Research Article

Use of the Thermal Chemical Vapor Deposition to Fabricate Light-Emitting Diodes Based on ZnO Nanowire/p-GaN Heterojunction

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The fabrication and characteristics of grown ZnO nanowire/p-GaN heterojunction light-emitting diodes are reported. Vertically aligned ZnO nanowire arrays were grown on a p-GaN substrate by thermal chemical vapor deposition in quartz tube. The rectifying current-voltage characteristics indicate that a p-n junction was formed with a heterostructure of n-ZnO nanowire/p-GaN. The room temperature electroluminescent emission peak at 425 nm was attributed to the band offset at the interface between the n-ZnO nanowire and p-GaN and to defect-related emission from GaN; it was also found that there exist the yellow band in the heterojunction. It would be attributed to the deep defect level in the heterojunction.

1. Introduction

Recently, nanowire- (NW-) based light-emitting diodes (LEDs) have become the focus of many researches and have also drawn considerable attention owing to their many advantages over conventional thin-film-based devices. NWs can improve light extraction without the use of a reflector because they can act as direct waveguides, and their nanostructure can overcome lower carrier injection efficiency because of a large band offset at the heterojunction interface. The nanojunction can also increase the contact area and aspect ratio and, hence, enhance carrier injection efficiency and recombination. Zinc oxide (ZnO) has a wide bandgap ($E_g = 3.37$ eV) and a stronger exciton binding energy (60 meV) than gallium nitride (GaN) (~29 meV) [1]. In addition, ZnO is a natural n-type semiconductor and has a wurtzite structure [2, 3]. These properties make ZnO a potential material to be used for ultraviolet (UV) photodetectors and other optoelectronic applications [4]. Moreover, ZnO-based one-dimensional (1D) materials are widely used because of their high surface-area-to-volume ratio. Therefore, a large contact area of the p-n junction

structure could be fabricated to produce many kinds of optoelectronic devices such as LEDs and detectors. However, ZnO homojunction devices are difficult to fabricate because p-type doping in ZnO is not stable or reliable enough. Therefore, a heterojunction of ZnO and another material is needed to realize a p-n junction, which is an important part of many devices. Heterojunction devices fabricated in previous studies utilized semiconductors such as Cu_2O , Si, SiC, and GaN [5–8].

Although several studies have investigated the use of p-type ZnO to realize homojunction devices, the fabrication of such devices is difficult because p-type ZnO is not stable or reliable enough. GaN is a wide-bandgap semiconductor ($E_g = 3.39$ eV) and has similar physical properties to ZnO, including a small in-plane lattice mismatch (~1.8%) and the same wurtzite structure [9, 10]. Therefore, n-ZnO NW-based LEDs can be realized through a GaN heterojunction structure. Recently, many researchers have grown ZnO NWs using various techniques, including metal organic chemical vapor deposition (MOCVD), and electrodeposition. LED performance is not satisfactory with MOCVD [11–13]. Lupan et al. fabricated low-voltage UV LEDs with

an electroluminescence (EL) emission wavelength at 397 nm at an applied voltage of 4.2 V [11]. However, these methods of growing NWs are complex and expensive. In this study, ZnO NW heterojunction was grown with a simple method by thermal chemical vapor deposition in quartz tube, because this method has many advantages such as process simply and short growth time, lower cost than MOCVD, and mass manufactures. The physical and electrooptical properties of the fabricated LEDs are discussed.

2. Experiment

A p-GaN epitaxial film was deposited on a c-plane (0001) sapphire substrate by MOCVD; the sapphire substrate was purchased commercially. The ZnO NWs used in this study were grown on the p-GaN substrate by thermal chemical vapor deposition. Zinc powder (99%, Strem Chemicals) was used as a zinc vapor source. The zinc powder and substrates were inserted into a quartz tube using an alumina boat. Constant streams of argon gas at a rate of 54.4 SCCM (standard cubic centimeters per minute at STP) and oxygen gas at a rate of 0.8 SCCM were then introduced into the reaction system. The evaporation process was carried out for 30 min after the reaction system had reached a reaction temperature of 550°C. A mechanical pump was utilized to maintain a reactive pressure of 10 Torr. Finally, a novel light-emitting diode was fabricated and packaged by the following method. A 3% HCl aqueous solution was used to etch out the n-ZnO NW to expose the p-GaN layer for a p-electrode. Ni/Au (15/120 nm) ohmic contacts were deposited on the p-GaN layer by thermal evaporation. Figure 1 shows the device processing steps used in this study. The fabricated sample was reversed and placed on the prepared ITO/glass substrate. The tips of the ZnO NWs contacted the ITO/glass substrate and formed a ZnO NW/p-GaN structure to be used for the LED. In order to achieve good ohmic contact between the ZnO nanowires and ITO, the LED was placed into a thermal furnace and annealed at 200°C for 10 min. The size distribution of the NWs and surface morphologies of the samples were elucidated using a JEOL JSM-7000F field emission scanning electron microscope (FE-SEM) operated at 10 KeV. The photoluminescence (PL) spectrum of the sample was measured at room temperature using a 325-nm HeCd laser, which acted as the excitation source.

3. Results and Discussion

Figure 2(a) shows a top-view FE-SEM image of as-grown ZnO NWs on GaN film. The SEM measurement shows that the ZnO NWs grow vertically and are connected to the GaN film. The ZnO NWs are 1 μm and 50–100 nm in diameter. Figure 2(b) presents an X-ray diffraction (XRD) pattern of ZnO NWs on a p-GaN substrate. In this figure, we can observe three clear peaks. The ZnO (0002) diffraction peak is to the left of the GaN (0002) peak, and the sapphire substrate (0006) exhibits a peak at 41.9°. This measurement shows that the ZnO NWs are oriented with the *c*-axis, perpendicular to the GaN film. The ZnO and GaN peaks of the XRD pattern

FIGURE 1: Structure of fabricated n-ZnO nanowire/p-GaN heterojunction LED.

are located close to each other at 34.2° and 34.8°, respectively, indicating that the strain existing between GaN and ZnO is very weak. The full width at half maximum (FWHM) values of GaN and ZnO are similar and sharp, indicating that the GaN film and ZnO NWs are of high quality. No other peak is observed, indicating that the preferred orientation of the NWs from the p-GaN film is achieved. Figure 2(c) shows an XRD rocking curve obtained for our sample. The extremely narrow FWHM observed from the rocking curve peak indicates that the ZnO nanowires prepared on the p-GaN substrate in this study are indeed single crystalline with high crystal quality.

Figure 3 presents the PL spectrum of the ZnO NWs and p-GaN film at room temperature. The PL spectrum of the p-GaN film consists of two broad bands, centered at maximum wavelengths (λ_m) of 432 and 583 nm. The broadband emission corresponds to a typical transition from the conduction band or shallow donors to the Mg acceptors. The PL spectrum of the ZnO NWs reveals a strong UV emission with a λ_m of 379 nm and a FWHM of 16 nm, because of near-band edge emission by ZnO with a wide bandgap.

In Figure 4, the current-voltage characteristics of the fabricated diode are plotted for bias voltages ranging from –5 to 10 V. This figure illustrates that the large turn-on voltage was approximately 5.5 V, which indicates that the thermal chemical vapor deposition procedure may produce a higher density of defects at the interface. From Figure 5, it is found that the EL emission rapidly increased with the applied forward bias, and the peak wavelengths were 425 nm, 425 nm, and 426 nm at 10 V, 15 V, and 20 V, respectively. The EL peak wavelength that is red shifted relative to the PL emission of ZnO is approximately 46 nm, which could be attributed to the recombination of electrons and holes in ZnO, causing an unexpected defect to occur in ZnO or at the interface between ZnO and GaN. Moreover, it is also found that there exists the yellow band in the heterojunction; it is attributed to the deep defect level in the heterojunction. The insert of Figure 5 shows the blue emission imaged with a CCD camera. The blue light radiating from

FIGURE 2: (a) FE-SEM image of as-grown ZnO nanowires on p-GaN film. (b) XRD pattern of as-grown ZnO nanowires. (c) XRD rocking curve of fabricated n-ZnO nanowire/p-GaN heterojunction structure.

FIGURE 3: Room temperature PL spectra of as-grown p-GaN film and ZnO nanowires.

the heterostructure LED under DC current injection is strong enough to be seen by the naked eye.

4. Conclusion

In conclusion, we fabricated the ZnO NW/p-GaN heterostructure by thermal chemical vapor deposition using a quartz tube furnace and packaged an LED with ITO/glass by a simple process. The photoluminescence spectrum of the p-GaN film exhibited broad bands at 432 and 583 nm; these bands are attributed to near-band edge emission by ZnO with a wide bandgap. The current-voltage characteristics of the fabricated diode indicated that the turn-on voltage was large (approximately 5.5 V), which may indicate that the thermal chemical vapor deposition procedure produces a high density of defects at the interface. The room temperature EL emission peak at 425 nm was attributed to the recombination of electrons and holes in ZnO, causing an unexpected defect to occur in ZnO or at the interface between ZnO and GaN. Furthermore, there has been the

FIGURE 4: Current-voltage characteristics of fabricated n-ZnO nanowire/p-GaN heterojunction LED.

FIGURE 5: EL spectrum of fabricated n-ZnO nanowire/p-GaN heterojunction LED.

yellow band in the EL spectrum; it is attributed to the deep defect level in the heterojunction.

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