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Fabrication of a White-Light-Emitting Diode by Doping Gallium into ZnO Nanowire on a p-GaN Substrate

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This study evaluated a process for fabricating white light emitting diodes (LEDs) by doping Ga into ZnO nanowires (ZnO:Ga NWs) on p-GaN substrates. Vertically aligned ZnO:Ga NWs were grown by thermal chemical vapor deposition to 0.7 μm in length and 50−300 nm in diameter. The white light LED was successfully fabricated by forming an n-p-n heterojunction on an ITO/glass substrate. The electroluminescence (EL) emission peak was 500 nm, and the broad band fwhm intensity was 200 nm. Finally, photographs show a white light from the ZnO:Ga LED.

Introduction

ZnO has attracted considerable attention in the recent decade owing to its potential applications in optoelectronic devices[1−3] and it advantages over nitride systems, such as its higher exciton binding energy (60 meV). Various research teams have developed ZnO-GaN heterostructures for optoelectronic devices by using various methods such as chemical vapor deposition,[4] the hydrothermal method,[5] plasma-assisted pulsed laser deposition,[6] and molecular beam epitaxy. A heterojuntion structure generally has a lower carrier injection efficiency than a homojunction structure does, owing to the large band offset that forms at the heterojunction interface. However, this issue can be overcome by using a nanojunction. A nanostructure can increase carrier injection efficiency and recombination rate by increasing the contact area and the aspect radio.

White light LEDs have attracted the attention of researchers because of their applications in black light modules in displays. White-light-emitting diodes have many advantages over traditional single light LEDs, including lower energy consumption and higher transfer efficiency. A blue light LED was successfully developed using a ZnO nanowire (NW) on a p-GaN substrate. A few teams have fabricated a white light LED successfully by using ZnO based heterojunction LEDs.

A report by Honghui Guo et al. described the fabrication of a white light LED using ZnO nanotubes[7] but did not include a clear photograph of the white light LED. Fabricating white light LEDs by increasing the emitted wavelength range of blue light LEDs is seldom discussed. Trivalent elements such as Al, Ga, and In can be used as n-type dopants to achieve precise control of n-type electrical conductivities of ZnO for optoelectronic device applications.[8−10] Kishwar et al. described the use of low temperature aqueous chemical growth for ZnO NWs in an n-ZnO NWs/p-GaN heterostructure LEDs. However, the spin-coated Shipley photoresist was still needed for spacer and evaporated electrodes on ZnO NWs and on p-GaN for ohmic contact.[11] M. Willander published several ZnO heterojunction LED papers describing the successful manufacture of white light LEDs by using p-4H-SiC and p-GaN on organic p-type polymers to form organic−inorganic hybrid junctions. The team focused on changing the p-type energy band gap to emission white light.[12,13]

This study successfully fabricated a white light LED by doping gallium into ZnO nanowires. A white light LED was packaged by a simple flip-chip package process without the evaporation of materials on the p-GaN and a ZnO nanowire. First, vertically aligned ZnO nanowires and ZnO nanowires doped with gallium were grown on a p-GaN substructure. A high-quality p-GaN substrate was used for the p-type contact layer.[14,15] Then, ITO/glass was used to combine and package the grown samples into heterojunction LEDs. The blue light emitted by the ZnO LED and the white light emitted by the ZnO:Ga LED were photographed at forward bias voltages. The current−voltage (I−V), photoluminescence (PL), and the electroluminescence (EL) emission of the white light and blue light LEDs were then measured.

Experimental Section

Metal organic chemical vapor deposition (MOCVD) was used to fabricate a p-GaN epitaxial film with a sapphire (0 0 0 1) substrate (1 cm·1 cm). GaN and ZnO have similar physical properties, including a small in-plane lattice mismatch (∼1.8%), similar wide band gaps (3.37 eV), and similar wurtzite structure.[16] Therefore, p-GaN was chosen as the buffer layer for growing ZnO nanowires. The ZnO NWs and gallium-doped ZnO (ZnO:Ga) NWs were grown on a p-GaN substrate by

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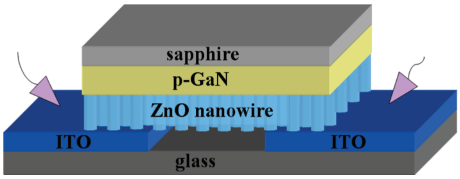


Figure 1. ZnO nanowires forming a heterojunction LED structure on the p-GaN substrate.

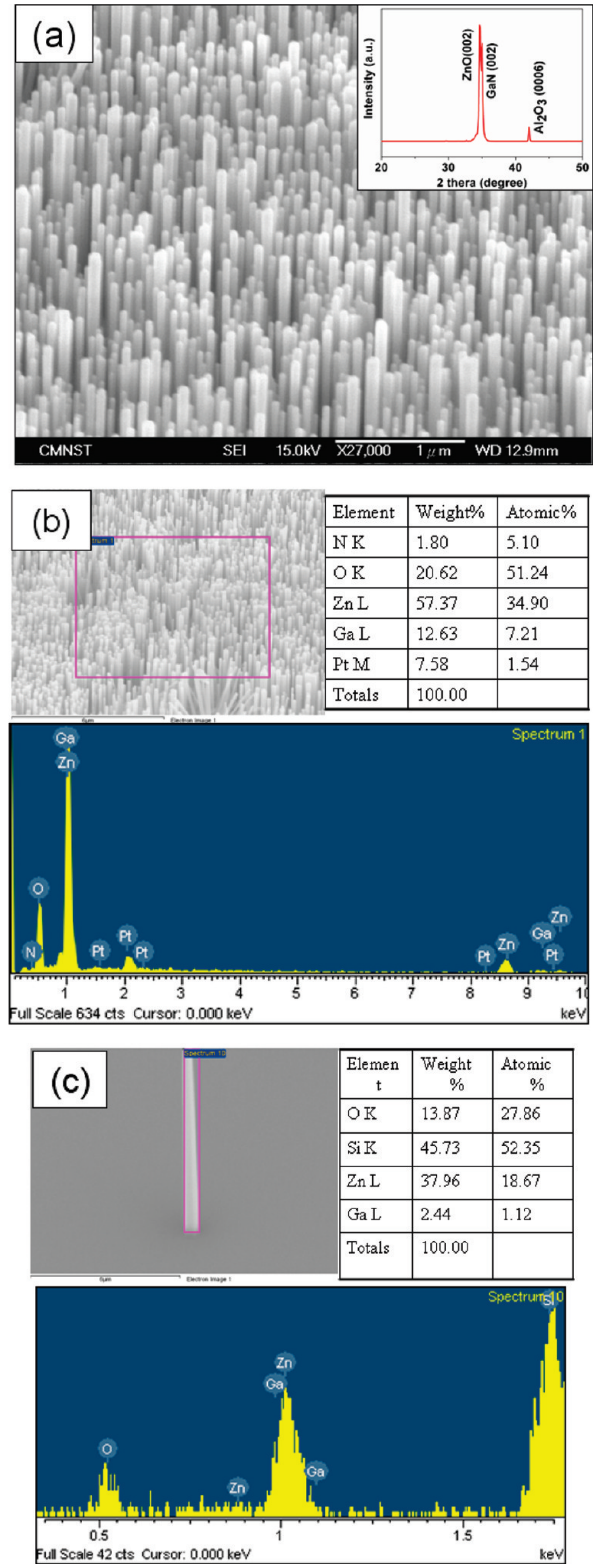
thermal chemical vapor deposition. Zinc metal powder (99.9% purity) purchased from Strem Chemicals was used as the zinc vapor source. A gallium metal ball (99.99% purity) purchased from Rasa Industries, Ltd. was used as the Ga source. The growth processes of ZnO NW and ZnO:Ga were almost identical except that the Ga metal in ZnO:Ga was placed in the alumina boat 5 cm upstream of the zinc powder. The Ga dopant was added by the vapor-solid synthetic method. Heating Ga to 600 °C in the upstream of zinc powder blew the Ga vapor to the downstream boat and simultaneously synthesized the ZnO nanowire on the downstream boat.

Because the gallium powder is close to the zinc powder, the Ga and Zn powder melts and mixes first, which forms a $ZnGa_2O_4$ nanowire rather than a ZnO nanowire doped with Ga.[17] The nanowire growth process was as follows. The zinc powder and p-GaN film were placed in the same alumina boat 1.5 cm apart. The boat was then placed in a thermal furnace. Argon (54.4 sccm) and oxygen (0.8 sccm) were continuously introduced into the thermal furnace with a constant temperature of 600 °C, and the vapor−solid growth process was performed for 50 min. The reactive pressure was maintained at 10 Torr using a mechanical pump.

After the growth process was complete, the heterojunction light emitting diode was fabricated and packaged using the method described below. To form an ohmic contact with GaN whose work function is very high, the commercial product must typically be evaporated on several materials (Ti/Al/Ni/Au). This study employed a flip-chip package process that uses ITO/glass substrates and a low-temperature furnace. Figure 1 displays a cross-sectional view of the heterojunction LED. To form an n-p-n heterojunction, a 0.25 cm wide ditch was etched into the ITO film to separate it into two electrodes. The heterojunction LED was then reversed and placed on the prepared ITO/glass substrate. As shown in the figure, the tips of the ZnO nanowire in direct contact with the ITO formed an n-p-n heterojunction structure for an LED. This LED was then placed in the thermal furnace and annealed at 200 °C for 10 min. After the thermal process, silicon on glass (SOG) was used to bind the LED. The flip-chip package process easily formed a good ohmic contact and did not deposit any material on the ZnO nanowire tips that would serve as contact electrodes.

Results and Discussion

The size distribution of the nanowires and surface morphologies was elucidated using a JEOL JSM-7000F field emission scanning electron microscope (FE-SEM operated at 10 keV). The photoluminescence properties of the ZnO NWs, ZnO:Ga NWs, and p-GaN at room temperature were characterized using a Jobin Yvon-Spex fluorolog-3 spectrophotometer. The excitation source used for PL measurement was an Xe lamp, which emitted at 254 nm. A voltage source, current meter (Keithley 237), and a probe station were used to measure the current−voltage (I−V) characteristics at room temperature. Electroluminescence (EL) spectra were obtained using an Avantes fiber optics photospectrometer.



Element	Weight%	Atomic%
N K	1.80	5.10
O K	20.62	51.24
Zn L	57.37	34.90
Ga L	12.63	7.21
Pt M	7.58	1.54
Totals	100.00	

Element	Weight %	Atomic %
O K	13.87	27.86
Si K	45.73	52.35
Zn L	37.96	18.67
Ga L	2.44	1.12
Totals	100.00	

Figure 2. (a) FE-SEM image (rotated 45°) of as-grown ZnO nanowires on p-GaN film. (Inset) XRD pattern of ZnO nanowire array on p-GaN epitaxy film. (b) EDX spectra of ZnO nanowire grown on the p-Gan substrate. (c) EDX spectra of a ZnO nanowire doped with a Ga on Si substrate.

Figure 2a shows the FE-SEM images of ZnO nanowires rotated through 45°, indicating that the ZnO nanowires were epitaxially grown on the p-GaN substrate by the thermal furnace system. The vertical ZnO nanowires were 0.7 μm long and 50−300 nm in diameter. Vertically aligned ZnO nanowires

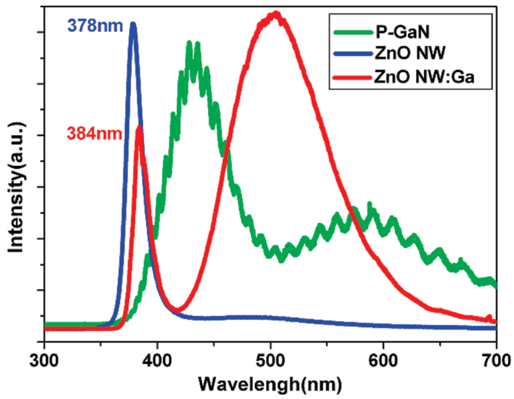


Figure 3. Room-temperature photoluminescence (PL) spectra of ZnO nanowire, Zno nanowire doped with Ga, and p-GaN film.

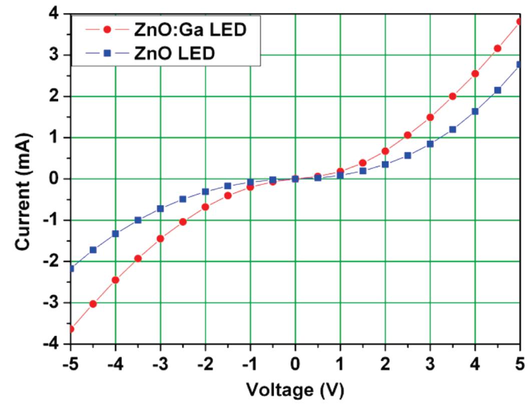


Figure 5. Current−voltage characteristics of ZnO LED and ZnO:Ga LED at room temperature.

synthesized on various substrates have been reported previously.[18−20] Since ZnO and GaN had a small lattice mismatch (~1.8%), ZnO nanowires grew along the *c*-axis. The grown p-GaN substrate was also an electron hole injection layer in the heterostructure LED. The inset in Figure 2a displays the X-ray diffraction (XRD) pattern of the ZnO nanowire on the p-GaN substructure. The diffraction peaks of the sample at 34.4°, 34.8°, and 41.9° were indexed to hexagonal wurtzite ZnO, GaN, and sapphire, respectively, which indicated an epitaxial relationship between the GaN epitaxy film and the ZnO nanowires. Figure 2b shows the EDX spectra of the ZnO nanowire on the p-GaN substrate. The EDX data showed that the nanowires were composed of Zn and O elements and that the substrate contained Ga and N atoms. Figure 2c shows that Ga was successfully doped into ZnO nanowire on Si substrate since ZnO nanowires doped with elemental Ga are indistinguishable on a p-GaN substrate. To synthesize the ZnO:Ga NWs, the Ga powder was placed in the furnace upflow. The Ga powder affected the oxygen flow so that the ZnO:Ga nanowire became thinner,[21] and the oxygen element increased. The PL peak at a further 500 nm confirmed this phenomenon.

The degree of doping with Ga was hard to determine by SEM but easily demonstrated by PL or EL spectroscopy. Figure 3 displays the room-temperature PL spectra of the ZnO nanowire, ZnO nanowire doped with Ga, and the p-GaN film. The PL spectrum of the ZnO nanowires revealed an ultraviolet emission at 378 nm, and the full width at half-maximum intensity is 13 nm, which is attributable to the near-band edge (NBE) emission of the ZnO with a wide band gap. The PL spectrum of the ZnO nanowires doped with Ga shows two peaks: one at 384 nm, shifted from 378 nm, and another large peak at 500 nm. According to the literature,[22] these results confirm the successful doping of the ZnO nanowire with gallium. The figure shows that the PL spectrum of a p-GaN substrate consists of two broad bands centered at maximum wavelengths of 432 nm and 583 nm. The broad band emission spectrum is attributable to the transition from the conduction band or shallow donors to the Mg acceptors.

After the flip chip package process, the heterojunction LED is formed from two back-to-back p-n junctions. The ohmic contact between ZnO and ITO was described in an earlier report by this research team.[23] Figure 4 presents the equivalent circuit of this n-p-n heterojunction structure. When a positive bias is applied to the right-hand side, the n-p junction on that side is forward biased and acts as a variable resistor, and the p-n junction on the left-hand side becomes an LED (Figure 4b). When a negative bias is applied to the right side, the n-p junction on that side becomes an LED, whereas the p-n junction on the left-hand side becomes a resistor (Figure 4c). Figure 5 plots the I−V characteristics of the ZnO LED and the ZnO:Ga LED measured when the bias voltage was reduced from +5 V to −5 V. These I−V characteristics demonstrate that these devices behave in a manner similar to that of two rectifying diodes. This figure, which exhibits reverse symmetry, demonstrates that one part of the structure is connected to another part like two diodes connected back-to-back. In this investigation, the turn-on voltage was successfully reduced and white light emitted by doping Ga into the ZnO nanowire. The turn-on voltage of the ZnO:Ga LED was lower than that of the ZnO LED, while the current of the ZnO:Ga LED was higher than that of the ZnO LED. The turn-on voltage of the ZnO:Ga LED still exceeded that of the commercial product but was lower than that obtained in other studies.[7,24] The forward current was approximately 4 mA at ±5 V, and the turn-on voltage was 1 V. One reason for the higher turn-on voltage is that one side of the p-n junction becomes a variable resistor when the opposite side is operating at forward bias. Another reason is that the interface and edge effect significantly influence the device characteristics when the p-n junction is shrunk to the nanoscale.[25,26] Figure 6a presents the electric luminescence (EL) spectra from the ZnO:Ga LED and ZnO LED. The peak wavelength and full-width-at-half-maximum (fwhm) intensity of the ZnO LED are 415 and 50 nm, respectively, at 20 mA.

The peak from the ZnO LED at 415 nm is attributable to radiative recombination at the defects that unexpectedly form

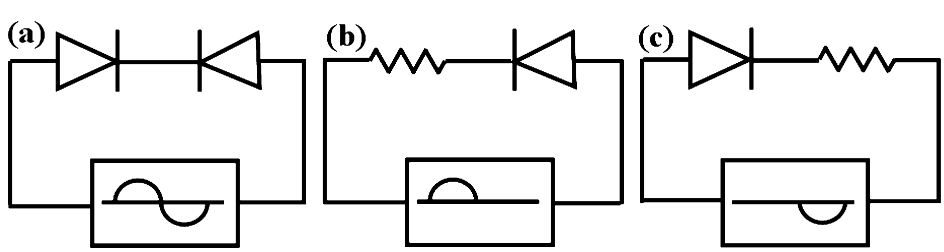


Figure 4. (a) Equivalent circuit of the n-p-n heterojunction structure (b) at positive bias and (c) at negative bias.

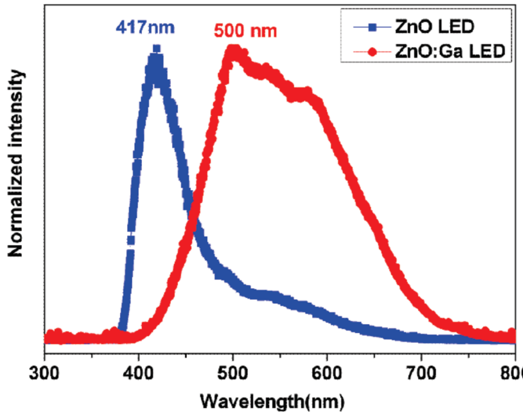


Figure 6. EL spectra of ZnO LED and ZnO:Ga LED at a DC current of 20 mA.

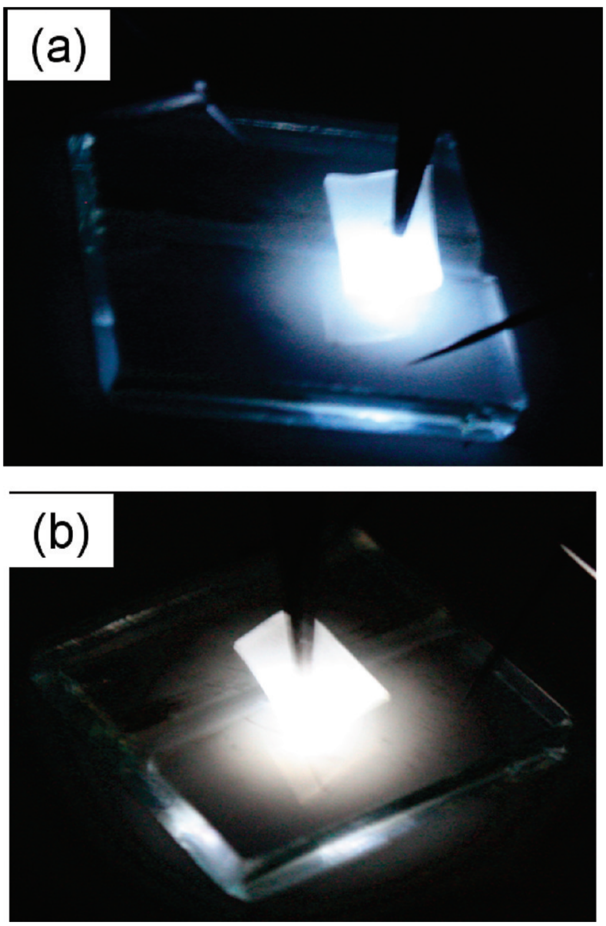


Figure 7. Photographs of a heterojunction LED, emitting (a) blue light (ZnO LED) and (b) white light (ZnO:Ga LED) under DC current injection.

when carriers are injected at forward bias. The peak wavelength and fwhm intensity of the ZnO:Ga LED are 500 nm and 200 nm, respectively, at 20 mA. The shift in the wavelength and increase in the fwhm of the EL peak between the ZnO LED and the ZnO:Ga LED are attributable to the successful doping of Ga into the ZnO nanowire and the unexpected defects between sapphire and p-GaN. As Ga doping increases the carrier density of the ZnO nanowire, the region of combination moves toward the p-GaN, and opportunities for combination in p-GaN increase. Figure 7a,b shows that under DC current, the LEDs emit blue and white light that is visible to the naked eye. Figure 8 shows the color coordinate measurements for the blue light (ZnO LED) and white light (ZnO:Ga LED).

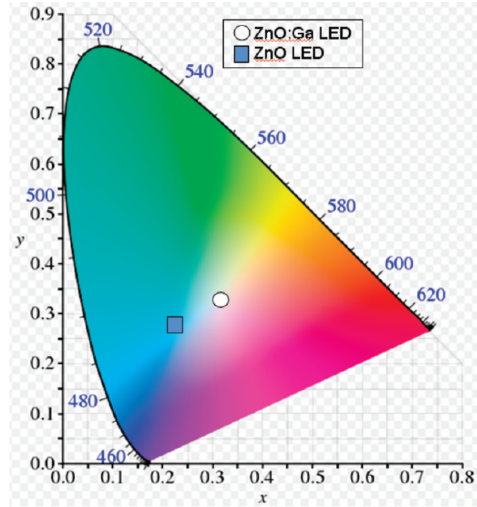


Figure 8. Color coordinate measurement of blue light (ZnO LED) and white light (ZnO:Ga LED).

Conclusions

In summary, ZnO nanowires and ZnO:Ga nanowires were fabricated on a p-GaN substrate by thermal chemical vapor deposition using a quartz tube furnace. The LED thus formed was packaged with ITO/glass by a simple flip-chip package process. The peak photoluminescence spectrum of the ZnO:Ga nanowire shifted from 378 to 384 nm and a broad band at 500 nm. The photoluminescence spectra of the ZnO:Ga nanowire exhibited two peaks, one at 384 nm, which shifted from 378 nm, and another large peak at 500 nm. At room temperature, the peak electroluminescence emission of the ZnO:Ga LED was 500 nm, and the fwhm intensity was 200 nm. When gallium was successfully doped into the ZnO nanowire, the EL peak shifted. A white-light LED was successfully fabricated, and no complex evaporation process was required to form an electrode on p-GaN.

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