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Plasma treatment of *p*-GaN/*n*-ZnO light-emitting diodes

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ABSTRACT

Zinc oxide (ZnO) is a material of great interest for short-wavelength optoelectronic applications due to its wide band gap (3.37 eV) and high exciton binding energy (60 meV). Due to the difficulty in stable *p*-type doping of ZnO, other *p*-type materials such as gallium nitride (GaN) have been used to form heterojunctions with ZnO. *p*-GaN/*n*-ZnO heterojunction devices, in particular light-emitting diodes (LED) have been extensively studied. There was a huge variety of electronic properties and emission colors on the reported devices. It is due to the different energy alignment at the interface caused by different properties of the GaN layer and ZnO counterpart in the junction. Attempts have been made on modifying the heterojunction by various methods, such as introducing a dielectric interlayer and post-growth surface treatment, and changing the growth methods of ZnO. In this study, heterojunction LED devices with *p*-GaN and ZnO nanorods array are demonstrated. The ZnO nanorods were grown by a solution method. The ZnO nanorods were exposed to different kinds of plasma treatments (such as nitrogen and oxygen) after the growth. It was found that the treatment could cause significant change on the optical properties of the ZnO nanorods, as well as the electronic properties and light emissions of the resultant LED devices.

Keywords: ZnO, nanorods, plasma treatment, light-emitting diodes

1. INTRODUCTION

Zinc oxide (ZnO) has been recognized as a promising candidate for short-wavelength photonic and optoelectronic devices due to its large band gap (3.37 eV) and high exciton binding energy (60 meV). ZnO-based optoelectronic devices such as light-emitting diodes (LED), photodetectors, etc. have been extensively investigated.[1-16] There are a few reports on devices based on ZnO homojunctions[1-5] due to the fact that *p*-type doping has been a major challenge. Other *p*-type materials such as gallium nitride (GaN),[6-14] silicon (Si),[15-16] or organic materials[17] have been utilized to form heterojunctions with ZnO. Among them, GaN is one of the most popular candidates. Like ZnO, GaN has wurtzite crystal structure and a band gap of ~3.4 eV. The similarity in crystal structures and the lattice spacing of GaN and ZnO (lattice mismatch ~2%) allows high quality and effective junctions to be made. Park and Yi demonstrated LED devices made with *p*-type GaN and ZnO nanowires array grown by metal organic vapor phase epitaxy (MOVPE).[6] Ng *et al.* also reported electroluminescence (EL) on heterojunctions of *p*-type GaN and ZnO nanorods array prepared by low-cost solution-based methods.[7] It was suggested that the emission color could be varied with different ZnO growth seed layers and nanorod growth method due to different interfacial states and energy band alignment across the junction.[7]

The energy band alignment can also be modified by the addition of an interlayer between the *p*-GaN and ZnO layers.[9-14] Li *et al.* suggested that the UV electroluminescence intensity and output power of a GaN/ZnO heterojunction could be enhanced by inserting an intrinsic magnesium oxide (*i*-MgO) layer at the junction interface.[10] Chen *et al.* also reported that the *p*-GaN/*n*-ZnO heterojunction lighted up under forward bias with the MgO interlayer, but exhibited no emission without the interlayer.[12] It was suggested that the MgO layer could block the electrons from the ZnO layer and

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change the electron-hole recombination position across the heterojunction.[12] Other than MgO, materials with large band gap such as gallium oxide (Ga_2O_3)[13] or polymer film[14] have also been employed. Recently, we have found that plasma treatment can significantly change the optical properties of ZnO.[18] The defect emission of ZnO nanomaterials was almost completely quenched by exposing to hydrogen plasma. It was suggested that hydrogen plasma could passivate the defects either on the surface or in the bulk.[18]

In this study, we demonstrate heterojunctions made with *p*-type Mg-doped GaN layer and *n*-type ZnO nanorods array grown by a facile solution method. The as-fabricated devices were subjected to different kinds of plasma (nitrogen and oxygen). The effects of the plasma treatment to the properties and performance of the resultant devices was studied.

2. EXPERIMENTAL

2.1 Device fabrication

The heterojunction was fabricated by growing ZnO nanorods on top of an Mg-doped GaN layer with MgO interlayer. The device structure is shown on Figure 1. The Mg:GaN layer was prepared by metal-organic chemical vapor deposition (MOCVD) as described elsewhere.[7,8,12] In short, a p-type Mg:GaN layer (550 nm) was deposited on a layered structure of highly resistive Mg:GaN (550 nm)/Undoped GaN (2.2 μm)/GaN nucleation layer (30 nm)/sapphire. The layer was thermally activated by annealing in N_2 atmosphere at 825 ºC. The resultant film has hole concentration of $\sim 5\times10^7$ cm^{-3} measured by Hall measurement. MgO interlayer was deposited on the Mg:GaN layer with electron-beam deposition.

ZnO nanorods array was grown by a hydrothermal method commonly reported.[5,7,19] A ZnO seed layer was firstly deposited by oxidation of zinc acetate ($Zn(CH_3COO)_2$) precursor. The substrate surface was wet with 5 mM solution of zinc acetate (99.99% purity, Sigma Aldrich) in ethanol, rinsed thoroughly with pure ethanol, and then blown dry with an Ar stream, followed by annealing at 350 ºC for 25 minutes. The samples were then put into an equimolar aqueous solution of 25 mM zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99.999% purity, Sigma Aldrich) and hexamethylenetetramine (99+% purity, Sigma Aldrich) and heated up to ~90 ºC for 3 hours.

Ni/Au electrode (55 nm Ni/40 nm Au, deposited by e-beam deposition and thermally activated at 600 ºC) was used as the contact for the *p*-type Mg:GaN layer. Ag electrode (200 nm, deposited by thermal evaporation) was used as the top contact for the *n*-type ZnO nanorods array. In order to insulate the top contact from the GaN layer, poly(methyl methacrylate) (PMMA, molecular weight: 950,000, MicroChem) was used to fill the gap among the ZnO nanorods. The tips of the nanorods were exposed by oxygen plasma before the deposition of the top contact.

Plasma treatment on the fabricated devices were performed with Oxford Plasmalab 80 Plus Reactive Ion Etcher. The gas flow rate (N_2 and O_2) and system pressure were 100 sccm and 700 mTorr respectively. The RF power was 150 W and the exposure time was 5 minutes.

2.2 Device characterization

The morphologies of the ZnO nanorods were examined with scanning electron microscope (SEM, JEOL-JSM 7001F). The photoluminescence (PL) and electroluminescence (EL) of the devices were measured with a fiber-optic spectrometer (PDA-512, Control Development Inc.). A He-Cd laser (325 nm) was used as the PL excitation source. A source meter (Keithley 2400 Sourcemeter) was used as the device power source for EL measurements.

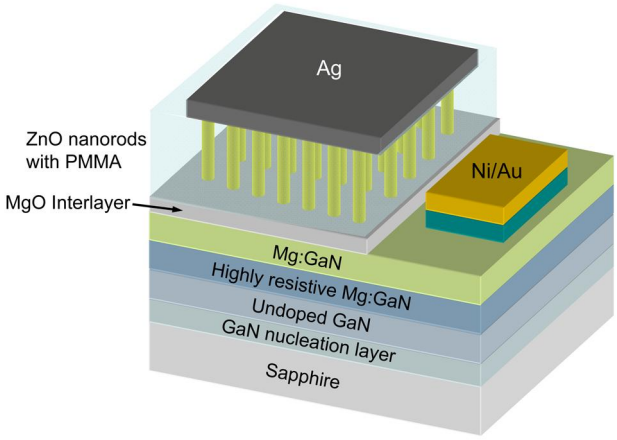

Figure 1. Schematic diagram of the *p*-GaN/*n*-ZnO nanorods array heterojunction device.

3. RESULTS AND DISCUSSION

Figure 2 shows the representative SEM image of the ZnO nanorods grown on the *p*-GaN substrate with MgO interlayer. The resultant nanorods are not well aligned perpendicularly to the surface similar to a previous report.[12] It is likely due to the lattice mismatch at the interface. No significant effects on the morphology of the nanorods (not shown here) was found for both nitrogen and oxygen plasma treatments. It was reported previously that hydrogen plasma treatment induced no observable changed on the morphologies of different ZnO nanostructures.[18]

The photoluminescence (PL) spectra of the whole *p*-GaN/ZnO nanorods array heterojunction devices are shown in Figure 3. All of the devices exhibit strong emission peaks at ~380 nm which is associated with the near band-edge emission of ZnO. The emission at ~440 nm is likely originated from the *p*-GaN layer.[7,8,12] Two of the samples also exhibit broad yellow or orange peak centered at around 650 nm which is probably due to the defect emission from ZnO. Several origins have been proposed to be associated to such emission, such as surface adsorbates and the presence of hydroxyl groups.[7,8,12] It can be observed that such yellow emission is significantly suppressed with nitrogen plasma treatment. It has been reported that the green defect emission of ZnO could be largely quenched by hydrogen plasma treatment as hydrogen plasma could passivate the defects either on the surface or in the bulk.[18]

Figure 4 shows the current-voltage (I-V) characteristics of the heterojunction devices with different plasma treatment. The devices without treatment and O plasma treatment exhibited typical diode curves. The contacts of Ni/Au/*p*-GaN and Au/ZnO nanorods were both ohmic in nature, as shown in the inset of Figure 4. It implies that the

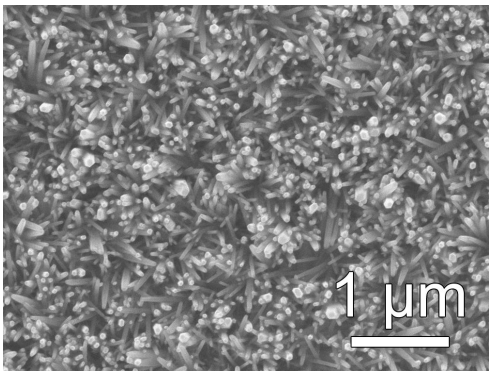

Figure 2. Representative SEM image of the ZnO nanorods array grown on the MgO/*p*-GaN substrate.

rectifying properties of the diodes are likely due to the *p*-*n* heterojunction. On the contrary, the device treated with N plasma exhibited a large leakage current under reverse bias. The electroluminescence (EL) spectra of the heterojunctions are shown in Figure 6. Under forward bias, all of the devices could light up, but with different emission spectrum. The untreated (Figure 6a) and O plasma treated device (Figure 6c) exhibited violet emission centered at ~400 nm, which was commonly observed in *p*-GaN/*n*-ZnO heterojunction devices with MgO interlayer.[9,11,12] The N plasma treated device showed a significantly different EL emission, as shown in Figure 6b. The emission consists of two peaks, one centered at ~400 nm and a shoulder peak at ~550 nm. The yellowish emission was likely attributed to the emission from GaN.[12] Under reverse bias, only the N plasma treated device showed EL emission as shown in Figure 6d. UV emission around 370-380 nm was possibly related to reverse breakdown, while the yellowish peak at ~570 nm was associated to GaN emission.[12] The difference in the behavior for N plasma treated device is not fully clear and requires further study.

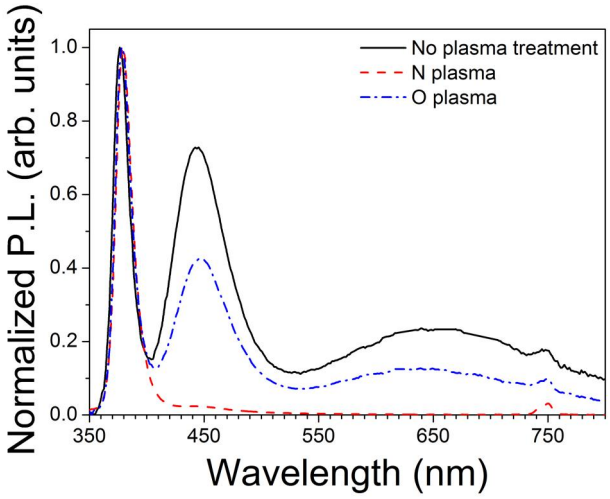

Figure 3. Photoluminescence (PL) spectra of the *p*-GaN/ZnO nanorods array heterojunction devices with different plasma treatments under excitation of 325 nm.

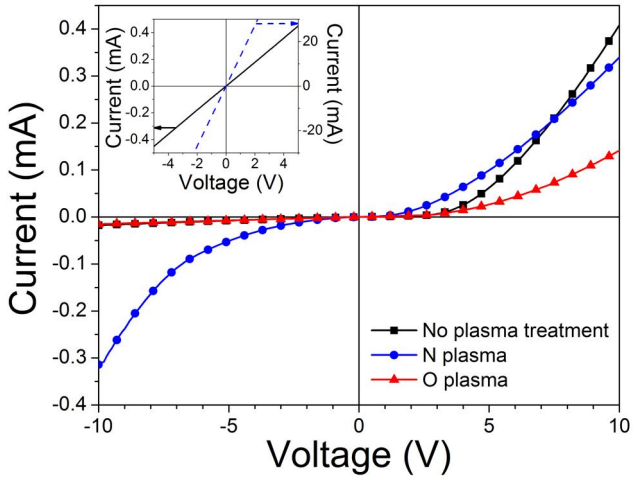

Figure 4. Current-voltage (I-V) characteristics of the *p*-GaN/ZnO nanorods array heterojunction devices with different plasma treatments. Inset shows the I-V characteristics of the Ni/Au to *p*-GaN contact (black line) and the Ag to ZnO nanorods contact (blue dashed line).

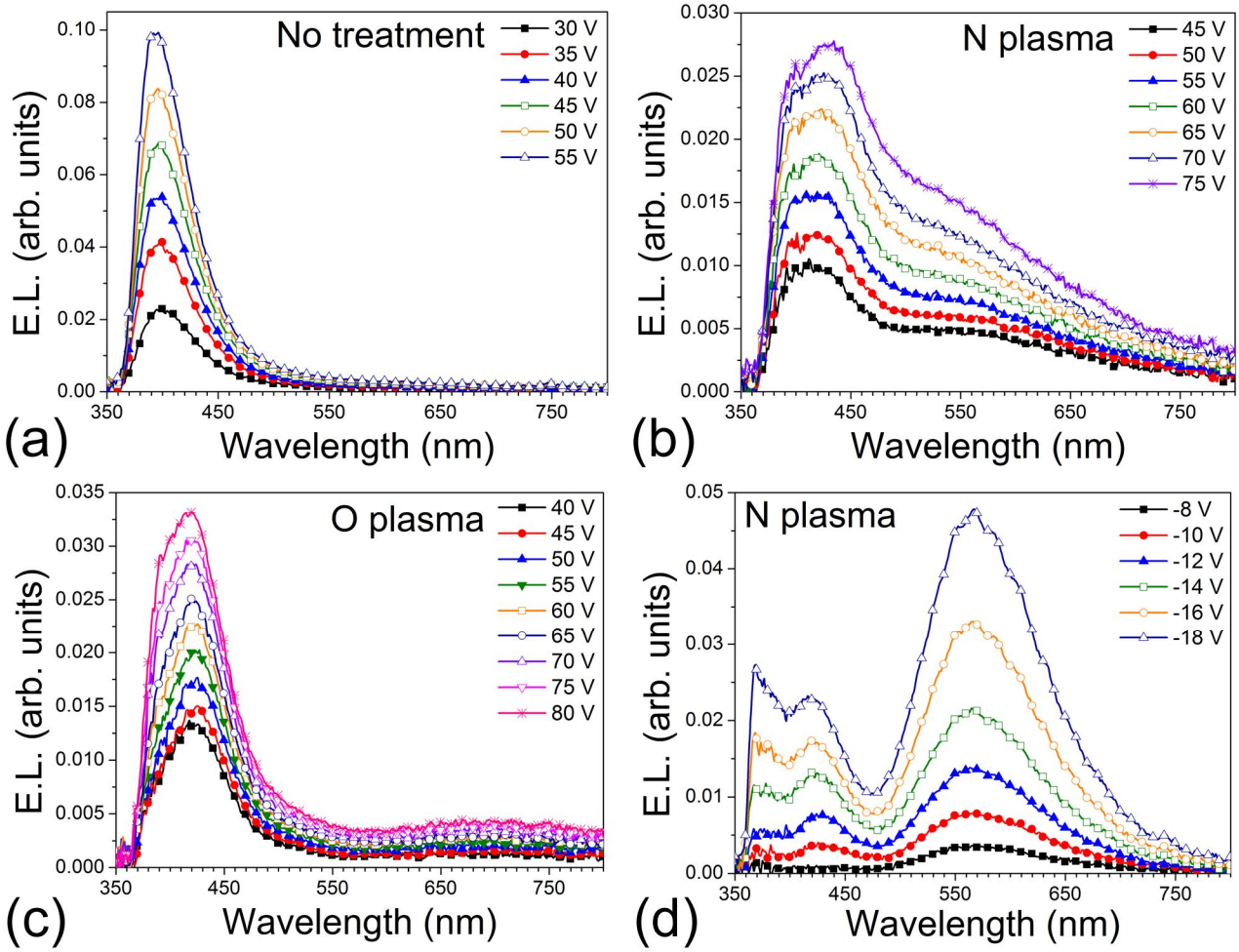

Figure 5. Electroluminescence (EL) spectra of the *p*-GaN/ZnO nanorods array heterojunction devices with a) no plasma treatment, b) N plasma treatment, c) O plasma treatment under forward bias. (d) EL spectra of device with N plasma treatment under reverse bias.

4. CONCLUSION

In summary, we demonstrated light-emitting diodes made with *p*-type Mg-doped GaN layer and *n*-type ZnO nanorods array grown by a solution method. The devices were treated with different plasma treatments and the EL emission was significantly affected. The variation on the EL emission was likely due to the change on the alignment of energy levels in the heterojunction.

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REFERENCES

[1] Guo, X.-L., Choi, J.-H., Tabata, T. and Kawai, T., "Fabrication and Optoelectronic Properties of a Transparent ZnO Homostructural Light-Emitting Diode", Jpn. J. Appl. Phys. 40, L177-L180 (2001).

[2] Tsukazaki, A., Kubota, M., Ohtomo, A., Onuma, T., Ohtani, K., Ohno, H., Chichibu, S. F. and Kawasaki, M., "Blue Light-Emitting Diode Based on ZnO", Jpn. J. Appl. Phys. 44, L643-645 (2005).

[3] Lim, J.-H., Kang, C.-K., Kim, K.-K., Park, I.-K., Hwang, D.-K. and Park, S.-J., "UV Electroluminescence Emission from ZnO Light-Emitting Diodes Grown by High-Temperature Radiofrequency Sputtering", Adv. Mater. 18, 2720-2724 (2006).

[4] Liu, W., Gu, S. L., Ye, J. D., Zhu, S. M., Liu, S. M., Zhou, X., Zhang, R. Shi, Y. and Zheng, Y. D., "Blue-yellow ZnO homostructural light-emitting diode realized by metalorganic chemical vapor deposition technique", Appl. Phys. Lett. 88, 092101 (2006).

[5] Leung, Y. H., He. Z. B., Luo, L. B., Tsang, C. H. A., Wong, N. B., Zhang, W. J. and Lee, S. T., "ZnO nanowires array *p*-*n* homojunction and its application as a visible-blind ultraviolet photodetector", Appl. Phys. Lett. 96, 053102 (2010).

[6] Park, W. I. and Yi, G.-C., "Electroluminescence in n-ZnO Nanorod Arrays Vertically Grown on p-GaN", Adv. Mater. 16, 87-90 (2004).

[7] Ng, A. M. C., Chen, X. Y., Fang, F., Hsu, Y. F., Djurišić A. B., Ling, C. C., Tam, H. L., Cheah, K. W., Fong, P. W. K., Lui, H. F., Surya, C. and Chan, W. K., "Solution-based growth of ZnO nanorods for light-emitting devices: hydrothermal vs. electrodeposition", Appl. Phys. B. 100, 851-858 (2010).

[8] Chen, X. Y., Ng, A. M. C., Fang, F., Djurišić A. B., Chan, W. K., Tam, H. L., Cheah, K. W., Fong, P. W. K., Lui, H. F. and Surya, C., "The Influence of the ZnO Seed Layer on the ZnO Nanorod/GaN LEDs", J. Electrochem. Soc. 157, H308-H311 (2010).

[9] Zhu, H., Shan, C.-X., Yao, B., Li, B.-H., Zhang, J.-Y., Zhang, Z.-Z., Zhao, D.-X., Shen, D.-Z., Fan, X.-W., Lu, Y.-M. and Tang, Z.-K., "Ultralow-Threshold Laser Realized in Zinc Oxide", Adv. Mater. 21, 1613-1617 (2009).

[10] Li, S. Z., Fang, G. J., Long, H., Mo, X. M., Huang, H. H., Dong, B. Z. and Zhao, X. Z., "Enhancement of ultraviolet electroluminescence based on *n*-ZnO/*p*-GaN isotype heterojunction with low threshold voltage", Appl. Phys. Lett. 96, 20111 (2010).

[11] Zhu, G. Y., Li, J. T., Shi, Z. L., Lin, Y., Chen, G. F., Ding, T., Tian, Z. S. and Xu, C. X., "Ultraviolet electroluminescence from *n*-ZnO/*i*-MgO/p^+-GaN heterojunction light-emitting diodes fabricated by RF-magnetron sputtering", Appl. Phys. B. 109, 195-199 (2012).

[12] Chen, X. Y., Ng, A. M. C., Djurišić A. B., Chan, W. K., Fong, P. W. K., Lui, H. F., Surya, C., Cheng, C. C. W. and Kwok, W. M., "GaN/MgO/ZnO heterojunction light-emitting diodes", Thin Solid Film 527, 303-307 (2013).

[13] Liu, Y., Liang, H., Xia, X., Shen, R., Liu, Y., Bian, J. and Du G., "Introducing Ga_2O_3 thin films as novel electron blocking layer to ZnO/*p*-GaN heterojunction LED", Appl. Phys. B 109, 605-609 (2012).

[14] Guo, Z., Zhang, H., Zhao, D. X., Liu, Y. C., Yao, B., Li, B. H., Zhang, Z. Z. and Shen, D. Z., "The ultralow driven current ultraviolet-blue light-emitting diode based on *n*-ZnO nanowires/*i*-polymer/*p*-GaN heterojunction", Appl. Phys. Lett. 97, 173508 (2010).

[15] Jeong, I.-S., Kim, J. H. and Im, S., "Ultraviolet-enhanced photodiode employing *n*-ZnO/*p*-Si structure", Appl. Phys. Lett. 83, 2946-2948 (2003).

[16] Choi, M. K., Han, W. S., Kim, Y. Y., Kong, B. H., Cho, H. K., Kim, J. H., Seo, H.-S., Kim, K.-P. and Lee, J.-H., "*n*-ZnO:Ga/*i*-ZnO/*p*-Si heterojunction light emitting diodes fabricated on patterned Si substrates", J. Mater. Sci.: Mater. Electron. 20, 1214-1218 (2009).

[17] Sun, X. W., Huang, J. Z., Wang, J. X. and Xu, Z., "A ZnO nanorod Inorganic/Organic Heterostructure Light-Emitting Diode Emitting at 342 nm", Nano Lett. 8, 1219-1223 (2008).

[18] Leung, Y. H., Chen, X. Y., Ng, A. M. C., Guo, M. Y., Liu, F. Z., Djurišić A. B., Chan, W. K., Shi, X. Q. and Van Hove, M. A., "Green emission in ZnO nanostructures-Examination of the roles of oxygen and zinc vacancies", Appl. Surf. Sci. 271, 202-209 (2013).

[19] Greene, L. E., Law, M., Tan, D. H., Montano, M., Goldberger, J., Somorjai, G. and Yang, P. D., "General Route to Vertical ZnO Nanowire Arrays Using Textured ZnO Seeds", Nano Lett. 5, 1231-1236 (2005).