copolymer thin film on GaN/c-Al_2O_3 substrates. Then, the nanostructures from PEO-*b*-PMMA-*b*-PS triblock copolymers were successfully transferred to GaN layers using ICP etching. Room temperature photoluminescence (PL) confirmed that the PL intensity was increased by about 30% around 450 nm wavelength after the pattern transfer onto GaN/c-Al_2O_3 substrates.

Keywords: plasma etching, GaN, self-assembly, block copolymer thin films

1. INTRODUCTION

There has been a huge amount of interest in the fabrication of nanoporous substrates whose surface is functionalized using various organic or inorganic materials.[1-4] Recently, anodized aluminum oxide (AAO) with a highly ordered structure of nano-sized pores was reported. However, it required a second anodization process after removing the first-anodized alumina, which is not only very complicated but also inapplicable to large substrates over 2 inches in size.[5] Soft lithography using a PDMS stamp is one of the potential methods of producing a nanoporous structure, but the scaling-up of this technique is still a major issue.[6] Another possibility is to use a nanostructured pattern obtained from self-assembled block copolymers, such as poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) diblock copolymers with cylindrical microstructures.[7-10] It has been well established that this is a very powerful method of producing nanoporous structures in large wafers. In this case, a secondary layer of PS-*r*-PMMA random copolymer under PS-*b*-PMMA is required because the interaction between the substrate and PS-*b*-PMMA needs to be controlled.[11-12] Once the surface is modified with the PS-*r*-PMMA random copolymer layer, the PMMA cylinders can be oriented normal to the substrate, and the nanoporous structures can be produced after the removal of PMMA via deep UV irradiation.[9] However, the introduction of a secondary layer of PS-*r*-PMMA random copolymer can be disadvantageous.

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Recently, it has been demonstrated that a novel triblock copolymer, poly(ethylene oxide-*b*-methyl methacrylate-*b*-styrene) (PEO-*b*-PMMA-*b*-PS) exhibiting core/shell (PEO/PMMA) cylindrical microstructures, can generate nanoporous structures.[13] In this case, nanostructured patterns with vertically oriented PEO/PMMA cylinders can be produced via solvent annealing techniques; furthermore, the nanoporous templates can be prepared by deep UV irradiation. From the fabrication viewpoint, this system is more desirable than that produced by PS-*b*-PMMA because nanoporous structures can be prepared on any semiconductor substrates without the need for secondary layers.

GaN-based light emitting diodes have attracted a lot of attention due to their low power consumption and better reliability than that of conventional light bulbs.[14] Internal quantum efficiency almost has matured due to the rapid progress in the epitaxial growth technique. However, due to large differences in the refractive index between GaN (2.5) and air (1), the light extraction efficiency is still a major concern. Schnitzer *et al.* reported that light extraction efficiency can be enhanced by surface texturing, which increases the probability for generated photons to escape from the GaN layer.[15]

Here we suggest a novel fabrication technique that combines the self-assembly of PEO-*b*-PMMA-*b*-PS triblock copolymers with inductively coupled plasma (ICP) dry etching. In this study, using chlorine-based ICP dry etching, we demonstrate the transfer of a pattern, whose diameter is as small as 20 nm, from a nano-patterned triblock copolymer to a GaN layer which has a very strong bonding energy.

2. EXPERIMENTS

The ABC triblock copolymer, poly(ethylene oxide-*b*-methyl methacrylate-*b*-styrene) (PEO-*b*-PMMA-*b*-PS), was synthesized via reversible addition fragmentation transfer (RAFT) polymerization as described elsewhere.[13] The total molecular weight of PEO-*b*-PMMA-*b*-PS is 36,000 g/mol and its polydispersity is as narrow as ~1.1. The mole fraction of PEO/PMMA is 28% and that of PS is 72%, and hence the microstructure exhibits a core/shell (PEO/PMMA) cylindrical morphology. The PEO-*b*-PMMA-*b*-PS triblock copolymers were spin coated from benzene solutions onto GaN on c-plane sapphire substrates. Film thicknesses of 30, 50, and 80 nm were obtained by adjusting the solution concentration and spinning speed. The thin films were then annealed in a saturated benzene atmosphere (controlled relative humidity of ~90%) for ~12 hours. To prepare the nanoporous template, the PMMA block was degraded by UV irradiation in vacuum (~10^{-2} Torr) for 10 minutes. The films were then successively rinsed in acetic acid and water to wash away the PMMA and PEO blocks.

A 2 mm thick GaN layer (carrier concentration of ~10^{17} cm^{-3}) was grown on a c-Al_2O_3 substrate by a horizontal atmospheric-pressure Metal-Organic Chemical Vapor Deposition (MOCVD) technique at ~1000°C. ICP dry etching was performed using a Multiplex ICP (STS). Firstly, the silicon wafers were coated with PS to calibrate the etch rate at a pressure of 5 mTorr, DC bias of 228 V, chuck power of 100 W, and ICP power of 800 W using a mixture of Cl_2 and BCl_3 at flow rates of 30 and 5 sccm, respectively. Under these conditions, the dry etch rates for PS and GaN were measured to be 7.1 and 9.0 nm/s, respectively. In the experiment, we chose a PEO-*b*-PMMA-*b*-PS thin film of 50 nm thickness for the pattern transfer to the GaN layer. To reveal the nanoporous GaN layer after completely removing the triblock polymer, ICP dry etching was performed for 8 seconds under the calibrated conditions. FE-SEM was employed to confirm the transfer of the nanoporous polymer pattern from the PEO-*b*-PMMA-*b*-PS triblock copolymers to the GaN layer. Room temperature photoluminescence (PL) spectra were collected from GaN layer when the backside of GaN/Al_2O_3 was exposed to the 325 nm line of a He:Cd laser.

3. RESULTS AND DISCUSSION

The production of nanostructured patterns from the self-assembly of block copolymers has been extensively investigated. The impetus behind this research is rooted in the potential applications of this technique, such as nanolithographic masks, high surface area supports for catalysts, separation membranes, and sensors, etc.[16] Among the several possible systems, we employed a newly developed triblock copolymer, PEO-*b*-PMMA-*b*-PS, which exhibits a cylindrical nanostructure, for the pattern transfer onto the GaN/c-Al_2O_3 substrate. By employing the solvent annealing process with a controlled relative humidity (~90%), the morphology of the thin film could be well controlled, such that the cylindrical nanostructures were oriented perpendicular to the substrate with a high degree of lateral ordering.[13] The most fascinating advantage of this system is that such a morphol-

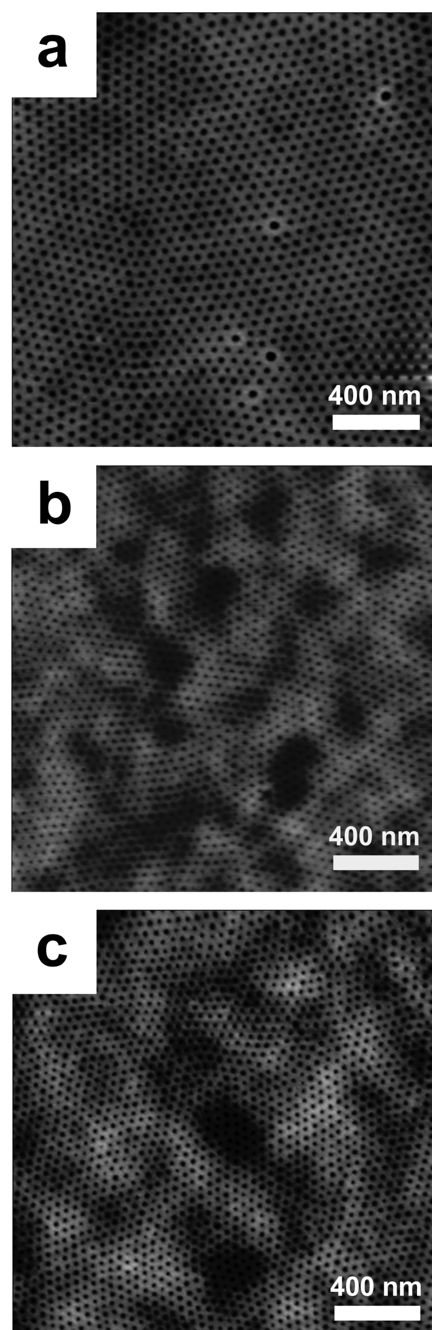

Fig. 1. AFM height images for PEO-*b*-PMMA-*b*-PS triblock copolymer films on GaN, with controlled thicknesses of (a) 30 nm, (b) 50 nm, and (c) 80 nm, after annealing for 12 hours in saturated benzene vapor under controlled humidity conditions (~90%).

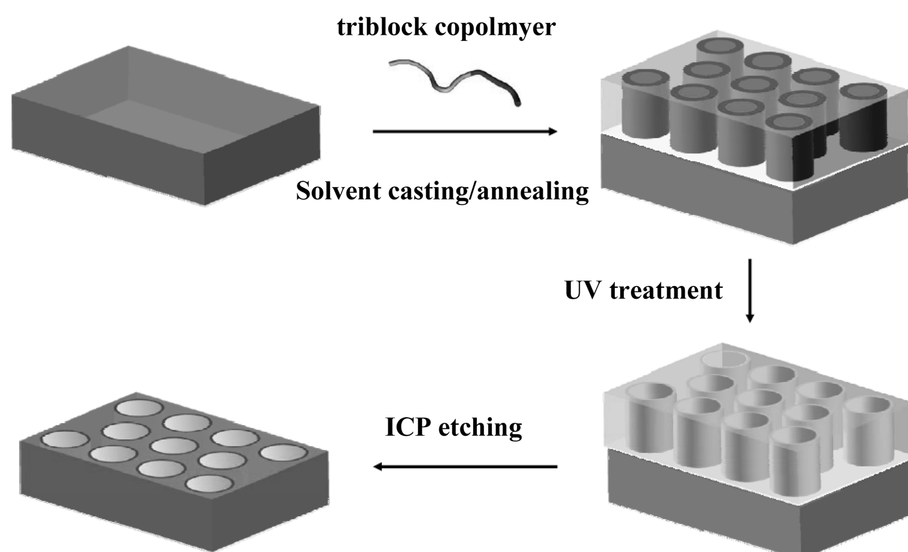

Fig. 2. Schematics to prepare the nanostructured pattern on GaN by the ICP dry etching of a nanoporous template from PEO-*b*-PMMA-*b*-PS triblock copolymer thin films.

ogy can be generated on any substrates without the aid of a secondary layer of either a random copolymer or SiO_2. Also, the thickness of the films can be varied from ~30 nm to ~200 nm. Figure 1 shows the AFM images of the triblock copolymer thin films on GaN/c-Al_2O_3 substrates with controlled thicknesses of 30, 50, and 80 nm after the solvent annealing process. All of the images look similar, as they can be depicted as hexagonally packed arrays. This suggests that the cylindrical microdomains are oriented perpendicular to the GaN layer. Note that the size of the cylindrical microdomains is ~22 nm and that the distance between the pairs of domains is ~40 nm as measured from the height profile in the AFM images.

After the removal of the PMMA block by UV irradiation, nanoporous structures, which can be used as a nanolithographic mask for pattern transfer, were produced. Figure 2 shows the process flow for the pattern transfer using ICP etching. When the silicon wafers were coated with polystyrene to calibrate the etch rate at a DC bias of 228 V, chuck power of 100 W, and ICP power of 800 W using a mixture of Cl_2 and BCl_3 at flow rates of 30 and 5 sccm, respectively, the etch rate was 7.1 nm/s. In the case of the 50 nm thick PEO-*b*-PMMA-*b*-PS triblock copolymer layer, we were able to successfully transfer the nanoporpous patterns to the GaN layer by the nanolithographic patterning method after 8 seconds of ICP dry etching under the same condition. Figure 3 confirms that the nano-sized pattern transfer was successfully achieved. In comparison, electron-beam lithography has often been used to define nano-sized patterns. After each spot across the entire area is exposed to electron beam, the sample is developed and then plasma etched. Focused-ion beam (FIB), which has been often employed in nanofabrication, employs Ga-ions to remove the undesired area in semiconductor wafer. In FIB fabrication, the nano-sized spots in the entire wafer should be processed one by one. Both methods are therefore inapplicable to mass production, thus rendering advantages to our method, which is based on block copolymer lithography. To the best of our knowledge, there is no report on the pattern transfer of block copolymer on the GaN surface using the ICP etching process.

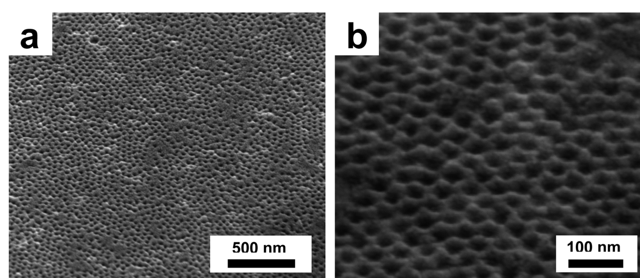

Fig. 3. SEM images of the nanostructured pattern on GaN after ICP dry etching (a) low magnification (b) high magnification.

GaN-based LEDs have shown very promising results for their device performances. However, due to the large difference in the refractive index between GaN (2.5) and air (1), these optical emitters suffer from a low extraction efficiency.[17] One solution to this problem is surface texturing to increase the extraction efficiency through multi-scattering. Therefore, the novel technique proposed herein was applied to surface roughening through the plasma etching of a nanoporous pattern of block copolymer template. As shown in Fig. 4, after surface texturing, the room temperature PL spectrum exhibits a ~30% intensity enhancement around 450 nm. This method has an advantage over electron-beam lithography in terms of the processing time and cost, and over soft lithography in terms of scale-up issues.

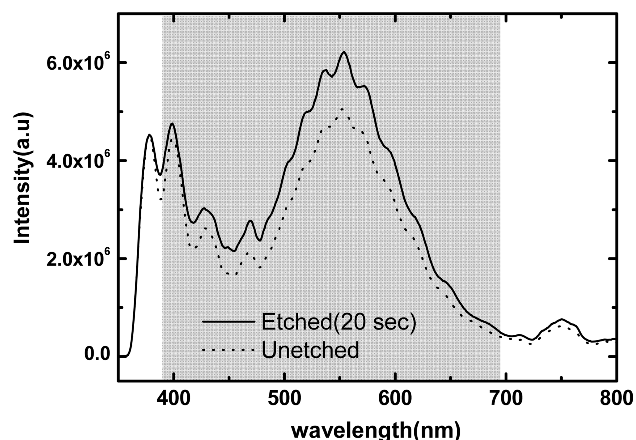

Fig. 4. Room temperature PL spectrum before and after surface texturing. Shaded area shows visible wavelength.

4. CONCLUSIONS

We have developed a novel method of defining a nanostructure on a generic semiconductor substrate using the nanolithographic technique. Nanoporous templates were prepared on a GaN/c-Al_2O_3 substrate by the spin-casting of PEO-*b*-PMMA-*b*-PS triblock copolymers followed by solvent annealing and UV treatment. Subsequently, ICP dry etching was employed to transfer the nanopattern to the GaN/c-Al_2O_3 substrate. This simple but powerful method was implemented to the surface texturing of GaN-based LEDs, where PL intensity was increased by about 30% from textured surface.

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