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Facile Fabrication of Free-Standing Light Emitting Diode by Combination of Wet Chemical Etchings

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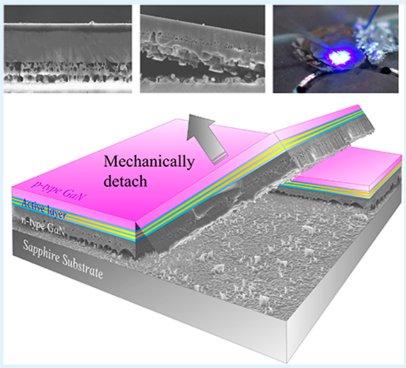
ABSTRACT: Free-standing GaN light-emitting diode (LED) structure with high crystalline quality was fabricated by combining electrochemical and photoelectrochemical etching followed by regrowth of LED structure and subsequent mechanical detachment from a substrate. The structural quality and composition of the regrown LED film thus produced was similar to standard LED, but the photoluminescence and electroluminescence intensity of the LED structures on the etched template were several times higher than for standard LED. The performance enhancement was attributable to additional light scattering and improved crystalline quality as a result of the combined etching scheme.



KEYWORDS: *EC-PEC, GaN LED, nanostructure, lift-off*

1. INTRODUCTION

GaN-based III-nitrides and their alloys are wide-bandgap semiconductors with properties favorable for fabrication of UV-to-visible light emitting diodes (LEDs) and photodetectors as well as high-frequency and high-power electronic devices.[1−3] Sapphire as a heterogeneous substrate has been widely chosen for the epitaxial growth of III-nitride, largely because of its structural similarity to the nitrides and its price competitiveness.[1] Actually nitride LEDs were first developed on sapphire and the heteroepitaxy technology on this substrate is very mature. However, its high electrical resistance and poor thermal conductivity imposes significant performance constraints on the GaN-based optoelectronic and electronic devices.[4−7] Homogeneous bulk substrates would be the best option to boost up the device performance.[8] Unfortunately, despite many years of intense research, the high equilibrium pressures and temperatures of the nitrides have so far made it difficult to grow the bulk substrates with production-grade sizes and quality.[9]

Hence, it looks very attractive to do epitaxial growth on sapphire and then detach the structure and transfer it to a substrate of choice. The advantages here include improved series resistance and more efficient carrier injection owing to the removal of the insulating substrate, enhanced light extraction efficiency because of the scattering on the roughened lower interface, and a better thermal conductivity when the structure is transferred to a substrate with good thermal properties.[10,11] To this end, several approaches have been developed.[10−13] For example, in a laser lift-off (LLO) method the LED structure is separated from the sapphire substrate by using deep ultraviolet laser.[10,11] However, the LLO process can produce in some cases additional defects and intermixing of the GaN/InGaN layer so that the procedure has to be carefully optimized.[14,15]

A chemical lift-off (CLO) is more accommodating in these respects, providing low etch-induced damages, cost effectiveness, simplicity and selective etching by using sacrificial layers.[12,13] Electrochemical (EC) etching can be used for such CLO processes, which rely on producing a nanoporous structure by EC etching with subsequent regrowth.[16,17] When used as a regrowth template, the nanoporous structure is believed to partially block the threading dislocations from penetrating into the active region of the GaN layer.[18] Moreover, high temperature annealing during growth has been reported to transform the pores into spherical voids facilitating subsequent mechanical separation. This detachment, however, is not always uniform and easy to achieve. As reported in our earlier paper,[19] a combination of front-side EC etching and back-side photoelectrochemical (PEC) etching improves the separation uniformity for GaN single layers. In the present study, we apply this combined method to produce free-standing

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blue LED structure and describe the optical and electrical properties of such a free-standing LED.

2. EXPERIMENTAL METHODS

The samples used in this study were grown on double-side polished (0001) sapphire (Al_2O_3) substrates using a metal organic chemical vapor deposition system. Compared to ref 19, the overall GaN thickness for chemical etching was thinner to facilitate the back-side PEC etching and easy separation. Detailed procedure for free-standing LED is shown in Figure 1. The structure of the reference sample is completely the same as for the free-standing LED except for the presence of the EC/PEC template. A 1 μm-thick unintentionally doped GaN (uid-GaN) layer and a subsequent 2 μm-thick n-type GaN (n-GaN) layer was grown at 1040 °C and 200 Torr (Figure 1a). The nanoporous GaN layer was prepared by the doping-selective EC etching[20] of the n-GaN layer in oxalic acid (0.2 M, 15 V) for 30 min at room temperature, with the pore diameter around 20−30 nm and the depth of 2 μm (Figure 1b). The back-side PEC etching was carried out in potassium hydroxide (KOH) solution (0.06 M, 9 V) for 30 min under UV illumination (Figure 1c). During this process the uid-GaN layer was preferentially etched in dislocation free areas because dislocations in GaN are very efficient centers of nonradiative recombination killing the density of holes produced by the back-side illumination. As a result the uid-GaN portion of the layer was turned into needles surrounding dislocations.[19,21] Three different regions (unetched reference, only EC etched, and EC-PEC etched region) were formed in a 2 inch sapphire substrate by applying a polyimide film with silicone adhesive as an etching mask. On this GaN template, a 4 μm-thick n-GaN layer, five InGaN/GaN multiple quantum wells (MQW), and a 150 nm-thick p-type GaN layer was regrown sequentially (Figure 1d). The GaN barriers and InGaN wells were grown at temperatures of 840 °C and 780 °C and pressure of 350 Torr, respectively. The p-GaN was grown at temperature and pressure of 920 °C and 300 Torr. Figure 1e shows a schematic drawing of the sample structure and the mechanically detached part. To detach the LED structure, an epoxy bond was coated on the LED surface and then a slide glass was attached on the epoxy. After heating at 100 °C for 12 h, the whole assembly was then forced to mechanically separate the grown film from the sapphire substrate. The LED on nanoporous structure detached from the substrate was transferred to another slide glass with indium contact. This transferred LED structure was turned upside down like conventional LED structure and free-standing LED with diameter of around 5 × 7 mm^2 was prepared as shown in Figure 1f. The photograph of the transferred LED structure luminescing under the current passing through the top indium contacts is shown in Figure 1g. To compare the forward current−voltage I−V characteristics and the relative intensities of the emitted light for various driving currents in the reference and the EC/PEC overgrown structures on-wafer probing of the LED structures with sapphire substrate not removed was done using In contacts. Furthermore, the residual GaN needles left on the substrate after detaching the LED structure could be easily removed by etching in molten KOH for 10 min.[19,22] This provides an additional merit of recycling the used sapphire substrate in subsequent processes.

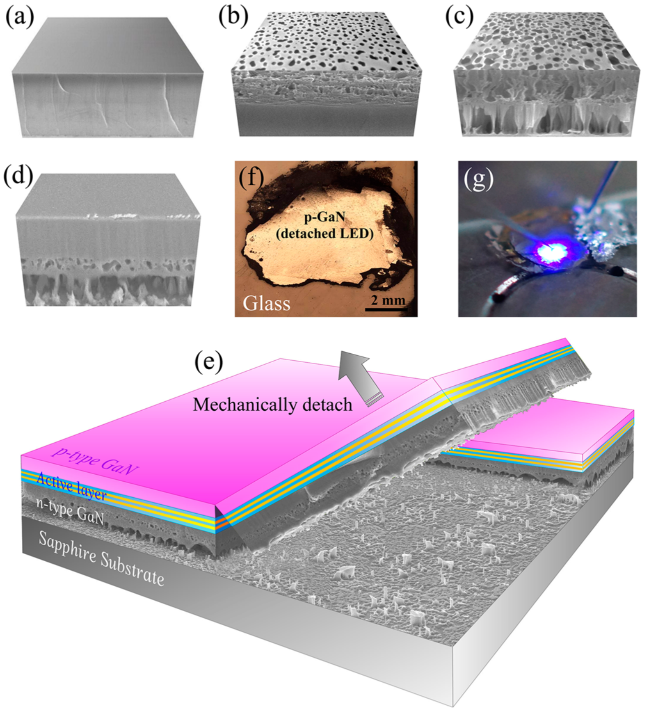

Figure 1. Fabrication process for the free standing LEDs: GaN template (a), EC etching (b), PEC etching (c), regrown LED structure (d), schematic drawing of sample structure (e), lift-off LED (f), and light emission by current injection (g).

The morphology of the etched and transferred sample was investigated by scanning electron microscopy (SEM) and optical microscopy (OM). Photoluminescence (PL) and electroluminescence (EL) measurements were carried out to study the optical and electrical properties of the LED sample. The EL properties were quantified by on-wafer probing of the device. A 25mW, He−Cd laser (325 nm) was used as the excitation source for the room temperature PL measurement. The luminescence imaging of the wafer was carried out by a PL mapper with a 375-nm-wavelength light source. The structural characterization was done by high resolution x-ray diffraction (HRXRD) measurements.

3. RESULTS AND DISCUSSION

It has been reported in the literature that regrown GaN layers on nanoporous GaN templates have a lower dislocation density and piezoelectric field and thus higher light emission efficiency.[18,23,24] Recently this has been also reported for free-standing structures prepared on such porous templates.[16,17] For the separation process to be of practical use the regrowth of GaN on porous templates should proceed crack-free and the lift-off of the regrown layer should not occur during the layer growth. At the same time, the film should be easily separated by mechanical force after regrowth. It has been demonstrated in previous papers that during regrowth the pores in the upper portion of the layer are commonly converted into approximately spherical voids produced by lateral overgrowth, while the nanoneedles in the lower portion of the template are transformed into nanocolumns with the spherical voids sitting on top.[25,26] The resultant structure is determined by the starting density of pores and by the conditions during growth. While avoiding detachment during growth, optimizing the morphology in such a way as to facilitate easy and uniform separation after growth is the key issue here.

Figures 2a and b show the cross sectional SEM images of regrown LED samples prepared on EC and combined EC/PEC etched templates, respectively. The nanoporous template formed by only EC etching clearly shows the row of approximately spherical voids formed instead of the pores at the interface between the regrown structure and the EC etched template (see Figure 2a). Lateral overgrowth giving rise to this morphology can play a certain role in improving the crystalline quality of the structure, but the presence of such a boundary is not sufficient to provide effective film separation. As reported in refs 16 and 17, EC etching alone can in principle be used for effective lift-off of the overgrown GaN, but a higher than usual growth temperature and lower than usual growth pressure are necessary to provide the desired change in the density and

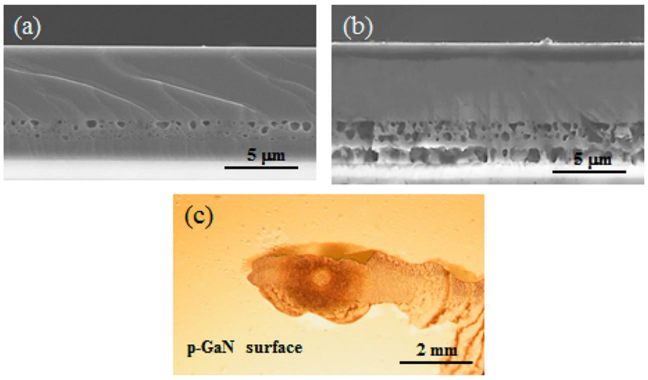

Figure 2. SEM images for the LED structure regrown on the EC etched template (a) and the EC and PEC etched template (b) and OM image for LED film separated during the regrowth (c).

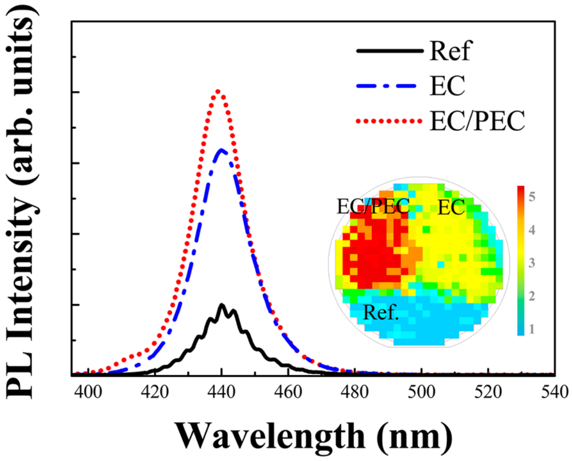

Figure 3. PL spectra of the LED structures on different templates. The inset shows PL mapping result.

shape of the pores.[25] These changes in growth conditions could pose a serious problem when optimizing the performance of the QW region. In our EC/PEC approach no such change of the growth conditions is required to obtain clean and uniform separation, which is, of course, a serious advantage. The nanoporous template formed by the combined EC and PEC etching provides the complicated interface with several layers of voids and a pronounced columnar structure transformed from the starting needles around dislocations (Figure 2b). The density of nanocolumns varies depending on the degree of PEC etching and influences the detachability of regrown films. When the columnar structure is too sparse the regrown film will be separated from the substrate during regrowth and will be broken into fragments as shown in the optical image in Figure 2c. This is minly the result of the thermal stress caused by the difference in thermal expansion coefficients during cooling down after re-growth. Empirically, we found that the planar density of the columnar structure of ~25% (the ratio of the area occupied by the GaN nanocolumns to the total area) is high enough to sustain the regrown layer on the template during LED growth. For films with a higher planar density the clean and uniform detachment becomes an issue, while for the templates with the column density of ~15% or lower the regrown film could be separated during growth. (In the case of Figure 2c, the density was 14%.) For column density of ~15–25%, therefore, clean and uniform separation after the regrowth could be achieved.

Using the regrown LED structures, we studied their optical and electrical properties. Figure 3 shows the room temperature PL spectra of regrown LED structures on the reference template (i.e. GaN layer not subjected to etching), EC etched template, EC/PEC etched template. The peak wavelengths of the PL spectra for the regrowth on reference MOCVD template was found to be close to 440 nm. For the EC etched and EC/PEC etched sample the peak was quite similar compared to the reference template, though slightly blue-shifted. Multiple interference PL fringes are clearly seen in the reference LED because of the Fabry–Perot resonance.[27] However, this interference completely disappeared in the LED on the etched template spectra because of the light scattering from the etched back surface. Moreover, the integrated PL intensity was increased by over 3 times. This improved intensity can come from increased internal quantum efficiency (IQE) and from the enhanced light extraction efficiency. Assuming that at low temperature the IQE is close to 1, the IQE value changes can be roughly estimated by comparing the PL efficiency at room temperature and at low temperature (10 K in our case).[28] The IQE of the reference LED sample thus determined was around 8%, while for the EC etched and EC/PEC etched LED sample it was 18% and 20%, respectively. The rational reason for the IQE improvement is the reduced strain and reduced density of defects in the active region of the etched LEDs.[16−18] These results could be due to the lateral overgrowth character for the GaN film grown around the EC etched pores. Mapping of the PL intensity in the LED structures on EC/PEC etched templates (the inset of Figure 3) demonstrates that this improvement is uniform throughout the area of 2-inch wafer.

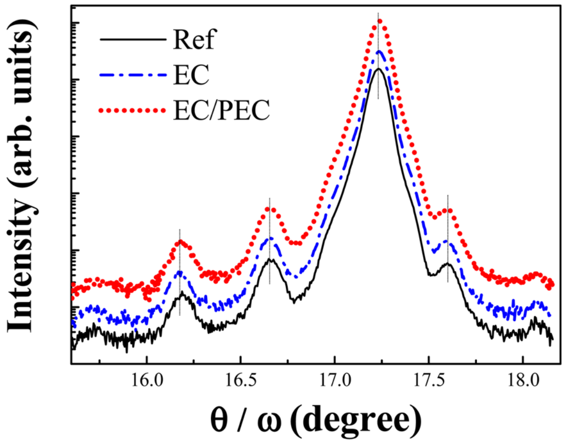

Figure 4. HRXRD θ–ω scans from InGaN/GaN MQWs.

The PL intensity could be influenced by the structure of MQWs and the indium content in the well layer because these can affect the quantum confinement effect and carrier recombination in well layer.[29,30] To check if the PL enhancement originated from these effects, we performed the HRXRD characterization as shown in Figure 4. The strongest peak in the diffraction pattern is due to the (0002) reflection of the GaN layer in all samples. The 0th order peak position and the number, intensity, and sharpness of the MQW related satellites peaks are virtually similar. This indicates that the indium compositions and the quality of MQWs and interfaces with the barriers should be similar among the three tested samples and are not affected by the nanoporous structure.

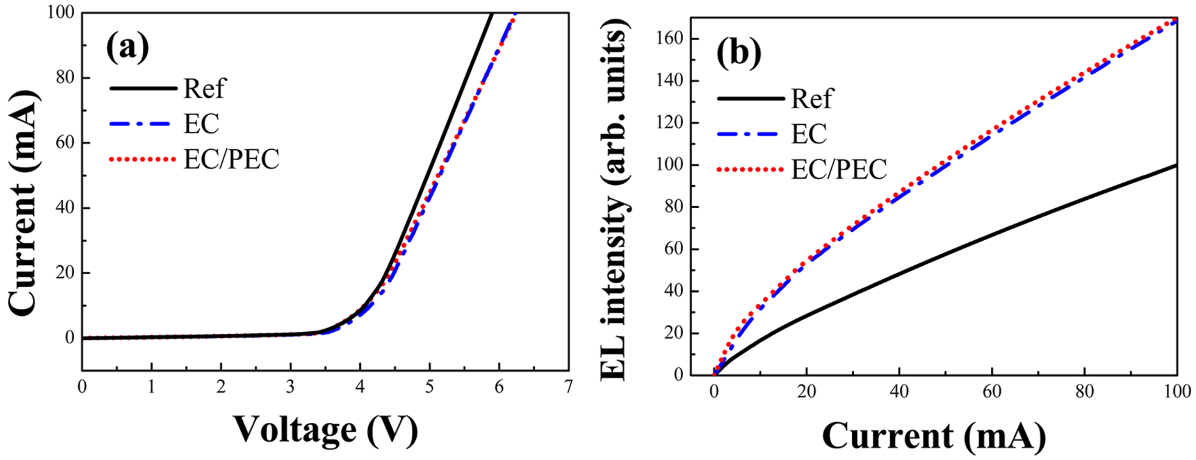

Figure 5. *I*−*V* characteristics (a) and *L*−*I*−*V* characteristics (b).

However, the FWHM of the (0002) reflection in the $\omega-\theta$ rocking curves was 273.6 s for the reference n-GaN layer and 259.2 s for the EC/PEC etching sample. Moreover the n-GaN layer on reference template before MQW, and p-GaN regrowth was more strained compared with the one obtained for the re-grown layer on the EC/PEC etched template, which is in reasonable agreement with results reported in refs 16−19. The observed phenomena is most likely explained by the fact that the etched template facilitates the strain relaxation and improves the light extraction efficiency via added scattering and the IQE through the decrease in defect density.

With a view to demonstrating the current induced luminescence, we measured the light output power versus current versus voltage (*L*−*I*−*V*) characteristics using on-wafer indium contacts (see Figure 5). *I*−*V* characteristics of the reference and overgrown samples in Figure 5a were very similar to each other with the forward voltages close to 4.5 V at 20 mA. However, the current flow in the nanoporous structures could be disturbed near the interface with the etched template resulting in the forward *I*−*V* curves of these structures being slightly slanted.[31,32] Nevertheless, the light output power of LED at 20 mA was found to be around 2 times higher for LEDs on nanoporous templates compared to the reference LED on standard template as shown in Figure 5b. These results are confirmed by measurements on standard 300 × 300 μm^2 LED chips prepared by photolithography and dry etching and using the standard metallization procedure (the detailed characterization results will be presented in a separate paper). Mind that the above results were obtained without separation of the overgrown LED structures from the substrate. This seems to be the only feasible way to provide a meaningful comparison of the EL efficiency between the standard and the EC/PEC overgrown structures. Measurements on the free-standing samples would be only possible in the latter case and the characteristics will be strongly dependent on the type of the substrate to which the layer is transferred and on the type of bonding. For example, for the free-standing LED structure transferred on sapphire using indium bond a very bright EL with the intensity considerably higher than for the non-separated structures could be observed, as illustrated in Figure 1g. Therefore, we can see that the MQW compositions and thickness are not affected by growth on porous templates, while the IQE value is increased due to reduced strain and reduced defects density. The light extraction efficiency is also increased owing to additional scattering. This results in a strong increase of the PL and EL efficiency. Together with the demonstrated detachability of the LED film this combined etching scheme will open very interesting possibilities in various applications.

4. CONCLUSIONS

We have fabricated free-standing LED structured by combining the EC and PEC etching. During the regrowth of LED structure, the holes formed by EC etching were transformed into the sphere shape and the GaN needle by PEC etching were transformed into columnar structure. These structures improved crystalline quality and facilitated easy detachment of the regrown films. The PL and EL intensity of regrown LED on nanoporous template were increased compared to the reference template, due to the improved external quantum efficiency.

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Notes

The authors declare no competing financial interest.

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