# Removal and passivation of surface defects in perforated GaN-based light-emitting diodes

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## ABSTRACT

Perforated GaN-based light-emitting diodes (LEDs) with an array of plasma-etched microholes penetrating through the active region were fabricated using lithography and plasma etching. Plasma damage on the microhole sidewalls led to an increase in junction leakage by up to seven orders of magnitude and a reduced light emission in the low injection regime. It was found that KOH can etch off the plasma-damaged materials, leading to a complete suppression of surface leakage currents. It however attacked metal contacts and increased the forward turn-on voltage. Thermal annealing removed damage in the near-surface bulk region, whereas $(NH_4)_2S$ treatment only passivated the defect states at the immediate surfaces. Both methods produced a partial restoration of the forward-bias characteristics. It has been demonstrated that annealing at 700 °C used in conjunction with prolonged sulfide passivation can remove or passivate all plasma-induced defects and result in a complete suppression of surface leakage in the perforated LEDs. This work is an important step toward developing high-efficiency photonic crystal-integrated LEDs, in which light can only be coupled to radiation modes but the undesirable guided light emission is inhibited.

**Keywords:** light-emitting diode, photonic crystal, plasma damage, sulfide passivation

## INTRODUCTION

According to Snell's Law, a large fraction of light emitted from the active region of a planar light-emitting diode (LED) is reflected at the semiconductor/air interfaces and lost inside the LED chip due to a large contrast of refraction index between semiconductor and the surrounding media.[1] The low light extraction efficiency is a primary obstacle to the development of high-brightness LEDs required for solid-state lighting.[2] For GaN-based blue LEDs grown on sapphire, light outside the escape cones is trapped within a thin epitaxial structure. The extraction efficiency is limited to $\sim 1/4n^2$ = 4% per GaN/air interface, and the overall extraction efficiency of a planar LED is found to be ~12% by ray-tracing calculation.[3] The incorporation of photonic crystals (PhCs) is one of the most promising approaches that are being explored to improve light extraction from LEDs.[4-8] With appropriate parameters, two-dimensional (2D) PhCs consisting of periodic arrays of nanoscale airholes may exhibit photonic band gaps in the visible wavelength range. The guided modes inside LED chips may be suppressed if the wavelength of interest falls into the photonic band gaps.

2D PhCs are typically fabricated using nanolithography and plasma etching. To date, almost all the studies of light extraction by means of PhCs have focused on a thin 2D PhC slab built away from the LED active region, i.e. the PhC was fabricated around or atop the light emitting region. [4-7] The PhC actually acts as a diffraction grating and outcouples the guided modes. While this approach offers the advantages of being amenable to implementation in real devices, it produces limited enhancement of light extraction. It has been suggested that more remarkable improvement in light extraction can be achieved if PhCs are incorporated into the light-emitting regions.[8] In this device scheme, the emitted light can only be coupled to radiation modes, whereas the undesirable guided modes are inhibited. Unfortunately, LEDs with a large number of airholes may severely suffer from increased junction leakage and nonradiative recombination due to the presence of surface states and plasma-induced defects.[9,10] In order to take full advantage of the photonic bandgap effects, it is essential to develop appropriate post-plasma etching treatment to remove plasma damage generated on the nanohole sidewalls. Various methods have been proposed to remove plasma damage in GaN, including thermal annealing,[11,12] wet etching,[13] dielectric passivation,[11,14] and plasma healing.[10] None of these methods, however, produces a full recovery, and in the meantime is compatible with device processing.

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In this work, we report on a study of the effects of thermal annealing and sulfide passivation on the electrical characteristics of perforated blue LEDs, which resemble PhC-integrated emitters. It is demonstrated that a complete restoration of the LED electrical characteristics can be achieved by a combination of these two techniques.

## EXPERIMENTAL

The InGaN/GaN multiple-quantum-well (MQW) blue LEDs were grown on a (0001) sapphire substrate with a low-temperature GaN buffer layer using metalorganic chemical vapor deposition. The structure consisted of a 2.2 μm *n*-GaN layer (Si~$5x10^{18}cm^{-3}$), a 8-period InGaN/GaN active region with ~2 nm wells and 12.5 nm quantum barriers, a 0.08 μm *p*-type AlGaN cladding layer and a 0.2 μm *p*-GaN contact layer (Mg ~$9x10^{19}$ $cm^{-3}$). A Ni/Au/Ni (10/10/100 nm) film was first deposited on the *p*-GaN layer. 300 μm × 300 μm LED mesas were formed using photolithography and inductively coupled plasma (ICP) etching. An array of microholes with a diameter of 1 or 3 μm and spacing of 2-10 μm were then created in the Ni/Au/Ni metal by lithography and wet etching. The microhole patterns were then transferred into the LED structure by ICP etching using the thick top Ni metal as a hard mask. The etch depth was ~0.7 μm to ensure that the holes were etched through the active region down to the n-GaN layer. The remaining Ni was selectively etched, leaving the bottom Ni/Au (10/10 nm) as a semitransparent p-contact. A Ti/Al/Ti/Au *n*-type metallization was deposited by e-beam evaporation and annealing at 600 $^{o}$C was performed for 2 min in air. The LED fabrication was completed after the deposition of Ni/Au (20/200 nm) bonding pads. For comparisons, standard LEDs without microholes were also fabricated and used as control. The total sidewall areas of the LEDs with microholes are 4-30× larger than that of the control LED.

To simulate the effects of plasma damage introduced during the mesa etching, the LEDs were treated with Ar ICP plasma (300 W ICP power, 100 W RIE power, and 20 mTorr) for 30 s. The samples were then divided into three sets and subjected to three different treatments. The first set was annealed in flowing $N_2$ at 400-800 $^{o}$C for 30 s. The second set was dipped in a 20% KOH solution heated to 100 $^{o}$C for durations of 10 min to 1 hour. The third set was immersed in a diluted $(NH_4)_2S$ solution ($C_3H_7OH$: $(NH_4)_2S$=1:1) for 10-60 min at room temperature. The electrical characteristics of the LEDs before and after the treatments were recorded using an Agilent 4156C semiconductor parameter analyzer. Light emission was detected using a silicon photodiode-array fiber-optic spectrometer under pulsed operation with a frequency of 1 kHz and a duty cycle of 1%.

## RESULTS AND DISCUSSION

The forward and reverse I-V characteristics of LEDs with and without microholes are shown in Fig.1. The total sidewall areas of the LEDs are normalized to that of the control LED and are shown in the legends. As expected, both the reverse-bias and low forward-bias leakage currents increase sharply in the perforated LEDs, by many orders of magnitude. The leakage current increases as the total sidewall area increases, suggesting the dominance of surface currents in the plasma damaged layer. However, it does not scale up with the sidewall area, presumably due to nonuniform current spreading in the perforated region.

The adverse effects of plasma damage on the optical characteristics are only seen at low and intermediate injection currents. Figure 2 displays the light output power – current (L-I) curve for a LED with 3 μm microholes in comparison with the control. A microphotograph of light emission from the microhole array is illustrated in the inset. Plasma-induced defects at the sidewall surfaces act as nonradiative recombination centers, and significantly reduce the radiative efficiency in the low injection regime. As the defect states are saturated at elevated current densities, the influence of plasma damage diminishes. This is also evidenced by the overlapped I-V curves above 1 mA in Fig. 1. At 20 mA, the LEDs with microholes are ~21% brighter due to enhanced light extraction. Since the holes are at the micron scale, we do not expect that there exist any photonic bandgap effects. However, the microholes improve the light extraction efficiency by outcoupling some guided light into radiation modes.

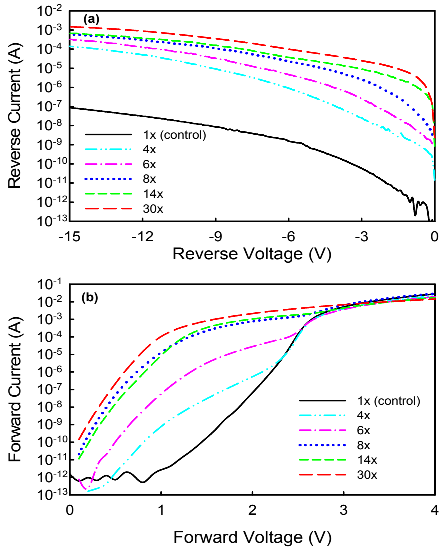


Fig. 1 I-V characteristics of perforated blue LEDs after plasma etching. The total sidewall surface areas are normalized to that of the LED without microholes and are shown in the legends.

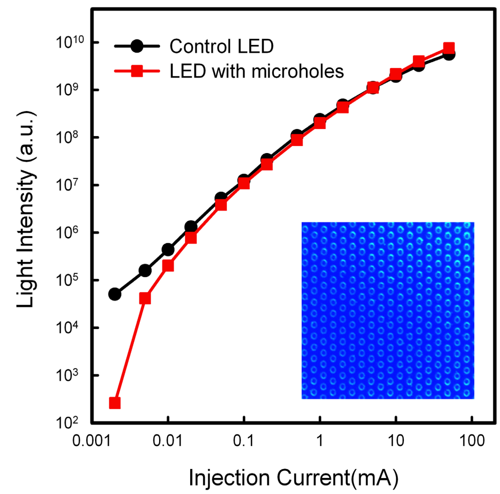


Fig. 2 L-I characteristics of blue LEDs with and without a microhole array. The data is plotted on a log-log scale. The inset shows a microphotograph of light emission from the microhole array.

Our previous studies showed that thermal annealing can effectively remove plasma damage in GaN and restore the electronic properties of plasma etched GaN surfaces.[11,12] Figure 3 shows the forward and reverse I-V characteristics of the LEDs with 3 μm microholes after annealing in $N_2$ at 400-800 °C. As the temperature is raised, the reverse leakage is increasingly suppressed and the I-V curve approaches the original one. Annealing at 700 °C leads to a nearly complete recovery of the reverse characteristics. As the temperature is further increased to 800 °C, the LED becomes leakier. This is due to the creation of thermal damage on the sidewalls as a result of a preferential loss of N during the annealing.[11,12] A substantial recovery of the forward characteristics is also seen upon annealing. However, after 700 °C annealing, the surface leakage at low forward bias (<2V) is still significantly larger compared to the control LED. This finding suggests that the forward-bias leakage currents may originate from carrier tunneling or recombination assisted by multiple bandgap states. The remaining forward leakage currents may be associated with N vacancies at the immediate surface generated during the plasma as well as annealing processes.

Plasma-damaged GaN can be slowly etched in a KOH.solution[13] To obtain a full recovery of the electrical characteristics of the perforated LEDs, the samples were immersed in boiled KOH for 10-60 min. As seen in Fig. 4, the I-V curves are gradually restored as the etch time is increased. The junction leakage currents at both reverse and forward biases are completely suppressed after 40-60 min treatment. It is estimated that several tens of nanometers of damaged materials were etched off the microhole sidewalls.[11] Unfortunately, the KOH etch also results in a significant increase in the forward voltage of the LEDs, as seen in Fig. 4 (b). We have fund that the metal contact/GaN interfaces were attacked by KOH during the treatment, resulting in a reduced contact area and thus an increased contact resistance. Therefore, even though KOH treatment is effective in removing plasma damage in nitride LEDs, it is not an acceptable processing step during device fabrication due to its destructiveness.

In an effort to seek a less aggressive wet chemical treatment, we found that $(NH_4)_2S$ treatment can reduce the surface leakage and yet does not compromise the performance of the LEDs. Sulfide passivation has been widely used to reduce nonradiative surface recombination velocities in conventional III-V semiconductors such as GaAs and InP.[15-17] Sulfide treatment removes unstable native oxides as well as the associated surface states on these materials and forms a monolayer of sulfides, which can physically and electronically passivate the semiconductor surfaces.[15-17] Figure 5 shows the forward and reverse I-V characteristics of the LEDs with 3 μm microholes after being soaked in $(NH_4)_2S : C_3H_7OH$ (1:1) for different lengths of time. As the process proceeds, the I-V curves are gradually recovered. This corresponds to a slow removal of surface oxides and probably a thin GaN layer which was severely damaged as well. Again, a nearly full

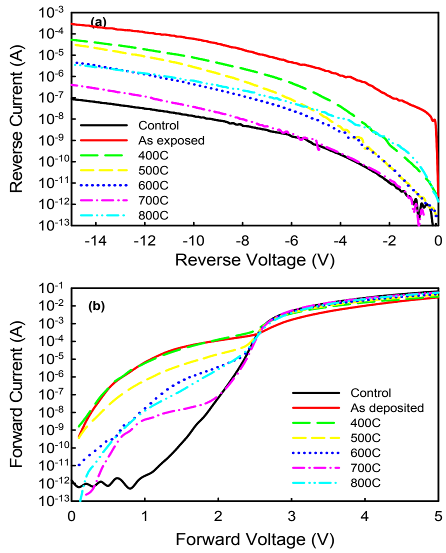


Fig. 3 I-V characteristics of perforated blue LEDs after annealing in $N_2$ at different temperatures

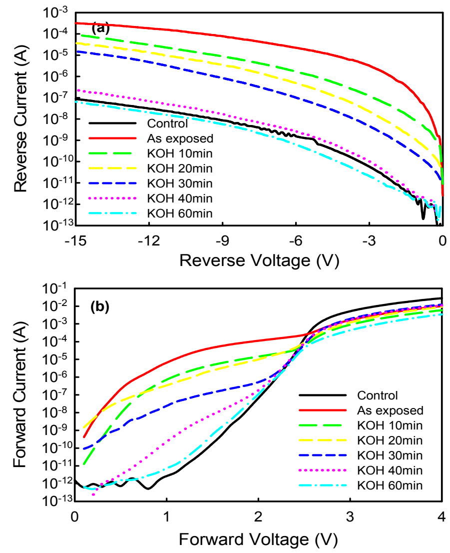


Fig.4 I-V characteristics of perforated blue LEDs after etching in a boiling KOH solution for different times.

recovery of the reverse-bias properties is obtained after 30 min. The forward I-V characteristics, however, is only partially restored. A significant amount of surface leakage remains in the low and intermediate injection regimes. Prolonged treatment does not further suppress the leakage. These findings are explained by the fact that the $(NH_4)_2S$ can only passivate the defect states in the immediate surface layer but cannot remove all the plasma damage which may be tens of nanometer deep. This is in contrast to the case of thermal annealing we investigated earlier, which can effectively remove bulk damage but may induce surface defects. Therefore, the best strategy for damage removal in GaN LEDs may be thermal annealing used in conjunction with sulfide passivation or a brief KOH etch.

Figure 6 shows the I-V characteristics of a perforated LED which was annealed in $N_2$ at 700 $^oC$ for 30 s and then was immersed in $(NH_4)_2S$ for 60 min. As expected, both the forward and reverse I-V characteristics are fully recovered after the treatment. The junction leakage becomes as low as that in the LED without microholes, indicating a complete removal or passivation of all the defect states on the microhole sidewalls. The sample was retested after exposure to air for more than one month and exhibited very good stability. This confirms that sulfide passivation on GaN is more stable than that on GaAs and InP due to the greater strength of N-S bonds compared to As-S and P-S bonds.[18]

## 4. CONCLUSIONS

In summary, the effects of thermal annealing and treatments in different reagents on the electrical characteristic of plasma-etched perforated InGaN/GaN MQW blue LEDs have been investigated. KOH treatment produces the greatest improvement and fully suppresses surface leakage currents induced by plasma damage, but leads to degraded metal contacts. Both thermal annealing and $(NH_4)_2S$ treatment fully recover the reverse I-V characteristics but only partially eliminate leakage at low forward bias. The former is effective in removing bulk damage whereas the latter can only passivate surface states. A complete suppression of surface leakage in the perforated LEDs is achieved by annealing followed by prolonged sulfide passivation.

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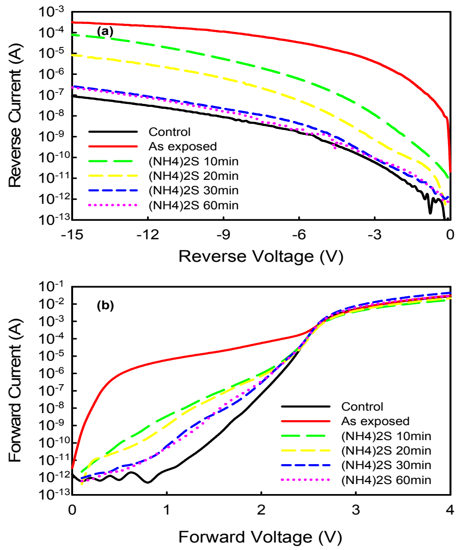


Fig. 5 I-V characteristics of perforated blue LEDs after soak in a $(NH_4)_2S$ :$C_3H_7OH$ (1:1) solution for different times.

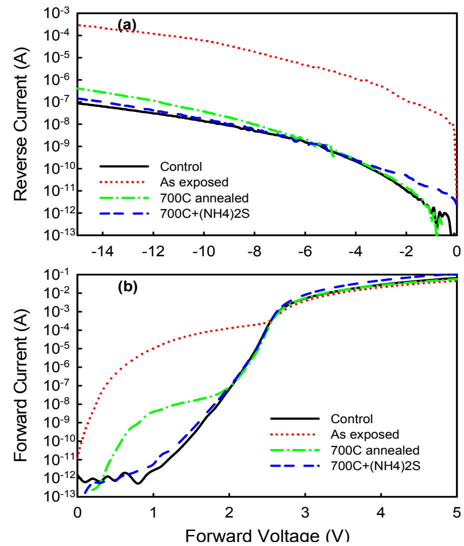


Fig. 6 I-V characteristics of perforated blue LEDs after annealing at 700 °C followed by treatment in $(NH_4)_2S$ for 60

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