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Light emitting diode based on n-Zn$_{0.94}$M$_{0.06}$O nanorods/p-GaN (M= Cd and Ni) heterojunction under forward and reverse bias

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Abstract

In this study, we report on the improvement in the optoelectronic properties of n-ZnO nanorods/p-GaN heterojunction. This was achieved by doping the ZnO with cadmium (Cd) and nickel (Ni). The ZnO and Zn$_{0.94}$M$_{0.06}$O nanorods grown hydrothermally on the p-GaN substrate were used to fabricate the light emitting diodes (LEDs). Structural measurement revealed that nanorods with wurtzite structure having a preferential orientation along the (002) c-axis. The UV-vis spectra show that the optical band gap of Zn$_{0.94}$M$_{0.06}$O nanorods is decreased in comparison to ZnO nanorods. Electrical measurements of the fabricated LEDs show an obvious rectifying behaviour with low threshold voltage. Electroluminescence (EL) characteristics of LEDs operated at forward and reverse bias were investigated. The EL spectra under forward bias show that doping ZnO nanorods with Cd and Ni led to an intensity enhancement of the broad peak in the visible region while the blue peak originating from the p-GaN substrate remains almost unaffected. The effect of doping was to reduce the valence band offsets and consequently more hole injection has occurred leading to the observed enhancement of the broad band in the visible region. Under reverse bias all heterojunction LEDs show the blue light emission peak originating from the p-GaN substrate.

Keywords: Nanorods, Heterojunctions, Doping, Optoelectronic properties, White light emitting diodes.
1. Introduction

The improvement of light emitting diodes (LEDs) has attracted much attention in the past few years [1]. Zinc oxide (ZnO) due to many interesting properties such as direct band gap (3.37eV), relatively large exciton binding energy (60 meV at room temperature) and the possibility of growth in the nanostructure form using many techniques on any substrate makes it a promising candidate for many optoelectronics devices [2-4]. Due to the absence of reliable p-doping ZnO, its homojunction diode application has been limited [5]. Some researchers have grown n-ZnO nanostructures on other p-type substrates such as GaN [6-8], SiC [9-11], GaAs [12,13] and Si [14,15] to provide another way to realize ZnO-based p-n heterojunctions. Light emitting diode based on the n-ZnO/p-GaN heterojunction is one of the best candidates for LEDs because of the ZnO and GaN both have the same wurtzite hexagonal structure and similar lattice parameters that lead to low lattice mismatch (1.8%) [16-18]. To use the advantages of the optical transitions of ZnO to improve the optoelectronic properties of n-ZnO/p-GaN heterojunction, it is necessary that the radiative recombination occurs in the n-type semiconductor. Several researchers have reported that radiative recombination mainly originates from defect related states in the p-GaN due to a prevailing electron injection from the n-ZnO with a weak holes injection from the p-GaN [19, 20]. To overcome this problem and have more holes injection from the GaN to the ZnO, the valence band offset (barrier for holes) should be lowered to a value less than the conduction band offset (barrier for electrons). To the best of our knowledge, there have been few detailed investigations reported about the use of doping to improve the optoelectronic properties of n-ZnO nanorods/p-GaN heterojunction based LEDs [21]. In the present work, we report on the structural, electrical and optoelectronic properties of n-ZnO.94M0.06O nanorods/p-GaN (M= Cd and Ni) heterojunction based LEDs under forward and reverse bias. The aim of this investigation is to manipulate the band offsets at the n-ZnO/p-GaN to balance the carrier’s injection over the heterojunction to enhance the defect assisted emission in ZnO.

2. Experimental

Commercially available p-GaN substrate was used in this study and all chemicals were purchased from Sigma Aldrich and were of analytical grade and used without further purification.
2.1. **Growth of pure and M-doped ZnO (M= Cd and Ni) nanorods**

At first, the p-GaN substrate was cleaned by sonication in acetone, deionized water, and isopropanol, respectively. Then the substrate preparation technique developed by Green et al. [22] was used to improve the quality of the grown nanorods. For the growth of pure and M-doped ZnO (M= Cd and Ni) nanorods, an equimolar concentration of hexamethylenetetramine (HMT), zinc nitrate hexahydrate (94%) and cadmium chloride (6%) or nickel nitrate hexahydrate (6%) (0.075 M) solutions were prepared and mixed together. Then the prepared solution was poured in a beaker and the pretreated substrates were immersed in the solution with the growth side facing downward. Then the beaker was sealed and heated in a laboratory oven at 95 °C for 5 hours and then it was allowed to cool down to room temperature. After the growth process, to remove the residual salts, the samples were rinsed with deionized water and dried with flowing nitrogen.

2.2. **Fabrication of n-Zn_{0.94}M_{0.06}O nanorods/p-GaN heterojunction LEDs**

Prior to the growth of the pure and M-doped ZnO nanorods on the p-GaN substrate, 10 and 40 nm thickness of Ni and Au were deposited, respectively, using thermal evaporation on the p-GaN substrate, followed by annealing at 350 °C for 15 minutes. After the growth of the pure and M-doped ZnO nanorods an insulating layer of Shipley 1805 photo resist (Marlborough, Ma, USA) was spin-coated on all samples for filling the spaces between the nanorods. Then reactive ion etching was used to expose the tips of the nanorods before the deposition of Al ohmic top contact (50 nm).

2.3. **Characterization**

The structural and morphological properties of the heterojunctions were studied by X-ray diffraction (XRD: Phillips PW 1729 powder diffractometer equipped with CuKα radiation) and field emission scanning electron microscope (FESEM: LEO 1550 Gemini). The optical characterization of the pure and doped ZnO nanorods was performed using a Perkin Elmer Lambda 900 UV–visible spectrophotometer. The light emission features of the pure and M-doped ZnO nanorods and GaN were studied by a micro-photoluminescence (µPL) setup at room temperature. The excitation was performed by a frequency doubled Nd:YVO laser as a continuous wave excitation source, giving a wavelength of λ=266 nm. The electrical properties
was investigated by semiconductor parameter analyzer (Agilent 4155B) and the electroluminescence (EL) measurement was performed using Keithley 2400 source to provide a fixed voltage and the emission spectra were collected using a detector (SR-303i-B).

3. Results and discussions

3.1.1. Morphological and structural properties

Figure 1 (a-d) shows a tilted and top view SEM images of the pure and M-doped ZnO (M= Cd and Ni) nanorods hydrothermally grown on the p-GaN substrate. As it can be seen relatively well aligned pure and M-doped ZnO nanorods with uniform spatial covering over the substrate is achieved. Also, they have hexagonal faces and the average diameter was approximately 50 nm. Almost no observable differences from the SEM images were observed for Zn_{0.94}Cd_{0.06}O nanorods when compared to the ZnO nanorods but in the case of Zn_{0.94}Ni_{0.06}O nanorods, the diameter was found be relatively larger. The typical XRD patterns of the heterojunctions are shown in figure 2(a) indicating that the pure and M-doped ZnO nanorods were highly oriented along the c axis (002) (JCPDS card NO.36-1451). As it can be seen the XRD patterns are dominated by the ZnO (002) and the GaN (002) reflection peaks. This confirms that the pure and M-doped ZnO nanorods have the same out of plane orientation with the GaN substrate. The observed (002) peak of the M-doped (M= Cd and Ni) was found to be shifted towards a lower angle for Cd doped and to a larger angle for the Ni doped compared to the angular position of the (002) of the pure ZnO. This is ascribed to the fact that substitution of larger Cd ions or smaller Ni ions with the Zn ions leads to expansion or contraction of the ZnO lattice. No additional peaks related to impurities phases are observed.

3.2. Optical properties of pure and M-doped ZnO nanorods

The optical band gap of the pure and M-doped ZnO (M= Cd and Ni) nanorods was obtained from the \((\alpha h \nu)^2\) versus \(h \nu\) plot shown in figure 2(b) which was measured using the following equation [23]:

\[
(\alpha h \nu) = A (h \nu - E_g)^{1/2}
\] (1)
Where $\alpha$ is an optical absorption coefficient, $h\nu$ is the photon energy, $A$ is a constant coefficient and $E_g$ is the optical band gap energy. The optical band gap values of pure and M-doped ZnO (M=Cd and Ni) nanorods, obtained by the extrapolation method were 3.3, 3.23 and 3.26 eV, respectively. So we can conclude that the interaction of Cd and Ni states with the ZnO host states resulted in creating an energy donor levels in the band gap that leads to reduce the optical band gap.

3.3. Electrical properties of heterojunction LEDs

The schematic diagram of the n-ZnO nanorods/p-GaN heterojunction LED is shown in Figure 3(a). Figure 4(a-c) presents the current-voltage (I-V) characteristics of the n-ZnO nanorods/p-GaN and n-Zn0.94M0.06O nanorods/p-GaN (M= Cd and Ni) heterojunction LEDs. The I-V curve shows an obvious rectifying behaviour with a threshold voltage of 3.5 V, 4.5 V and 3.75 V, for the undoped, Cd doped and Ni doped LEDs respectively. The rectification ratio ($I_F/I_R$) where $I_F$ and $I_R$ are current under forward and reverse bias of the n-ZnO nanorods/p-GaN and the n-Zn0.94M0.06O nanorods/p-GaN (M= Cd and Ni) heterojunction LEDs were found to be 36.82, 13.30 and 14.60, respectively. This rectification ratio was evaluated at 8V. The series resistance ($R_s$) of the n-ZnO nanorods/p-GaN and n-Zn0.94M0.06O nanorods/p-GaN (M= Cd and Ni) heterojunction LEDs can be determined by calculate the slope of the curve of the $I/(dI/dV)$ versus $I$ as shown in figure 4(d-f) that was 244.37 $\Omega$, 317.57 $\Omega$ and 272.26 $\Omega$, respectively. It can be seen that by doping ZnO with Cd and Ni, the rectification ratio is decreased and the $R_s$ of the heterojunctions is increased. Despite the reduction of the band offsets due to doping, the increase of the series resistance is more pronounced and has led to increase the threshold voltage of the heterojunction.

3.4. Optoelectronic properties of the n-ZnO nanorods/p-GaN and n-Zn0.94M0.06O nanorods/p-GaN (M= Cd and Ni) heterojunction LEDs

The EL spectra of the n-ZnO nanorods/p-GaN and n-Zn0.94M0.06O nanorods/p-GaN (M= Cd and Ni) heterojunction LEDs were measured under forward and reverse bias of 25V as shown in
Figure 5 (a-f). However, below 25V the light emission can be observed by the naked eye but it was too weak. As can be seen from the Figure 5(a), under forward bias the emission of n-ZnO nanorods/p-GaN heterojunction has a sharp blue peak centred at 408 nm and a broad emission peak with low intensity extended from 490 nm up to 700 nm. The EL spectrum of the n-Zn_{0.94}Cd_{0.06}O nanorods/p-GaN heterojunction shows a red shift in the sharp blue peak (421 nm) and the broad emission peak centred at 560 nm has higher intensity compared to the n-ZnO nanorods/p-GaN heterojunction as shown in Figure 5(b). Figure 5(c) shows that the EL spectrum of the n-Zn_{0.94}Ni_{0.06}O nanorods/p-GaN heterojunction has a sharp blue peak centred at 400 nm and broad emission peak centred at 650 nm. The EL spectra of n-ZnO nanorods/p-GaN and n-Zn_{0.94}M_{0.06}O nanorods/p-GaN (M= Cd and Ni) heterojunction LED under reverse bias shows a relative broad peak centred at about 405 nm, 412 nm and 403 nm, respectively. To understand the origin and the mechanism of the emissions from the n-ZnO nanorods/p-GaN and the Zn_{0.94}M_{0.06}O nanorods/p-GaN (M=Cd and Ni) heterojunction LEDs, we performed PL measurement and band diagram model. The room temperature PL spectra of the pure ZnO, Zn_{0.94}M_{0.06}O (M= Cd and Ni) nanorods and GaN are shown in Figure 6 (a-d). All the spectra were taken at the same excitation power and integration time and are therefore comparable. It can be seen that the ultraviolet (UV) emission which is called near band edge emission (NBE) and the deep level emission (DLE) peaks are observed for ZnO nanorods centred approximately at 375 nm, 520 nm (DLE1, green emission) and 680 nm (DLE2, red emission), respectively. The UV emission is attributed to the recombination of free excitons and the green and red peaks can be ascribed to the recombination between the conduction band and zinc interstitial (Zn_i) energy level to oxygen vacancy (V_O) and oxygen interstitial (O_i), respectively [24]. Also, the green emission can be attributed to the Zn_iV_Zn defect pairs [25]. The PL spectra of the Zn_{0.94}M_{0.06}O nanorods (M= Cd and Ni) show a red shift in the NBE peak which is expected and is consistent with the UV-vis data. The I_{UV}/I_{Vis} ratio was measured to be 2.87, 1.52 and 1.11 for the pure ZnO, Zn_{0.94}Cd_{0.06}O and Zn_{0.94}Ni_{0.06}O nanorods, respectively, where I_{UV} is the integrated band intensity of the UV emission peak and I_{Vis} is the integrated band intensity of the green emission peak. The reduction of I_{UV}/I_{Vis} ratio can be attributed to the substitution of Cd and Ni ions with Zn ion which can lead to produce new defects in ZnO nanorods. Basak et al. reported that surface related defects in the form of a complex V_{Zn}^{-}H_2O can limit the green emission [25]. For the case of Zn_{0.94}Ni_{0.04}O nanorods, the diameter was found to be relatively larger compared to ZnO
nanorods. The relative increase of the diameter leads to decrease of the surface area to volume ratio which consequently results in decreasing possible surface defect sites to form V_{Zn}H_2O. Therefore, addition of Ni leads to the reduction in surface defect states which limit the green emission. The PL spectrum of the GaN shows a blue peak centred at 406 nm which is known and attributed to transition from the conduction band to deep Mg acceptor levels in the p-GaN [26]. According to the electron affinity (χ) and band gap of pure ZnO (4.35 eV, 3.3 eV) and GaN (4.2 eV, 3.34 eV) the energy band diagram under zero, forward and reverse bias were drown via Anderson model [27] which is shown in Figure 3(b-d). The conduction band offset of the n-ZnO nanorods/p-GaN heterojunction was estimated to be 0.15 eV. The valence band offsets of the n-ZnO nanorods/p-GaN and n-Zn_{0.94}M_{0.06}O nanorods/p-GaN (M=Cd and Ni) heterojunctions were calculated to be 0.11 eV, 0.04 eV and 0.07 eV, respectively. Since the carrier mobility in the n-ZnO is larger than of the p-GaN, electrons could not be blocked in the n-ZnO region and will be injected into the p-GaN site to recombine with holes. Under forward bias, electron and hole barriers is decreased and the electrons in the conduction band of the n-ZnO move towards the p-GaN and the holes in the valence band of p-GaN move towards the n-ZnO. According to the PL spectra, the blue peak at about 408 nm can be attributed to the transition from the conduction band of p-GaN to deep Mg acceptor levels in the p-GaN substrate and the broad peak with low intensity in the visible region can be attributed to deep defect states in n-ZnO site [19, 20, 26]. For the n-Zn_{0.94}Cd_{0.06}O nanorods/p-GaN heterojunction LED the blue peak has red shift (421 nm) that this can be ascribed to the transition from the conduction band of the n-ZnO to Mg acceptor levels of the p-GaN [26]. The blue peak (403 nm) of the n-Zn_{0.94}Ni_{0.06}O nanorods/p-GaN is almost not change. The reduction in the valence band offsets of the n-Zn_{0.94}M_{0.06}O nanorods/p-GaN (M=Cd and Ni) heterojunction LEDs results in increasing hole injection from the p-GaN towards the n-Zn_{0.94}M_{0.06}O site. Therefore, the recombination in the n-Zn_{0.94}M_{0.06}O region is increased and it leads to increase the EL peak intensity under forward bias in the visible region. Since the valence band offset of the n-Zn_{0.94}Cd_{0.06}O nanorods/p-GaN heterojunction is lower than that of n-Zn_{0.94}Ni_{0.06}O nanorods/p-GaN heterojunction, the visible peak intensity is higher in n-Zn_{0.94}Cd_{0.06}O nanorods/p-GaN heterojunction. Under reverse bias, since a large barriers formed at the heterojunction, the occupied valence band maximum of p-GaN would be higher than the unoccupied conduction band maximum of n-ZnO which this results in decreasing the movement of holes from p-GaN towards the n-ZnO. Therefore, most of recombination will
occur in p-GaN site which leads to blue light emission. Inset of Figure 5 (a-f) shows the CIE 1931 color coordinate measurements for the n-ZnO/p-GaN and n-Zn$_{0.94}$M$_{0.06}$O/p-GaN (M= Cd and Ni) heterojunction LEDs under forward and reverse bias. As it can be seen under forward bias by doping Cd and Ni with ZnO the emission light turns from blue to almost white but under reverse bias the emission light was almost blue.

4. Conclusion

In summary, we have fabricated n-ZnO nanorods/p-GaN and n-Zn$_{0.94}$M$_{0.06}$O nanorods/p-GaN (M= Cd and Ni) heterojunction LEDs. Structural study revealed that pure and M-doped ZnO nanorods have the same out of plane orientation with GaN along the c-axis (002). Current-voltage characteristics of heterojunctions show an obvious rectifying behaviour for all of them. Optical measurement shows that M-doped ZnO nanorods has smaller optical band gap than that of pure ZnO nanorods. The reduction of the optical band gap results in decrease of the valence band offset of the n-Zn$_{0.94}$M$_{0.06}$O nanorods/p-GaN (M= Cd and Ni) heterojunction LEDs compared to the n-ZnO nanorods/p-GaN heterojunction LED. In turn, this reduction has led to more holes injection from the GaN to ZnO. Hence, under forward bias we have demonstrated that the visible broad deep defect peak emission in ZnO nanorods can be enhanced by doping. Under reverse bias only blue light emission was observed for all LEDs.

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References


Figure 1. Different SEM images of the grown nanorods, in (a) top view of the pure ZnO nanorods, (b) titled view of the sample shown in (a), (c) Top view SEM image of Cd-doped ZnO nanorods, and finally in (d) top view SEM image of the Ni-doped ZnO nanorods.
Figure 2. (a) XRD patterns of the n-ZnO nanorods/p-GaN and n-Zn_{0.94}M_{0.06}O nanorods/p-GaN (M= Cd and Ni) heterojunctions and (b) Plot of $(\alpha h\nu)^2$ versus $h\nu$ of the pure and M-doped ZnO nanorods (M= Cd and Ni).
Figure 3. Schematic diagram of the n-ZnO nanorods/p-GaN heterojunction (a) and energy band diagram of the n-ZnO nanorods/p-GaN heterojunction under (b) zero, (c) forward and (d) reverse bias.
Figure 4. Typical current-voltage (I-V) characteristics of the (a) n-ZnO nanorods/p-GaN, (b) the n-Zn_{0.94}Cd_{0.06}O nanorods/p-GaN, and (c) n-Zn_{0.94}Ni_{0.06}O nanorods/p-GaN heterojunction. Insets show the threshold voltage of the heterojunctions. Plot of $I/(dI/dV)$ versus $I$ of the (d) n-ZnO nanorods/p-GaN, (e) n-Zn_{0.94}Cd_{0.06}O nanorods/p-GaN and (f) n-Zn_{0.94}Ni_{0.06}O nanorods/p-GaN heterojunction.
Figure 5. EL spectra measured from the different fabricated LEDs at forward bias, in (a) the EL spectrum of the n-ZnO nanorods/p-GaN LED. In (b) the EL spectrum of the n-Zn$_{0.94}$Cd$_{0.06}$O nanorods/p-GaN LED, and in (c) the EL spectrum of the n-Zn$_{0.94}$Ni$_{0.06}$O nanorods/p-GaN. While in (d), (e), and (f) the spectra of the samples shown in (a), (b), and (c), respectively, is again displayed but for reverse bias. The inserts are the corresponding chromaticity coordinates of the different heterojunction LEDs.
Figure 6. Room temperature photoluminescence (PL) spectra of (a) ZnO, (b) Zn$_{0.94}$Cd$_{0.06}$O, (c) Zn$_{0.94}$Ni$_{0.06}$O nanorods and (d) GaN substrate.