Preparing nano-hole arrays by using porous anodic aluminum oxide nano-structural masks for the enhanced emission from InGaN/GaN blue light-emitting diodes

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Abstract

We report on the achievement of the enhanced cathodoluminescence (CL) from InGaN/GaN light-emitting diodes (LEDs) by using roughening surface. Nanoporous anodic aluminum oxide (AAO) mask was utilized to form nano-hole arrays on the surface of InGaN/GaN LEDs. AAO membranes with ordered hexagonal structures were fabricated from aluminum foils by a two-step anodization method. The average pore densities of $\sim 1.0 \times 10^{10} \text{ cm}^{-2}$ and $3.0 \times 10^{10} \text{ cm}^{-2}$ were fabricated with the constant anodization voltages of 25 and 40 V, respectively. Anodic porous alumina film with a thickness of $\sim 600 \text{ nm}$ has been used as a mask for the induced couple plasma etching process to fabricate nano-hole arrays on the LED surface. Diameter and depth of nano-holes can be controlled by varying the etching duration and/or the diameter of AAO membranes. Due to the reduction of total internal reflection obtained in the patterned samples, we have observed that the cathodoluminescence intensity of LEDs with nanoporous structures is increased up to eight times compared to that of samples without using nanoporous structure.

Keywords: light-emitting diode, nanopatterning, light scattering, anodic aluminum oxide

Classification number: 2.07

1. Introduction

High-performance GaN-based light-emitting diodes (LEDs) have recently attracted considerable interest for full-color displays, and future phosphor free solid state lighting applications [1, 2]. However, the external quantum efficiency of GaN-based LEDs is still low even though the internal efficiency has been significantly improved [3–5]. Several approaches have been investigated to enhance the LED external quantum efficiency including the surface texturing, roughening, omni-directional reflectors, transparent electrodes, patterned substrates and photonic crystals [5–8]. Among these techniques, nanoporous anodic aluminum oxide (AAO) membrane with self-assembled periodic pore structure is widely used as a template for the formation of various nanostructures for opto-electronic devices due to its low cost and simple fabrication method [9–11]. In this paper we report on the enhanced cathodoluminescence of the InGaN/GaN blue LEDs by using nano-hole arrays on p-GaN surface using AAO masks. The AAO membranes have been fabricated from...
an aluminum foil by a two-step anodization method with anodization voltages in the range of 25 and 40 V in sulfuric acid or oxalic acid electrolyte. The pore density and pore size can be controlled by adjusting anodization voltage, while the film thickness can be changed by varying the anodization time and considering the dependence of growth rate on the applied voltage and electrolyte. Inductively coupled plasma (ICP) dry etching method was used to etch and define nano-hole array pattern on LED surface through an AAO mask. The diameter and depth of the holes can be controlled by optimizing the etching time. The nano-hole arrays are finally formed on the LED wafers after removing the AAO masks. Cathodoluminescence properties of LED with nanoporous structures are recorded as eight times stronger compared to that of samples without using nanoporous structure.

2. Experimental procedures

A mirror-like surface of Al surface has been formed from the pretreatment of electropolishing in a mixed solution of perchloric acid and ethanol (1:4 in volume) for 60 min. Nanoporous AAO layers have been fabricated through a two-step anodization process from an aluminum foil (99.99%, 100 µm in thickness, Tokai). The first anodization process is performed in the 0.3 mol l\(^{-1}\) oxalic acid with the applied voltages from 30 to 40 V or 0.3 mol l\(^{-1}\) sulfuric acid at 25 V for 8 h at 1°C, then the anodized oxide layer on the Al foil is removed in a mixture solution of H\(_2\)PO\(_4\) and CrO\(_3\) at 65°C for 3 h. The sample is then exposed for the second anodization step, resulting in a thin alumina film on top of the Al foil by controlling anodizing time. The remaining aluminum substrate is removed in a saturated HgCl\(_2\) solution, leaving a thick anodized alumina layer. The removal of the barrier layer and pore widening are conducted in a 5 wt% H\(_3\)PO\(_4\) solution at 30°C for 10–50 min.

In this study InGaN/GaN blue LED wafers have been grown on sapphire (0001) substrates by low-pressure metalorganic chemical vapor deposition (LP-MOCVD). The AAO mask is subsequently placed on top of the LED structure. ICP etching is then applied to make the nanopattern on the \(p\)-GaN top layer of InGaN/GaN LED. The etchants are BCl\(_3\) and Cl\(_2\) under an ICP source power of 800 W and an RF bias power of 100 W. The nano-hole arrays are revealed on top of the LED wafers after removing AAO mask by using acetone solution. The morphologies of the AAO masks and patterned LEDs are studied by field emission scanning electron microscopy (FESEM). A CL microscope (Gatan MonoCL3) which is composed of a high-sensitivity photomultiplier tube (thermoelectrically cooled to \(-20°C\)) attached to an SEM (S-4300SE from Hitachi) is used to study the light extraction properties of the LED structures with and without nano-hole arrays. The measurement is performed at room temperature.

3. Results and discussion

3.1. AAO membrane preparation results

The formation of the highly ordered hexagonal pore arrays of the alumina membranes is a self-organization process during the Al anodization. Sulfuric, oxalic and phosphoric acid solutions, used as electrolytes for the anodization process, are suitable for the preparation of alumina membranes with small-, medium- and large-sized pores, respectively. A good tuning of the pore diameter and cell size of the alumina membranes can be obtained for the small- and medium-sized pore membranes [12]. However, for alumina membranes with
large pores, a narrow size distribution of pore diameter and cell size and regular arrangements of pores cannot be easily obtained. Therefore, in this work, sulfuric and oxalic acids are chosen for the preparation of alumina membranes. Normally the regularity of the pores and pore arrangement increases with the anodization time, especially in the first several hours. After a long first anodization, alumina membranes with disordered pores on the top and regular pores at the bottom of the membranes are observed. Then a second anodization was carried out on this surface-patterned Al foil, resulting in alumina membranes with regular pore arrays as shown in figure 1. The nano-hole arrays have a hexagonal structure, and the distances between the holes or pore density vary when we change the anodic voltages. The pore densities are approximately of $1.08 \times 10^{10}$, $2.20 \times 10^{10}$ and $2.96 \times 10^{10}$ cm$^{-2}$ in the cases of 40 and 30 V in oxalic acid and 25 V in sulfuric acid, as shown in figures 1(a)–(c), respectively.

The pores extend down to an alumina barrier layer between the pore bottom and the Al foil. The remaining aluminum substrate was removed in a saturated HgCl$_2$ solution, leaving a thick anodized alumina layer. Use acid solution H$_3$PO$_4$ to remove the barrier layer and etch the pore walls resulted in alumina membranes with regular pore arrays at both sides of the membranes. By controlling the hole-widening time, the different pore diameters of AAO films are obtained. The AAO films with different pore sizes 20, 35 and 50 nm, were prepared by varying the hole-widening time as 10, 20 and 40 min, respectively, while setting the applied voltage and the anodization time to 40 V and 10 min in order to maintain a fixed pore number density and similar film thickness. This could be obtained by increasing the second anodization time from 5 to 30 min. A cross-section view FESEM image of a typical nanoporous AAO mask with highly uniform through hole is displayed in figure 2.

### 3.2. The CL properties of LED with nanoporous structures

The AAO masks fabricated at a voltage of 40 V with a thickness of ~600 nm are used for the ICP etching processes. Figure 3 shows FESEM image of the nano-hole arrays formed on top of the LED wafer after a 10 s ICP etching and removal of the AAO mask. The mean diameter and depth of the nano-holes are estimated to be ~50 and 3.5 nm, respectively. The holes that formed on top of the LEDs are slightly larger than those of the AAO templates since the AAO masks may be etched out during the plasma etching process and/or the surfaces of LEDs in contact with the AAO masks are not completely smooth. As the ICP etching time increases to 15 s, the diameter of the nano-holes increases to 70 nm. The nano-hole arrays on top of the LEDs still maintain a quasi-hexagonal structure as in the case of the AAO templates.

Figure 4 shows the CL spectra of LEDs with and without nano-hole arrays. The CL measurements are carried out at room temperature with electron beam energy of 10 kV. It is clearly observed that, after the ICP etching process and removal of the AAO mask, the CL intensity of the LEDs with 50 nm nano-hole arrays increases ~ eight times compared to that of the unpatterned LEDs. The increased CL intensity of the LEDs with nano-hole arrays may be attributed to the light scattering by the textured surfaces [13]. Because the nano-holes have a cone shape, the incident light from quantum wells with an angle higher than the critical angle might be refracted to the air by side walls of the etched holes [14]. As a result, more blue light may escape from the nano-patterned LEDs compared to the as-grown LEDs. The blue peak emission of the LEDs with 70 nm hole arrays decreases and slightly shifts to a longer wavelength compared
to that of the LEDs with 50 nm hole arrays. As ICP etching time increases, the nano-holes are broadened, because the AAO masks may be etched out during plasma etching process or because the surface of the LEDs’ contact to the AAO masks may not be completely smooth. The broadening of the nano-holes might cause their cone shapes to change and decrease the refraction of the blue light by the side walls of the etched holes. This may contribute to the reduced CL intensity observed from the patterned LEDs with 70 nm hole arrays compared to that from the samples with 50 nm hole arrays. Overall, both LEDs with roughening surfaces exhibit much stronger cathodoluminescence over the unpattern samples.

4. Conclusion

Nanoporous AAO membranes with ordered hexagonal structure have been fabricated from an aluminum foil by a two-step anodization method. By applying the anodization voltages in the range of 25 and 40 V, the number of nanopores in the AAO membrane was controlled between $1.0 \times 10^{10}$ pores cm$^{-2}$ and $3.0 \times 10^{10}$ pores cm$^{-2}$. By controlling anodizing time, the anodic porous alumina films with around 400–1600 nm thickness have been obtained. A hole diameter from 20–60 nm could also be obtained by controlling the aging time in 5–wt% H$_3$PO$_4$ solution. Nanoporous array structures on blue InGaN/GaN LEDs were successfully fabricated using AAO templates as etching masks. The FESEM analysis showed that nanoporous arrays with pore diameters of approximately 50–70 nm were fabricated in a $p$-GaN layer after dry etching. The CL intensity of LEDs with the nano-hole array is enhanced up to eight times compared to that of LED samples without using nano-hole array.

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