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Dong, Zhili

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Ultraviolet emission from a ZnO rod homojunction light-emitting diode

X. W. Sun,^{1,a)} B. Ling,¹ J. L. Zhao,¹ S. T. Tan,² Y. Yang,³ Y. Q. Shen,⁴ Z. L. Dong,⁴ and X. C. Li¹

¹*School of Electrical and Electronic Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore*

²*Institute of Microelectronics, Agency for Science, Technology and Research (A*STAR),*

11 Science Park Road, Science Park II, Singapore 117685, Singapore

³*Data Storage Institute, Agency for Science, Technology and Research (A*STAR), 5 Engineering Drive 1, Singapore 117608, Singapore*

⁴*School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore*

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Ultraviolet electroluminescence was demonstrated at room temperature from a ZnO rod homojunction light-emitting diode array. The *p*-type doping was realized by phosphorous (P) ion implantation into defect-free ZnO rods followed by annealing. High resolution transmission electron microscopy shows the lattice compression of annealed single crystalline P-doped ZnO rod compared to the as-grown ZnO rod, suggesting atomically incorporation of P into the ZnO wurtzite structure. *p*-type doping was confirmed by low temperature photoluminescence spectra and single rod current-voltage characterization. © 2009 American Institute of Physics.

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Ultraviolet light-emitting diodes (UV LEDs) hold the promise for a variety of applications including solid state lighting, UV photolithography, high density data storage, and biomedical analysis.¹ As a potential UV emitting material with band gap of ~ 3.37 eV at room temperature (RT), ZnO has attracted considerable attention due to its large exciton binding energy of ~ 60 meV, band gap engineering capability, high thermal and chemical stability, and feasibility of wet chemical etching.² It is well known that nominally undoped ZnO is *n*-type and reliable *p*-type doping remains a big challenge. Although there have been some reports on ZnO *p*-type doping since 2007,³ few studies have realized ZnO nanowire/nanorod homojunction LEDs.^{4,5} As a result, most of the currently developed ZnO LEDs are based on heterojunctions. In our previous work, *p*-type ZnO rods and *p-n* homojunction LEDs were achieved by arsenic (As) ion implantation.⁵ Phosphorous (P) is also an effective acceptor dopant for ZnO, capable of achieving high hole concentration and mobility.^{6,7} In this work, we report a UV-emitting ZnO rod *p-n* homojunction LED with an ion-implanted P-doped *p*-type ZnO.

Vertically aligned ZnO rods with diameters of 200–500 nm and length of ~ 3.5 μm were uniformly grown on fluorine-doped tin oxide (FTO) coated sapphire (*c*-plane) substrates by a vapor phase transport (VPT) method.⁵ It is worth mentioning here that no metal catalyst were used during the growth, which otherwise may induce electronic defects (trap states). The as-grown ZnO rod arrays were implanted with P⁺ ions using a VARIAN E-220 implanter with 50 keV (device I) and 100 keV (device II) at a dosage of 1×10^{14} cm⁻² perpendicular to the aligned rods. Dopant activation of the as-implanted ZnO rods was performed by annealing at 900 °C for 1 h with an O₂ flow rate of 100 SCCM (standard cubic centimeters per minute) at 1 Torr. The obtained *p*-ZnO:P/*n*-ZnO rod homojunctions were further em-

ployed to fabricate LEDs. Different from our previous work,⁵ in this paper, we used a bottom emitting configuration, i.e., constructing the LED on FTO coated sapphire with light emitting from sapphire side. The transparent conductive FTO film (resistance: ~ 8 Ω/square) functioned as the cathode and the top Au layer fabricated by sputtering through a shadow mask acted as the anode. To prepare top Au electrode on ZnO:P rods, spin on glass (SOG) (Honeywell) was adopted as a spacer. Reactive ion etching (RIE) was adopted to expose ZnO rod tops for contact formation. During the RIE process, CF₄ gas of 70 SCCM and O₂ gas of 5 SCCM was applied. The radio frequency power supply is 100 W and the vacuum level is 50 mTorr. The whole etching process lasted 3–5 min.

Figure 1(a) and the inset show respectively the top- and side-view images of the as-grown ZnO rods characterized by a JEOL JSM 5910LV scanning electron microscope (SEM). High density vertically aligned rods with slightly larger diameters on top were intentionally grown since such a morphology was found to effectively avoid ion implantation into the sidewalls of the rods.⁵ The average diameter and length of the ZnO rods were 350 nm and 3.5 μm , respectively. Figure 1(b) and the inset show, respectively, the top-view and 45° tilted-view SEM images of ZnO:P rods embedded in SOG. It can be seen that ZnO rods remained vertically aligned after the P⁺ implantation. Figure 1(c) shows the low magnification transmission electron microscopy (TEM) image of an annealed ZnO:P rod, of which the implantation was performed at 100 keV P⁺ ions with a dosage of 10^{14} cm⁻². The interference lattice fringes from both [0001] and [10 $\bar{1}$ 0] directions were investigated carefully along the growth direction of the rods. Figures 1(d)–1(f) are typical high resolution TEM (HRTEM) images taken from different parts of the rod, corresponding to the denoted regions d–f in Fig. 1(c). The lattice spacing corresponding to the *d*-spacing of (0001) planes of wurtzite ZnO changes from 0.504 to 0.519 nm from the rod top [region d in Fig. 1(c)] to bottom region

^{a)}Electronic mail: exwsun@ntu.edu.sg.

FIG. 1. (Color online) (a) Top view and (inset) side view of the as-grown ZnO rods. (b) Top view and (inset) 45° tilted view of ZnO:P rods embedded in SOG layer. (c) Low-magnification TEM image of an annealed ZnO:P rod. In the inset is the change in lattice spacing along the a -axis and c -axis of the ZnO rod. [(d)–(f)] High-resolution TEM images from different parts of the rod denoted by the rectangular regions in Fig. 1(c). The white arrowhead indicates the growth direction of the rod. (g) SAED pattern of region d from the p -ZnO:P rod.

[region f in Fig. 1(c), ~ 400 nm away from the rod top]. Similarly, the lattice spacing corresponding to the d -spacing of (10 $\bar{1}0$) planes shows the same increasing tendency from the top to the bottom regions (0.554–0.562 nm). Beyond region f, no further lattice spacing change could be observed. The spacing between a - and c -ZnO:P planes of the ZnO:P are expected to be smaller than those of intrinsic ZnO nanowires (i.e., 5.629 and 5.207 Å).² The lattice compression is due to the P doping and possibly the formation of P_{Zn} defects as the P_{Zn}–O bond has a smaller bonding length (~ 1.68 Å) than that of Zn–O bond (~ 1.93 Å).³ According to the variation of the lattice spacing along the rod [inset of Fig. 1(c)], we can roughly estimate the implantation depth of the rods to be around 150–250 nm from the rod tops. The above results were confirmed after checking more than 20 rods. Figure 1(g) is a selected area electron diffraction pattern taken from region d, confirming the single crystal structure.

The impurity bound excitons in the ZnO:P rods were analyzed by low temperature photoluminescence (LTPL) carried out at 5 K, using the 325 nm line of a He–Cd laser as the excitation source. Figure 2 shows the LTPL spectra of the as-grown ZnO rods, ZnO:P rods from devices I and II, respectively. The as-grown ZnO rods show only two neutral donor-bound exciton peaks (D_1^0X : 3.358 eV and D_2^0X : 3.362 eV) (Refs. 2 and 8) and one two-electron satellite (TES) peak (~ 3.313 eV) related to the excited state of the donor-bound exciton.³ Device I shows two predominant neutral acceptor-bound exciton peaks (A_1^0X : 3.357 eV and A_2^0X : 3.353 eV) with a very weak donor-bound exciton peak (~ 3.361 eV).³ In the LTPL spectrum of device II, another broad weak peak appears at ~ 3.316 eV (inset of Fig. 3) besides A_1^0X peak (~ 3.357 eV) and D_2^0X peak

FIG. 2. (Color online) PL spectra of the as-grown ZnO rods, device I and device II taken at 5 K. The inset shows the enlarged area as marked for device II.

(~ 3.360 eV), which can be attributed to free electron-to-acceptor (eA^0) emission.^{9,10} The neutral acceptor-bound exciton peaks shown in LTPL spectra confirm the acceptor behavior of P in ZnO. The intensity ratio of donor-bound to acceptor-bound exciton peaks of device II is higher than that of device I, suggesting more donor defects (such as V_O) were induced in device II during implantation with higher ion energy. The well-known deep level emissions around 2.5 eV, cannot be detected in all our annealed ZnO:P sample, indicating low concentration of deep-level defects in our p -ZnO:P rods.^{3,11} The acceptor binding energy (E_A) in ZnO:P rod can be estimated by $E_A = E_{\text{gap}} - E_{eA} + k_B T/2$,¹² where E_{eA} is the transition energy of eA^0 , k_B is the Boltzmann constant, and T is the temperature. Using the intrinsic band gap of $E_{\text{gap}} = 3.437$ eV at 1.6 K,¹² the acceptor binding energy of E_A can then be calculated to be about 121 meV, which agrees well with the reported value in P-doped p -ZnO films.¹³

To study the electrical properties of the single ZnO rod homojunction, we employed Zyvyx KZ100 Nanoprobe and Nanomanipulating system attached to a LEO 1550 SEM for current-voltage (I - V) measurement. Figure 3 shows the typical I - V characteristics of different regions in a single vertically aligned p -ZnO:P/ n -ZnO rod where the implantation is performed by 50 keV P⁺ ions with a dosage of 10^{14} cm⁻². The schematic diagram and the SEM image of the probing measurement are shown in the insets at top left and bottom right, respectively. Curves p - p , p - n , n - n , and n -FTO (tested between a-b, a-c, c-d, and d-e, respectively) represent I - V characteristics of p -ZnO:P, p -ZnO:P/ n -ZnO, n -ZnO, and

FIG. 3. (Color online) I - V characteristics of p - p , p - n , n - n , and n -FTO regions in a single ZnO rod. The upper left and lower right insets show the schematic diagram and a SEM image of probing by Zyvyx nanomanipulator, respectively.

FIG. 4. (Color online) EL spectra of (a) device I and (b) device II under various injection currents, respectively. The insets show the UV light output intensities as a function of forward injection current. The photographs of corresponding light emissions collected from both [(c) and (e)] front side (Au anode) and [(d) and (f)] back side (single-sided polished sapphire substrate) in these two devices under the same bias voltage of 25 V.

n-ZnO/FTO, respectively. Rectifying behavior can be clearly seen from the *p*-*n* junction while the near-linear relationship of *I*-*V* from *p*-*p*, *n*-*n*, and *n*-FTO curves indicates an Ohmic behavior. The low turn-on voltage of ~ 0.8 V is in good agreement with our previous study on *p*-ZnO:As/*n*-ZnO rod homojunction (Ref. 6) and other previous reports on *p*-ZnO:P/*n*-ZnO film homojunction diode, in which the turn-on voltage was about 1 V.^{14,15} The diode ideality factor *n* of our devices is 3.8–17.5, which is higher compared to that of the ideal *p*-*n* junctions (*n*=1), but similar to other ZnO:P thin-film homojunctions.¹⁴

The electroluminescence (EL) spectra of devices I and II were measured at various injection currents. Strong UV emission was observed from both devices under forward bias [Figs. 4(a) and 4(b)], which corresponds to near band edge emission of ZnO. Besides the UV emission, device I shows a relatively weak and broad emission band in the visible range, indicating a low density of deep-level defects. However, the defect-related emission becomes stronger in device II, which consists of one green emission at ~ 510 nm and one near-infrared peak at ~ 800 nm. These results are consistent with LTPL studies. The insets in Figs. 4(a) and 4(b) show the UV peak intensities as a function of forward injection current of devices I and II, respectively. The UV light output intensities increase linearly with injection current above a threshold current (*I*, *I*=18.6, and 23.5 mA for devices I and II, respectively). The photographs of the emitting devices I and II under the same forward bias of 25 V are shown in Figs. 4(c)–4(f), where Figs. 4(c) and 4(e) are taken from the front

side (Au pad) of the devices while Figs. 4(d) and 4(f) are from the back side (single-sided polished sapphire substrate). For both devices, the light emission observed from the back side is much brighter than that from the front side.

It is worth mentioning that the VPT grown ZnO rods using pure Zn and O₂ are defect-free inside (i.e., very few defects inside and the defects are primarily located at the surface). By P ion implantation and annealing, we can convert the top parts of these rods to *p*-type. From the HRTEM images, the lattice constant in the *p*-type region is significantly different from that in the intrinsic region, which indicates that it is difficult to grow *p*-type epilayers even on a ZnO substrate. There will be a lot of dislocations/defects formed in the *p*-type region with such a lattice mismatch ($\sim 2\%$). These defects contribute to *n*-type conductivity of ZnO, hence *p*-type can hardly be obtained. However, in the case of a rod, less dislocations/defects could be formed due to the limited dimension of the rods. Thus we expected that it is easier to realize *p*-type doping in ZnO (nano)rods.

In conclusion, we have achieved *p*-type doping in ZnO rods via P⁺ implantation, and further demonstrated ZnO rod *p*-*n* homojunction LEDs with UV light emission at RT. Our approach may provide a relatively simple and low-cost process of UV LEDs with some commercial implications.

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