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Letter

Inductively coupled plasma etching of nano-patterned sapphire for flip-chip GaN light emitting diode applications

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Abstract

The flip-chip configuration is employed for the production of high-brightness GaN-based light emitting diodes to improve the extraction of heat. A lithographic approach based on a sacrificial SiO_2 nanosphere etch mask was developed to enhance the external extraction of light from the sapphire substrate. Closed-packed arrays of SiO_2 nanospheres were prepared by a simple solution-based method on the sapphire substrate. Subsequent dry-etching via inductively coupled plasma using a gas mixture of BCl_3 and Cl_2 transferred a pattern into the sapphire substrate with the lowest etching at the center of the SiO_2 nanosphere. This process created an array of circular cones in the surface of the sapphire that were found to be effective in enhancing the light extraction efficiency through multi-photon scatterings. Room temperature photoluminescence exhibited an increase of 22.5% in intensity after the surface of sapphire was textured.

Keywords: Light emitting diodes; Surface texturing; Plasma etching; Sapphire; GaN

1. Introduction

Gallium nitride-based light emitting diodes (LEDs) are a critical component in numerous applications including cell phones, lap-top computers, automobiles, and traffic lights. Over the past decade, the external efficiency of GaN LEDs has continuously increased based on improvements in internal and, more of late, extraction efficiency [1–5]. The external quantum efficiency (η_{external}: the number of photons emitted/the number of electrons supplied) can be expressed as $\eta_{\mathrm{internal}} \times \eta_{\mathrm{extraction}}$, where η_{internal} is the internal quantum efficiency, and $\eta_{\mathrm{extraction}}$ is the light extraction efficiency [3]. Recent advances in epitaxial growth technique made it possible that the internal quantum efficiency is almost maximized (~80%) [6]. But the low light extraction efficiency metric is still an issue resulting from the narrow semiconductor-air extraction cone. The critical escape angle is limited by the large differences in refractive index (n) of semiconductors ($n_{\mathrm{GaN}}=2.5$) and sapphire ($n_{\mathrm{sapphire}}=1.78$) with air ($n_{\mathrm{air}}=1$) [7–10]. Focused-ion beam and masked lithographic etching of photonic crystal structures, KOH-based wet etching for surface roughening, and etching of anodized aluminum oxide have been used to increase the light extraction efficiency [9–13]. However, these techniques are not applicable to large wafers and remain difficult to control, particularly for the lack of selectivity in KOH-based wet etching. In this paper, we present a production-ready technique to enhance the light extraction efficiency in reproducible way.

The flip-chip configuration is widely employed in high power GaN-based LEDs because the thermal conductivity of sapphire is extremely poor (42 W/m K at 25 °C) and sapphire is transparent up to deep UV range [3]. In this configuration, the top layer is sapphire and the GaN layer is in close contact to thick metal carrier. Unfortunately, there is no wet etchant available for sapphire. Also, the dry-etch rate of sapphire is considerably slower than the etch rate of standard photoresist [14,15]. Therefore, a very thick and unreliable photoresist or

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metal-mask is required to generate a pattern on sapphire. Here, we suggest a simple method to texture the sapphire surface by inductively coupled plasma etching (ICP) of ordered SiO_2 nanospheres. In this approach, spin-casted SiO_2 nanospheres served as a sacrificial dry-etch mask.

2. Experimental details

Gallium nitride was grown by metal-organic chemical vapor deposition (MO-CVD) directly on *a*-plane sapphire substrate. Growth was carried out in a modified vertical impinging flow CVD reactor. A 25-nm AlN buffer layer was deposited at 680 °C and 6670 Pa. Subsequently, a 4-μm n-type GaN:Si was deposited at 1020 °C and 33,300 Pa. The n-doping of GaN was accomplished with disilane. In-situ reflectance monitoring with a 534.5-nm HeNe laser was used to monitor the growth process in real time. Further details of the growth process and equipment are available elsewhere [5,8].

The monodisperse silica (SiO_2) nanoparticles were synthesized according to the Stöber method, via hydrolysis of tetraethylorthosilicate (TEOS) in an alcohol medium in the presence of water and ammonia [16]. The size of the SiO_2 particles were controlled to 240 nm by setting the concentrations of ammonia, TEOS, and water to 0.1, 17.0, and 0.2 M, respectively [17]. The resulting mean diameter of SiO_2 particles was measured by Scanning Electron Microscopy.

First, the sapphire surface was covered with a 50-nm thick layer of polystyrene (PS) to secure the SiO_2 nanospheres. Then the surface was made hydrophilic by exposing it to UV radiation. SiO_2 nanospheres with a diameter of 240 nm were spun-cast on the surface of PS/sapphire, followed by annealing at 160 °C for 10 min to embed the SiO_2 nanospheres into the PS layer. Then, the sample was loaded in multiplex ICP (STS) equipment for dry-etching at a pressure of 0.667 Pa. A mixture of Cl_2 (7.5 sccm) and BCl_3 (30 sccm) was used at a radio-frequency power of 150 W and coil power of 600 W. Hsu *et al.* reported that the etch rate of sapphire is 100 nm/min under the same conditions [18].

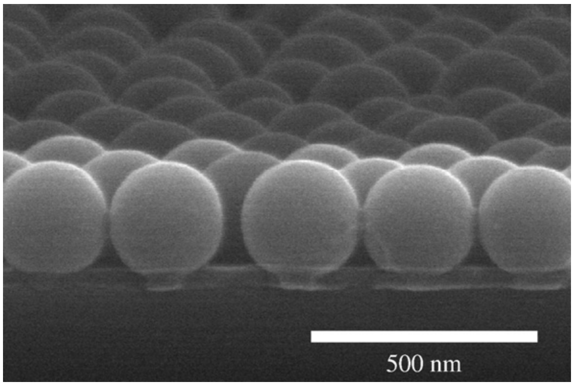

Fig. 2. Cross-section scanning electron micrograph of SiO_2 nanospheres embedded in the surface of a PS layer of the surface of the sapphire wafer.

Scanning electron microscopy was used to monitor the surface structure before and after ICP dry-etching. Room temperature photoluminescence spectra were obtained using 325 nm line of UV lamp before and after surface texturing.

3. Results and discussion

The four step process flow to create arrayed nano-cones in the surface of the sapphire substrate by ICP etching SiO_2 nanospheres embedded in a PS layer is depicted in Fig. 1. The PS layer was prepared on the sapphire surface, and then arrays of SiO_2 nanospheres were subsequently deposited on the PS layer. After heating to 160 °C, well above the glass transition temperature of

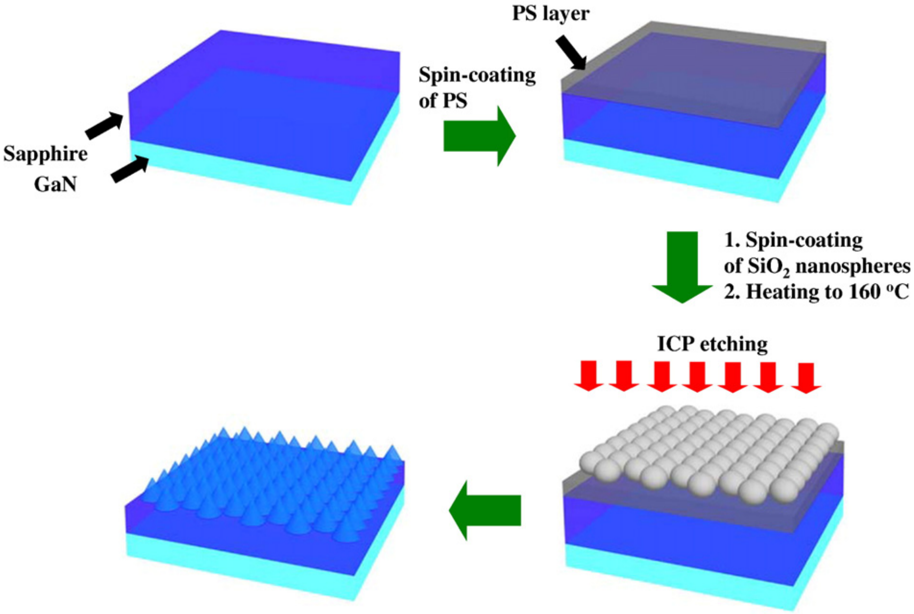

Fig. 1. (Step 1) the GaN/Sapphire was mounted in a flip-chip configuration, and (Step 2) a 50-nm PS layer was deposited to bind the SiO_2 nanospheres, (Step 3) which were subsequently deposited by spin-coating. After SiO_2 nanospheres were embedded in the PS layer by heating, (Step 4) nano-patterns were created in the sapphire by ICP dry-etching via the SiO_2 nanosphere mask.

PS, SiO_2 nanospheres were embedded into the PS layer. The cross-sectional electron micrograph in Fig. 2 shows that each SiO_2 nanosphere has sunk into polystyrene layer. The ensuing dry-etch of SiO_2 nanospheres on the sapphire substrate created a high-density of circular sapphire cone structures, as can be clearly observed in an inclined and top view in Fig. 3(A) and (B), respectively. The geometry of the sapphire cone structure is based on the geometry of the sacrificial SiO_2 nanosphere. Essentially, the thickness variation across the spherical SiO_2 sacrificial etch mask results in the different etched depth in the sapphire, thereby leading to the cone structures.

According to Snell's law, the critical angle for escape can be calculated using $\theta_C = \sin^{-1}(n_2/n_1)$, where n_1 is the refractive index of semiconductor and n_2 is the refractive index of air [3]. By Snell's law the extraction from a bi- or multi-layer structure only depends on the index of the entrance (GaN) and exit (air). Any planar inter-layer does not affect this fundamental relation, e.g., $n_{\mathrm{air}}\sin(\theta_{\mathrm{air}}) = n_1\sin(\theta_1) = n_2\sin(\theta_2) = \ldots = n_{\mathrm{GaN}}\sin(\theta_{\mathrm{GaN}})$. Thus, a fixed amount of light generated in GaN will escape into air regardless of the number of planar (optically-thick optically-transparent) layers. To increase light extraction efficiency in GaN LED with flip-chip configuration, surface-texturing of sapphire would be desired [19]. At the fixed critical angle between semiconductor and air, it is very important to give photons more opportunities for escape from sapphire. Textured surface has advantage over flat surface in increasing the number of photon scattering events. In this case, textured surface can randomize the reflection angle, which can reduce the number of photons permanently trapped within sapphire [19].

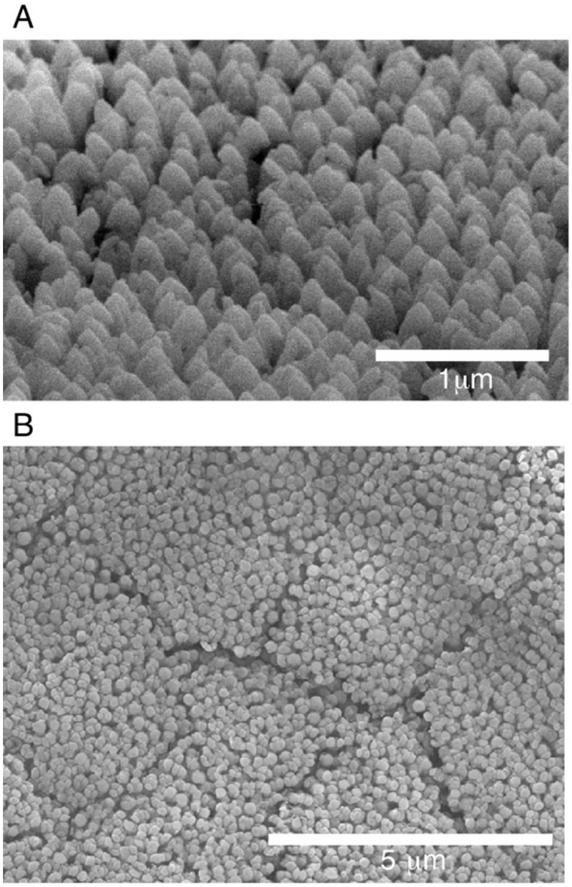

Fig. 3. Scanning electron micrographs of the sapphire substrate following the ICP etch in a (A) tilted view and (B) top-view.

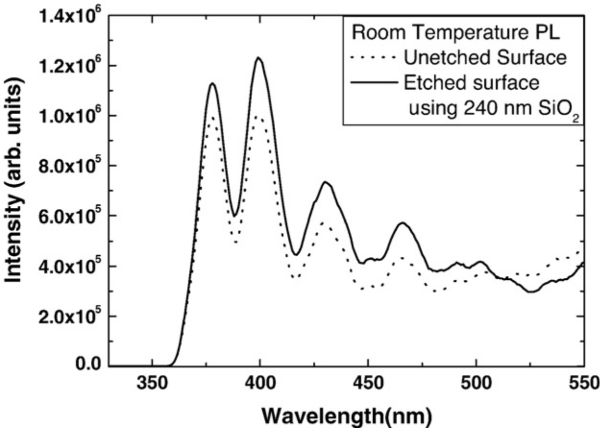

Fig. 4. Photoluminescence spectra at room temperature of the flip-chip GaN/Sapphire before and after texturing of the sapphire surface.

A room temperature photoluminescence spectrum was collected from the (top side in the flip-chip configuration) sapphire, while the GaN was excited with a 325 nm line of UV lamp exposed to (bottom-side) GaN layer (Fig. 4). The photoluminescence response at 400 nm was increased by 22.5% after surface texturing. Additionally, the increase of emission over a broad range of energies indicates that the nano-textured surface, compared to a flat surface, increases the number of photon scattering events.

This natural lithography approach using ordered SiO_2 nanospheres as mask material is superior for large area, volume processes as it is very simple and fast compared to other methods such as imprinting, electron-beam lithography, focused-ion beam pattering and conventional photolithography [20–22]. Furthermore, this approach is highly reproducible, particularly compared to a photo-electro-chemical wet etch process based on a KOH solution.

4. Conclusion

Closed-packed arrays of SiO_2 nanospheres with a diameter of 240 nm were prepared on the surface of a sapphire substrate. The sapphire was dry-etched with a mixture of BCl_3 and Cl_2 gas, with the SiO_2 nanospheres serving as a sacrificial mask material. It was demonstrated that texturing of the sapphire surface into patterned circular cone shapes is very effective at increasing light extraction efficiency. After this surface texturing approach was applied to a GaN/Sapphire in a flip-chip configuration, the intensity of light extracted increased by 22.5%. This approach provides a simple and scalable process to enhance the extraction of light from high-brightness GaN-based LEDs.

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