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Solution-Growth ZnO Nanorods for Light Extraction in GaN-Based Flip-Chip LEDs

Nan-Ming Lin,[a] Shih-Chang Shei,[a,z] and Shoou-Jinn Chang[b]

[a]*Department of Electrical Engineering, National University of Tainan, Tainan 70005, Taiwan*
[b]*Institute of Microelectronics & Department of Electrical Engineering, Institute of Nanotechnology and Microsystems Engineering & Department of Materials Science and Engineering, Advanced Optoelectronic Technology Center, Center for Micro/Nano Science and Technology, National Cheng Kung University, Tainan 701, Taiwan*

A simple and low-cost successive ionic layer adsorption and reaction and hydrothermal method was used to form ZnO nanorods sapphire surface for GaN-based power flip-chip (FC) light-emitting diodes (LEDs). With 350-mA current injection, it was found that the output powers were 361.7 and 448.2 mW for the FC LED without ZnO nanorods and with ZnO nanorods, respectively. The FC LED with ZnO nanorods was 24% larger than that of the FC LED without ZnO nanorods. Furthermore, it was also found that the formation of ZnO nanorods on the surface of sapphire will not degrade the electrical properties.

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III-NITRIDE compound semiconductors, which include GaN, InGaN, and AlGaN, have become the most important material system for short-wavelength light emitters in recent years. Indeed, GaN-based LEDs have attracted extensive attention for many important applications, especially for solid-state lighting.[1–4] Compared with conventional light sources, GaN-based LEDs are compact in size and consume less power. Lifetime of GaN-based LEDs is also much longer. However, output power of current LEDs is still low. Conventional GaN-based LEDs emit photons from the p-side indium–tin–oxide (ITO) contact.[5] With this configuration, however, a significant amount of photons will be obscured by the bonding pads and wires. One effective way to enhance LED output power is to use flip-chip (FC) technology.[6–8] Without the blocking of bonding pads and wires, photons can be emitted freely from the sapphire substrates. By flipping the LEDs, one can also shorten the thermal path between the active light-emitting region and the heat sink. To fabricate FC LEDs, it is necessary to solder the flipped LED chips onto a Si submount prior to packaging. Electrical connections are then made to the FC LEDs via the submount. It is known that thermal conductivity of Si (149 W/m K) is much larger than that of sapphire.[9] Together with the shorter thermal path, the higher thermal conductivity of Si submount thus results in much better thermal property of GaN-based FC LEDs as compared with conventional GaN-based non-flip-chip (NFC) LEDs. For practical solid-state lighting, one needs to deliver large power into large-size devices. The inputted electrical power will be partially converted into output light while the remaining power will be converted into heat. Without a good thermal property, the generated heat can easily fail the devices. Thus, it is extremely important to enhance thermal properties of high-power LEDs. However, the reflective index of sapphire is higher than that of air. This will result in Fresnel reflections, most of the generated lights in the active layer are absorbed inside LEDs and then converted into heat. Rough sapphire surface is a simple technique and has been used to destroy the total internal reflection.[10] It has been reported that one can increase the light extraction efficiency of GaN-based LEDs by using SiO_2, ITO, and SiNx nanopillars.[11–13] Recently, using ZnO nanopillars to increase the light extraction of GaN-based LEDs has been reported due to simplicity and cost effectiveness.[14–15] Among these, the solution approach based on soft chemical technique has attracted increasing attention in recent years. Although the ZnO zeed layer can be grown by rf magnetron sputtering,[15] the rf magnetron sputtering needs the long-time and vaccum process. This process is complicated and expensive. In this paper, we reported the solution-growth ZnO nanorods on the surface of sapphire to enhance light extraction of GaN flip-chip LEDs. The ZnO nanorods were formed by SILAR-based and Hydrothermal method. It should be noted that the ZnO zeed layer was formed by SILAR due to the fact that the SILAR can shorten the growth time. The combination of SILAR and Hydrothermal presents a simple, low-temperature, low-cost, high-reliability and large-area growth. This will not destroy the Ni/Ag mirror property for GaN-based FC LEDs. The detailed procedure will be reported.

The samples used in this experiment were all grown by a metallorganic chemical vapor deposition on c-face 2 in. sapphire Al_2O_3 (0001) substrates. The LED structure consists of a 30 nm thick GaN nucleation layer grown at 550°C, a 3 μm thick Si-doped n-GaN buffer layer grown at 1050°C, an unintentionally doped InGaN/GaN multi-quantum well (MQW) active region grown at 770°C, a 50 nm thick Mg-doped p-$Al_{0.15}Ga_{0.85}N$ electron-blocking layer grown at 1050°C and a 0.25 μm thick Mg-doped p-GaN layer grown at 1050°C. The InGaN/GaN MQW active region consists of five pairs of 3 nm thick $In_{0.23}Ga_{0.77}N$ well layers and 7 nm thick GaN barrier layers. The samples were subsequently annealed at 750°C in N_2 ambient to active Mg in the p-type layers. After annealing to activate Mg in the p-type layers, we partially etched surfaces of the LED samples until the n^+-GaN layers were exposed. We subsequently deposited a 15-nm-thick ITO layer, a 1-nm-thick Ni layer, and a 200-nm-thick Ag layer onto the sample surfaces. Here, the 15-nm-thick ITO layer and the 1-nm-thick Ni layer serve as the transparent ohmic contact while the 200-nm-thick Ag layer serves as the reflective mirror. Rapid thermal annealing was then performed at 300°C for 35 s to improve electrical properties of the p-contacts. On the other hand, Cr/Pt/Au was deposited onto the exposed n^+-GaN layers to serve as the n-contacts. We then deposited SiO_2 films as passivation onto the wafers by plasma-enhanced chemical vapor deposition. Photolithography and hydrofluoric (HF) solution etching were subsequently performed to define the P/N pad pattern for bump electroplating. Sn/Au (15 μm/5 μm) layers were then electroplated onto the wafers before the bumps were formed by liftoff. We then thin the sapphire substrate to around 90 μm by back side grinding without polishing. The samples were subsequently chemically treated in HCl:DI water (1:5) at 50°C for 90 s to remove the remaining contaminant. The ZnO was grown on the top of sapphire as the seed layer by successive ionic layer adsorption and reaction (SILAR) method. The detailed procedures of a ZnO seed layer in four cycles described as follows. The rinsing procedure by SILAR method: (a) Dipping samples in the zinc complex $[Zn(NH_3)_4]^{2+}$ solution for 20 s. (b) $Zn(OH)_2$ precipitation is formed on the samples by dipping in unheated DI water for 20 s. (c) dipped samples in ultrasonic-assisted DI water for 30 s to remove counterion Cl^- and loosely attached Zn $(OH)_2$ grains. (d) dipped samples in 95°C DI water:ethylene glycol = 1:4 for 20 s to form ZnO nanoparticles. (e) kept samples in ultrasonic-assisted DI water for 30 s to remove the loosely attached ZnO and unreacted $Zn(OH)_2$ grains. After the deposition of a ZnO seed layer on the top of sapphires, ZnO nanorods sequentially were grown on the ZnO seed layer by Hydrothermal method (Hm). The mixed solution of 0.2 mM znic nitrate $[Zn(NO_3)_2]$ and hexamethylenetetramine

[z]E-mail: scshei@mail.nutn.edu.tw

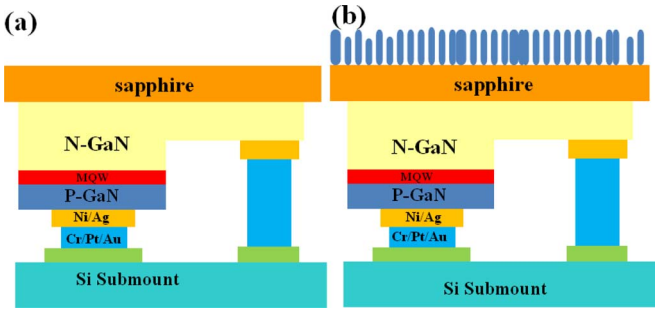

Figure 1. Schematic diagrams of (a) the FC LED without ZnO nanorods and (b) the FC LED with ZnO nanorods.

$[C_6H_{12}N_4]$ dissolved in DI water at 95°C for 1.5 h. For comparison, the conventional FC LED without ZnO nanorods was prepared. After Hm, the ZnO nanorods were formed on the top of sapphire. A schematic diagram of the GaN-based power FC LED with ZnO nanorods is shown in Figure 1. The current-voltage (I–V) characteristics of the two FC LEDs with ZnO nanorods and current-power were measured at room temperature using Keithley 2430 source meter combined with an integrating sphere. The near-field (NF) emission of fabricated LEDs with ZnO nanorods images was also taken by a calibrated CCD camera mounted on the microscope.

Figure 1a and 1b show the schematic diagrams of the FC LED without ZnO nanorods and FC LED with ZnO nanorods, respectively. It can be seen that the ZnO nanorods grow on the top of sapphire.

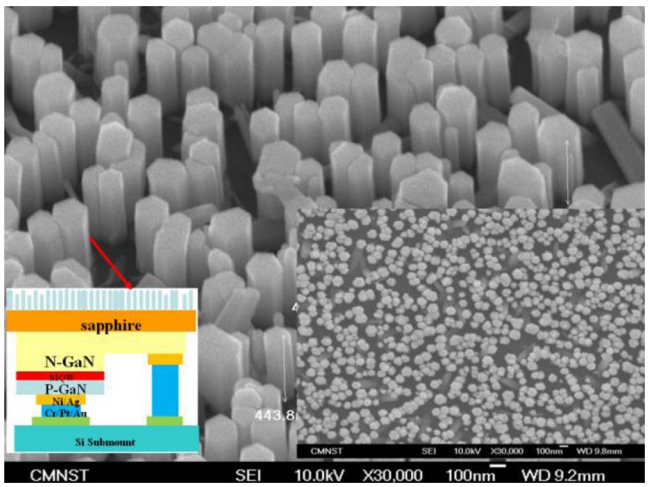

Figure 2. SEM images of the FC LED with ZnO nanorods.

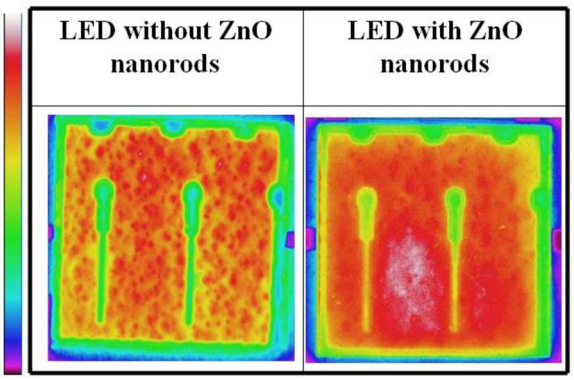

Figure 4. Output power mappings for the FC LED without and with ZnO nanorods.

Figure 2 shows the tiled-view SEM images of the FC LED with ZnO nanorods after SILAR-based and Hm methods. It can be seen clearly that an average height of the ZnO nanorods were 450 nm. The inset is a ZnO seed layer. It should be noted that ZnO nanorods were dense. The density of the ZnO nanorods was calculated as 7.0×10^9 number/cm^2. Our results demonstrate that the ZnO nanorods can effective be formed on the FC LEDs. This is due to SILAR-based and Hm methods. On the other hand, it was found that the entire sapphire was also covered by ZnO nanorods.

Figure 3a shows current-voltage (I-V) characteristics of the two LEDs. With 350 mA current injection, we obtained forward voltages of 2.97 V for the two LEDs. This indicates that the formation of ZnO nanorods did not degrade the FC LEDs. Figure 3b shows the current-output power characteristics of the two LEDs. With 350 mA current injection, it was found that the output powers were 361.7 and 448.2 mW for the FC LED without ZnO nanorods and with ZnO nanorod, respectively. It was also found that the FC LED with ZnO nanorods was significantly larger than that of the FC LED without ZnO nanorods. On the other hand, it was found that the FC LED with ZnO nanorods was also 24% larger than that of the FC LED without ZnO nanorods. This improvement can be attributed to the fact that the ZnO nanorods on the top of sapphire can reduce Fresnel reflection. Our result is similar to that of an approach.[14]

Figure 4 shows the emission intensity images for the FC LED without ZnO nanorods and with ZnO nanorods. The red color of the light emission image indicates the highest light emission intensity of the FC LEDs. Obviously, the emission intensity of the FC LED with ZnO nanorods was distributed more highly than that of the FC LED without ZnO nanorods. This indicates that ZnO nanorods can guide and extract the most light from the sapphire. This result agrees with that observed in Figure 4. Once again, the formation of ZnO nanorods is a simple way to enhance the output power of FC LEDs without

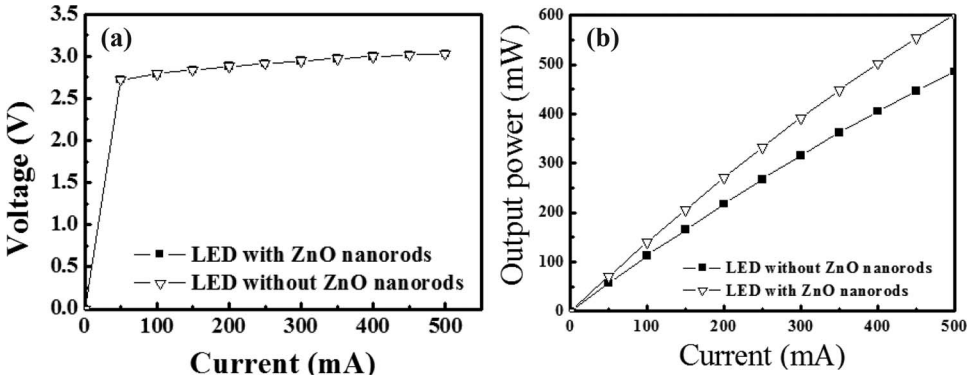

Figure 3. (a) I–V characteristics of the two LEDs, (b) Output power as a function of injection current for the FC LED without and with ZnO nanorods.

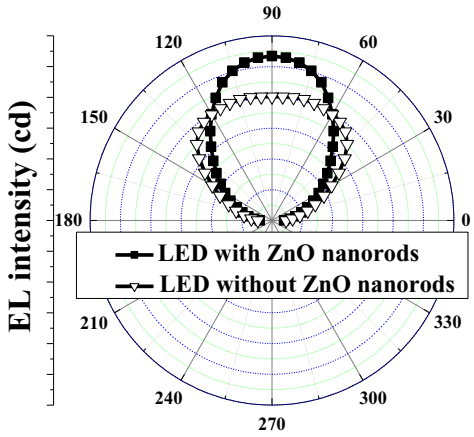

Figure 5. Light output patterns measured from the FC LED without and with ZnO nanorods.

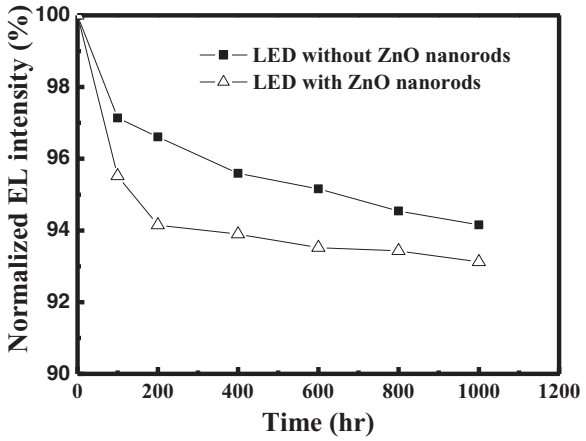

Figure 6. Life-time tests of relative luminous intensity measured from the two LEDs.

extra expensive equipments. In Fig. 4, the output power mapping for the LEDs with and without ZnO nanorods also have small light spots on the emission area. It is also possible that the samll light spots on the emission area are due to the filling of band-tail states (i.e., localized states) in which carriers or excitons recombined for emission as the low-injection current.[16] The localized states may be formed with indium compositional fluctuation (i.e., dot formation) in the InGaN well layers due to phase separation or indium segregation. However, phenomenon is less sensitive to the LED with ZnO nanorods caused by the high-density nanorods as multiple waveguides and then increasing the light extraction.

Figure 5 shows light output patterns measured from the two LEDs. During measurements, we injected a 350 mA dc current into the two LEDs. With 350 mA current injection, it can be seen clearly that the FC LED without ZnO nanorods was in the near horizontal direction. On the other hand, the EL intensity observed from the FC LED with the ZnO nanorods in the near vertical direction was larger than that observed from the FC LED without ZnO nanorods. The ZnO nanorods can effective guide internal light to escape from the sapphire. Figure 6 shows life-time tests of relative luminous intensity measured from the two LEDs, normalized to their respective initial readings. During life test, the two LEDs were driven by 550 mA dc current injection at 55°C. It can be seen that EL intensity decreased by 6% and 7% for the LED without ZnO nanorods and with ZnO nanorods, respectively. Compared with the LED with ZnO nanorods, the better reliability observed from the LED without ZnO nanorods should be attributed to that the heat can be removed in the device. On the other hand, the slight poor reliability observed from the LED with ZnO nanorods could be attributed to that the heat results in degradation in ZnO nanorodes. The slight drop (7% after 1000 h) in the reliability of the LED with ZnO nanorods under test conditions is still reasonably good for most applications.

In summary, we present a simple and low-cost solution growth with SILAR-based and Hm methods to form ZnO nanorods for GaN-based power FC LEDs. It was found that we achieved 24% enhacement in the FC LED output power by the formation of ZnO nanorods. The emission intensity of the FC LED with ZnO nanorods was distributed more highly than that of the FC LED without ZnO nanorods. This result agrees with that observed in the current-output power characteristics. It was also found that SILAR-based and Hm methods did not degrade the electrical properties of the FC LEDs.

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