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2016

Oh, S., Kim, S., Shin, S.-C., Su, P.-C., Yoon, Y.-J., Lee, K. J., . . . Kim, K.-K. (2017). Morphology effect of the ZnO surface via organic etchants for photon extraction in III-nitride emitters. *ECS Journal of Solid State Science and Technology*, 6(1), Q13-Q17.
doi:10.1149/2.0131701jss

<https://hdl.handle.net/10356/85356>

<https://doi.org/10.1149/2.0131701jss>

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Morphology Effect of the ZnO Surface via Organic Etchants for Photon Extraction in III-Nitride Emitters

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We demonstrate that the morphology effect on the ZnO surface using organic acids significantly improves the photon extraction efficiency of III-nitride emitters. Oxalic ($C_2H_2O_4$), citric ($C_6H_8O_7$), and formic (CH_2O_2) acids were used for modulating the nanostructured surface of the ZnO layer with various shapes, including random nanoblocks, nanoholes, and nanorods. The transmittance of the nanostructured ZnO layer fabricated with formic acid for 3 min was 91% at 450 nm wavelength. The optical output power intensities of the emitters with the nanostructured ZnO surface layer were enhanced by 22.14%, 30.58%, and 22.46% with oxalic, formic, and citric acid, respectively, compared with the emitter with the flat ZnO layer.

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Manuscript submitted November 1, 2016; revised manuscript received December 5, 2016. Published December 15, 2016.

The photon extraction of III-nitride emitter devices is mainly governed by the probability of the photons generated in the active layer escaping from the higher refractive index of the semiconductor into the lower refractive index of the surrounding material (air or resin). To increase the probability, the angular randomization of photons can be achieved through surface scattering by surface roughening the top-most layer of the emitter. Several methods to increase the photon extraction efficiency (PEE), such as surface texturing,^{1,2} antireflection coating,^{3,4} omnidirectional reflection,^{5,6} photonic crystal structure,^{7,8} and surface plasmons,^{9,10} have been suggested so far.

Among these methods, the surface morphology of the ZnO layer is often modulated to create a nanostructured surface for better PEE in emitter devices.¹¹ The morphologic modulation can be achieved by using a simple wet chemical etching process, which has very low process costs and is capable of performing isotropic or anisotropic etching. The solution process usually involves one or more chemical reactions that consume the original reactants and produce new species.^{12–15} Strong acids, such as HCl, HNO_3 , H_2SO_4 , and H_3PO_4 , have been used for the nanostructured surface of the ZnO layers as wet etchants, by which anisotropic patterns can also be obtained.¹⁶ The etching rate of the ZnO layer using such strong acid solutions is usually high, so the concentration was kept low for better control of the etching rate and the surface morphology. If a higher concentration of acid is used for such inorganic acids, the etching rate can be significantly increased, but the control of the ZnO surface morphology becomes very difficult. Therefore, many research groups have been trying to find alternative etchants to maintain a high etching rate but obtain better control of the ZnO surface morphology for higher device efficiency.^{14,15}

In this study, we use organic acids to further stabilize the etchant for modulating the surface morphology of the ZnO layer. Organic acids usually have a chemical formula composed of elements such as C, H, and O. These differ from inorganic acids, or forming weak organic acids with huge anions, as opposed to a strong halogenide acid. It seems likely that most acids, regardless of whether they are strong or weak, inorganic or organic, behave like hydrochloric acid (HCl).

Three acids – oxalic, formic, and citric acids – with various concentrations were prepared for the morphological modulation of the ZnO surface layer, as summarized in Table I. The pH values of the acids used in our experiments were maintained between 3 and 3.5. To obtain

various surface morphologies of the ZnO layers, the etching time was tested from 1 to 5 min for all three etchants. The concentrations of all three etchants were formulated to completely etch away the ZnO layer within 5 min. Formic acid with a monoprotic acid, oxalic acid with a diprotic acid, and citric acid with a triprotic acid release one H^+ , two H^+ , and three H^+ per mole, respectively. $pH = -\log_{10}[H^+]$, where H^+ is a concentration of weak acid, and because of $pK_a = -\log_{10}K_a$, $K_a = [H^+][A^-]/[HA]$, the A^- (the concentration of conjugate base) can be found from this equation. When the concentrations of weak acid and its conjugate base are equal, the pH of the solution equals to pK_a of the weak acid. For $pH < pK_a$, the weak acid (protonated form) predominates. On the contrary, for $pH > pK_a$, the conjugate base (deprotonated form) predominates. Because of lower acidity by addition of DI water and a relatively higher amount of OH^- ion, the three organic acid solutions used in this experiment were quantitatively more in the conjugate base than in the weak acid. Thus, these oxalic, formic, and citric acids have advantages of the etch rate in terms of controlling for the nanopatterning experiment. The surface morphology was examined by scanning electron microscopy (SEM) (Hitachi, S-4700). The transmittance results of the ZnO layer with modulated surface morphology from the etching process were analyzed by a spectrometer (HELIOS OMEGA UV-VIS). An emitter device with morphology change of the ZnO layer by the organic etchants under various etching times was fabricated to improve the PEE. The epilayers consisted of a p -GaIn (0.25 μm), 5-period InGaIn/GaN multiple-quantum wells (MQWs), an n -GaIn (1.5 μm), and an undoped GaIn (u -GaIn) layer grown on sapphire substrate (430 μm thickness). For an n -contact, we partially etched the layers using the inductively coupled plasma (ICP) equipment of the grown emitter samples until the n -GaIn layer was exposed. A Ti/Au (50/200 nm) layer was deposited by E-beam evaporation as an n -electrode. To obtain ohmic contact for the p -GaIn layer, the p -contact transparent copper indium oxide and ITO electrode (3/400 nm) were deposited onto the p -GaIn layer by E-beam evaporation and annealed at 600°C in O_2 ambient for 1 min by a rapid

Table I. Solution etchant conditions, including pH, etching time, and ratio of acid/DI.

Acids	Dilute Solution (Acid/DI)	pH	Etching Time
Oxalic ($C_2H_2O_4$)	0.025 g/300 ml	3.02	1 min. ~ 5 min.
Formic (CH_2O_2)	0.020 g/300 ml	3.18	
Citric ($C_6H_8O_7$)	0.035 g/300 ml	3.38	

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Figure 1. (a) SEM top views of nanostructured ZnO layer through etching time with diverse etchants. (b) shows the cross-section view of ZnO layer and nanostructured ZnO layer with formic acid.

thermal annealing (RTA) process. The annealed ITO layer is resistive to acid etchant and at the same time serves as a current spreading layer. The bonding pad electrodes of Cr/Au (50/200 nm) were formed on an ITO transparent conducting layer. After the formation of the electrodes, an *n*-ZnO (Al-doped ZnO) layer with a thickness of 400 nm was selectively deposited using the photolithography process on top of the ITO layer by radio frequency (RF) magnetron sputtering at room temperature (RT). Current–Voltage (*I*–*V*) measurements of the fabricated emitter devices were carried out using a parameter analyzer (Keithley-2420 source meter), and luminance–injection current (*L*–*I*) characteristics were measured using an Ocean optics-US 4000 spectrometer.

As shown by the SEM images in Fig. 1a, the surface morphologies of the modulated ZnO layers are very different with diverse organic etchants. Random block and hole shapes with nanostructures were obtained through the etching process using oxalic and citric acids, respectively, while the ZnO nanorod structure shown in Fig. 1b was obtained after etching with formic acid. The nanostructural fabrication, such as ZnO nanorods, is an interesting result, since the nanorod structure was only reported to be achievable through hydrothermal growth or the chemical vapor deposition (CVD) process.^{16–20}

Figure 2 shows the schematic of the etching shapes, the chemical formula, and the molecular structure of the etchants. Since the formic acid has a small number of elements per molecule compared with the

Figure 2. The chemical formula and etched images of ZnO layer using (a) oxalic, (b) formic, and (c) citric acids.

Figure 3. (a) Transmittance images of nanostructured ZnO layer using oxalic, formic, and citric acids. (b) Transmittance results from etching times from 1 min to 5 min at 450-nm wavelength.

other two etchants, it tended to diffuse more quickly to the surface defects with high surface energy, such as grain boundaries, cracks, and pits formed during the initiation of wet etching.^{21,22} After the diffusion into the surface defects of the ZnO layer, the etching continued in both vertical and lateral directions; consequently, a nanorod structure was obtained, as shown in Fig. 2b. For the other two etchants, oxalic and citric acid, the etching rates in both lateral and vertical directions were similar and the finally etched morphology was more isotropic, as seen in Figs. 2a and 2c. Oxalic acid, unlike the monoprotic formic acid, is diprotic and shows a large acid dissociation constant or acidity constant, producing a larger number of hydrogen ions in the aqueous solution under the same concentration and temperature. Therefore, the oxalic acid etched a larger area of the ZnO layer than formic acid at similar pH values in the same etching time. For the triprotic citric acid in an aqueous solution, it was partially dissociated into hydrogen ions and partially deprotonated in citric acid species $[(H_2C_6H_5O_7)^-]$ and $(HC_6H_5O_7)^{2-}]$, and the degree of partial dissociation depended on its concentration and solution temperature. The incompletely deprotonated citric acid species that entered the pores would produce additional hydronium ions, causing a rapid lateral etching reaction and consequently widening the pores aggressively.^{23–25}

The transmittance of the modulated surface of the ZnO layers etched with oxalic, formic, and citric acid over 1–5 min is shown in Fig. 3. Figure 3a shows the transmittance results of the morphology modulation in the ZnO layers with an etching time of 3 min. As shown in Fig. 3b, a transmittance of up to 90.9% was obtained from the ZnO layers etched with formic acid. This is a 20.1% improvement compared with the transmittance of 75.7% of the flat ZnO layer. Additionally, the transmittance of the nanostructured ZnO surface

Figure 4. I–V characterization of ref-emitter and nanostructured ZnO layer-based emitters.

layer etched with formic acid was improved compared with that of the morphological modulation in the ZnO layers with oxalic or citric acid. This resulted from the ZnO layer etched with formic acid shaped like nanorods with high PEE, as shown in Figs. 1b and 2b.

The electrical and optical properties of emitters with the modulated morphology of the ZnO layer and the flat surface of the ZnO layer (ref.) were measured. Figure 4 shows the I–V characteristics of the emitters with the three organic etchants and the ref. Nearly identical slopes on the I–V curves were observed in all samples. In addition, the operating voltage of the nanostructured surface of the ZnO layer and ref-emitters at the injection current of 20 mA increased only slightly from 3.34 V to 3.43 V. It is shown that the surface morphology modulation in the ZnO layer using three organic etchants maintained the good electrical properties of emitters without significant degradation.

Figure 5a shows the light output L–I characteristics of the emitters. The light output power increased with an etching time of 3 min, and the maximum light output power was obtained by the emitter that demonstrated a 22% (using oxalic acid), 31% (using formic acid), and 22% (using citric acid) enhancement in optical power compared with the ref-emitter. After the 3-min etching process for surface morphology modulation of the ZnO layer, the emission spectrum of the emitter with a nanostructured surface was measured, as shown by the electroluminescence (EL) of Fig. 5b, and the emitter with the nanostructured ZnO layer maintained approximately the same wavelength for the input currents 20 mA and 100 mA. ZnO nanostructures can lead to a gradual decrease of the refractive index at the interface between ITO ($n = 2.0$) and air ($n = 1.0$), reducing the total internal reflection (TIR) and the Fresnel reflection through the effective medium theory, $n_{\text{eff}} = [n_{\text{ZnO}}^2 V_{\text{ZnO}} + n_{\text{Air}}^2 (1 - V_{\text{ZnO}})]^{1/2}$, where n_{ZnO} and n_{Air} are the refractive indexes of ZnO and air, respectively, and V_{ZnO} is the volume fraction of ZnO.²⁶ Therefore, the optical output power was largely increased much more with the nanostructured surface of the ZnO layer on emitters than the ref-emitter.

Figure 6 shows the EL emission images at the 0.05 and 1.0 mA input currents, and the results demonstrate that the surface morphology modulation of the ZnO layer using formic acid shows the strongest and more uniform emission. These results show that the light output power depends on the surface morphology that is modulated by the etching condition. Nevertheless, it is worth nothing that all the emitters with the nanostructured ZnO layers still perform better than the ref-emitter. In addition, these results imply that the nanostructured surface with the morphology modulated by using the new solutions on ZnO layers enhance the extraction of trapped photon inside the emitter.

Figures 7a to 7d show the three dimensional finite different time domain (3D-FDTD) simulation results of PEE with various surface

Figure 5. (a) L-I properties of emitters with ref. nanostructured ZnO layers. (b) Emission spectrum of emitter with ref and nanostructured ZnO layer with formic acid.

Figure 6. Emission images of emitters with ref. nanostructured ZnO layers at 0.05 and 1.0 mA.

structure, such as ZnO nanorods, and nanostructured ZnO by organic acids. In this simulation, considering the PEE structure of modulated surface morphology such as nanorods or nanopattern, the density of nanostructured ZnO which is etched by formic acid is higher than that of nanorods grown by hydrothermal process. Therefore, the PEE with etched ZnO-based emitter by formic acid was improved, compared with the nanorods-based emitter, as shown in Fig. 7e. Nanostructured ZnO-based emitters etched by oxalic and citric acids have similar PEE values.

In conclusion, the surface morphology modulation of the ZnO layer using three organic etchants was successfully fabricated with enhanced PEE for III-nitride-based emitters. The new ZnO layer etchants, such as diluted oxalic, formic, and citric acid solution, were used, and about 31% enhancement in optical output power at 100 mA from the emitter with a nanostructured ZnO layer etched with formic acid for 3 min was observed without a significant degradation in electrical properties compared with the ref-emitter. In particular, emitter with the nanoscaled surface morphology, such as nanorods fabricated

Figure 7. 3D-FDTD simulation results of PEE with nanorods and nanostructured ZnO fabricated by formic, citric, and oxalic acids.

with a wet chemical process using formic acid etchant, demonstrated uniform and strong surface light output profiles at various injection current levels. Therefore, these results show that a nanostructured surface with various morphologies can be achieved by wet etching using organic acids and the pH value without the growth technique or photolithography process.

Acknowledgments

This work was supported by the Human Resource Program in the Transportation Specialized Lighting Core Technology Development of the Ministry of Trade, Industry & Energy (No. N0001364) and the Advanced Technology Research Center Program of the Small and Medium Business Administration (SMBA) (No. 10052274), Republic of Korea.

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