Electroluminescence Properties of a Zinc Oxide Nanorod Array Heterojunction Light-Emitting Diode

HUA JIANG,¹ YOUMING LU,^{1,2} XIMING RONG^{1,3} , SHUN HAN,¹
PEIJIANG CAO,¹ YUXIANG ZENG,¹ WANGYING XU,¹ MING FANG,¹
WENJUN LIU,¹ and DELIANG ZHU¹

1.—College of Materials Science and Engineering, Shenzhen Key Laboratory of Special Functional Materials, Shenzhen Engineering Laboratory for Advanced Technology of Ceramics, Guangdong Research Center for Interfacial Engineering of Functional Materials, Shenzhen University, Shenzhen 518060, China. 2.—e-mail: ymlu@szu.edu.cn. 3.—e-mail: xmrong@szu.edu.cn

A *p*-GaN/*i*-MgO/*n*-ZnO nanorod array (NRA) heterojunction light-emitting diode has been fabricated. Its room-temperature electroluminescence spectra under different forward biases revealed a strong emission band across the whole visible region, which was blue-shifted when increasing the forward bias. The origin of this visible emission is considered to be related to oxygen vacancy (V_O) defects in different valence states, where the blue emission (~ 460 nm) comes from neutral oxygen vacancy (V_O^X) defects and the green emission (~ 520 nm) from singly charged oxygen vacancy (V_O^+) defects, while the yellow (~ 580 nm) and red emission (~ 670 nm) are attributed to doubly charge oxygen vacancy (V_O^{++}) defects. These V_O defects in different states can convert into one another under different excitation conditions, resulting in the blue-shift of the emission peak as the forward voltage is increased.

Key words: ZnO nanorod array, heterojunction, electroluminescence, oxygen vacancy defect, pulsed laser deposition

INTRODUCTION

As an important group II–VI compound, zinc oxide (ZnO) has been widely explored for its potential use in solid-state light sources due to its wide bandgap (3.37 eV) and exciton binding energy (60 meV) above room temperature.^{1–3} The ability to grow ZnO with preferred orientation is another unique advantage, and ZnO nanorod array (NRA) structures can even be obtained easily using the solution method.^{4,5} Such one-dimensional waveguide-type rod-shaped ZnO exhibits excellent photoconductivity, and ZnO-based light-emitting diodes (LEDs) based on such structures have been studied extensively in recent years.^{6–13} Although the luminescent properties of ZnO-based LED devices with

different structures are not the same due to differences in their structure and fabrication processes, they can be roughly classified into those exhibiting ultraviolet emission originating from excitons¹² and those showing visible luminescence associated with impurities or defects.¹⁴

For luminescence caused by defects, the greatest controversy regards the origin of the luminescence in the visible region. Due to the rich intrinsic defects in ZnO materials, luminescence related to various types of defect has been reported, including oxygen vacancies (V_O), interstitial oxygen (O_i), zinc vacancies (V_{Zn}), interstitial zinc (Zn_i), etc.^{15–24} As early as 1996, Vanheusde et al. demonstrated that the green (~ 510 nm) emission from ZnO is caused by singly charged oxygen vacancies (V_O^+), and they found that free-carrier depletion can strongly influence its emission intensity, particularly for small particles¹⁵; Panigrahy et al. established a direct link between the magnetization and the relative occupancy of V_O^+ defects present on the surface of ZnO

(Received November 13, 2019; accepted January 9, 2020;
published online January 23, 2020)

NRs,¹⁶ and also confirmed the attribution of the yellow light (~ 580 nm) emission to the combination between doubly charge oxygen vacancies (V_O^{++}) for the deep acceptor level and conduction-band electrons, while the blue (~ 450 nm) emission may be related to neutral oxygen vacancies ($V_O^\times$). The origin of the red light emission is controversial, but it is generally considered to be related to interstitial zinc (Zn_i).^{6,7,17,19} Nanostructured ZnO materials, apart from a large number of intrinsic defects, also exhibit strong adsorption on their highly active surface, which complicates the visible luminescence.^{21,25,26} In addition, Zhu et al. synthesized ZnO nanoparticles (NPs) and NRA film by the sol-gel method, confirming that the ZnO NRA film contained more V_O defects and chemisorbed oxygen, which led to a special charge storage property.²⁶ Similarly, V_O defects and chemisorbed oxygen also play an important role in the work described herein.

In this study, a highly vertically oriented one-dimensional NRA was prepared on a *p*-type gallium nitride (*p*-GaN) substrate by a solution method, and a strong electroluminescence (EL) spectra was observed in the prepared ZnO NRA heterojunction at room temperature. The resulting band was in the visible region, and as the forward bias was increased, a significant blue-shift was observed in its peak position. By analyzing the correspondence between the different visible light emission bands and V_O defects, the visible light emission band can be attributed to V_O defects, and its shift to different states of V_O .

EXPERIMENTAL PROCEDURES

An insulating magnesium oxide (i-MgO) layer (temperature 600°C, oxygen pressure 2 Pa, laser frequency 5 Θ z) and ZnO seed layer (temperature 600°C, oxygen pressure 3 Pa, laser frequency 3 Θ z) were fabricated on a *p*-GaN substrate by the pulsed laser deposition (PLD) method. The *p*-GaN doped with magnesium was synthesized by metalorganic chemical vapor deposition (MOCVD), having carrier concentration and mobility of $3.14 \times 10^{17} \text{ cm}^{-3}$ and $7.96 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The vacuum deposition system was a PLD-450 device (SKY Technology Development Company), and the laser was a COMPEXPro205 samarium fluoride (KrF) laser (248 nm) (Lambda Physics Company). The ZnO NRA was prepared by a solution method. Zinc acetate dehydrate (0.01 mol L^{-1}) and hexamethyleneimine (HMT, 0.01 mol L^{-1}) were dissolved in 40 ml deionized water, being left for 24 h after stirring for 2 h, then the solution was heated to 95°C. Finally, the substrate with the insulating and seed layers was immersed in the growth solution at a tilt angle of 90° and grown for 2 h. A gold (Au)/nickel (Ni) electrode with thickness of 5 nm/5 nm was prepared by vacuum thermal evaporation then annealed at 500°C for 5 min in oxygen atmosphere. The indium (In) electrode was prepared by vacuum

sintering. The morphology of the ZnO NRs was studied by thermal field-emission scanning electron microscopy (SEM, SU-70). The *I*-*V* curve of the device and electrode were measured using a UV-2450 power supply equipment. EL measurements were carried out using a Zolix ultraviolet-visible (UV-Vis) spectrometer (ZLX-FS Omni λ -3005), photoluminescence (PL) measuring using a 30-mW helium (He)-cadmium (Cd) laser (325 nm), and confocal Raman spectrometry (Renishaw inVia model) by placing the samples in a closed-loop liquid-helium refrigerator for temperature-dependent measurements.

RESULTS AND DISCUSSION

Figure 1a shows a top-view SEM image of the ZnO NRA, while the inset displays an enlarged image from the same perspective. Figure 1b shows a SEM image of the ZnO NRA tilted at a viewing angle of 25°, while the inset shows its cross section, revealing a typical ZnO NR with hexagonal structure with length of about 500 nm and diameter of 50 nm to 100 nm. Meanwhile, note that, due to the small distance between the ZnO NRs, some of them joined into larger-diameter NRs and even irregularly shaped columns. Figure 1c shows the a schematic of the structure of the ZnO NRA heterojunction LED, where the thickness of the MgO is about 15 nm, its main function being to inhibit electron transfer to the *p*-GaN side to achieve more efficient composite emission from the ZnO side; The thickness of the seed layer (ZnO) was about 85 nm, mainly being used to improve the growth perpendicularity of the ZnO NRA. Figure 1d shows the *I*-*V* curve of the LED device. At reserve bias of 15 V, the current was approximately 2 mA, while under forward bias of 15 V, it exceeded 4 mA. These results show that the device exhibited significant rectification characteristics. The inset shows the *I*-*V* curve of the Au/Ni electrode, confirming a good ohmic contact.

The room-temperature EL spectra of the prepared *p*-GaN/i-MgO/*n*-ZnO NRA heterojunction LED are shown in Fig. 2g, revealing mainly a wide band in the visible region. As the forward bias was increased, the intensity of the band increased and the peak position gradually shifted to shorter wavelength. When the applied bias voltage was 15 V, the center wavelength of the luminescence peak was about 620 nm, but when the bias voltage was increased to 35 V, the center wavelength moved to 525 nm. Figure 2a-f shows photographs of the luminescent device at different bias voltages (in a dark environment), where the camera was fixed at (12 cm, 20 cm, 15 cm) away from the sample in three-dimensional space (~ 28 cm, see inset of Fig. 2a for coordinates). The photographs in Fig. 2a-f display weak red light at bias of 10 V and yellow emission at bias of 20 V, while the device begins to emit bright white light at bias of 30 V.

Fig. 1. (a) SEM image of ZnO NRA (inset displays enlarged image from same perspective). (b) SEM image of ZnO NRA tilted at viewing angle of 25° (inset shows cross section of NRA). (c) Schematic of structure of *p*-GaN/*i*-MgO/*n*-ZnO heterojunction LED device. (d) *I*-*V* curve of device under different bias voltages (inset confirms good ohmic contact between Au/Ni and *p*-GaN).

To study the causes of the blue-shift of the EL spectrum of the device, we performed temperature-dependent PL spectroscopy on the prepared ZnO NRA. Firstly, the PL spectrum of the GaN substrate measured at 298 K is shown in Fig. 3a, revealing an emission band that originates from the doped Mg acceptor energy level at 440 nm in *p*-GaN. Comparing the PL spectra of the sample in Fig. 3a, there is only one very broad visible emission band with a central wavelength of 500 nm to 600 nm. It can be seen that the PL luminescence curve is completely different from that of *p*-GaN, indicating that the luminescence originates from the ZnO NRA. The PL luminescence intensity decreased and the peak position changed with increasing temperature. The corresponding peak positions at 298 K and 773 K were ~ 574 nm and ~ 544 nm, respectively. Figure 3b displays the PL spectra under nitrogen-cooled condition, while the inset shows the trend of the peak position as a function of temperature, revealing a delayed blue-shift from 78 K to 773 K. At a certain temperature between 423 K and 523 K, the peak position changed from ~ 571 nm to ~ 546 nm; we call this the transition temperature for the large change of peak position. In general, Fig. 3a and b demonstrates that the PL spectra presented a ~ 30 -nm blue-shift of the peak position overall, of which ~ 25 nm occurred at the transition temperature. To clarify why the temperature-

dependent PL spectra exhibited such a blue-shift, multipeak fitting was applied. Figure 3c shows the Gaussian fitting results for the PL spectra at 298 K, 523 K, 623 K, and 773 K, yielding four visible light emission bands, viz. P1 (blue light ~ 452 nm), P2 (green light ~ 525 nm), P3 (yellow ~ 590 nm), and P4 (red light ~ 685 nm). Comparison of these four visible light emission bands reveals that P2 and P3 were strong, and the relative intensity of P2 increased with temperature, while gradually P3 decreased. P1 and P4 were weak, with an increasing trend of the relative intensity of P1 but no obvious change in P4.

Generally, the visible luminescence of ZnO is attributed to defect-related recombination, while ZnO NRs grown by the solution method are considered to exhibit a large number of donor-like V_O effects.^{13,17,27} Figure 4 shows the energy level distribution of the ZnO NRs according to the fitting results shown in Fig. 3c. In these ZnO NRs, the energy levels of V_O^X and V_O^+ are 2.74 eV and 2.36 eV higher than the valence-band maximum, respectively, while those of Zn_i and V_O^{++} are 0.29 eV and 2.36 eV lower than the conduction-band minimum. These results are consistent with previous reports.^{21,26}

The highly active surface of ZnO NRs can easily adsorb O₂ molecules, which capture electrons from V_O , resulting in V_O^+ , V_O^+ , and V_O^X in different charge

Fig. 2. Photographs of device under forward bias of (a) 10 V, (b) 15 V, (c) 20 V, (d) 25 V, (e) 30 V, and (f) 35 V. (g) EL spectra of the device under forward bias of 15 V, 20 V, 25 V, 30 V, and 35 v.

states, as shown in Fig. 5. Under certain external conditions, V_O also exhibits a certain transformation relationship between its different states.^{4,16,21,26} V_O^+ can be converted into V_O^{++} by capturing a hole, or into V_O^X by capturing an electron. Under strong irradiation, V_O^{++} can also be converted into V_O^+ .¹⁵ Figure 6 shows the V_O distribution of the ZnO NRs from the surface to bulk. Closer to the surface, the electrons of V_O are trapped more easily by adsorbed O_2 , resulting in a lower electron concentration near the surface, which

forms a surface depletion region of a certain thickness.^{21,26} The thickness of this depletion layer can change the distribution of V_O in different states. Also, its thickness can be calculated as

$$W = \left(\frac{2\epsilon_{ZnO} V_{bi}}{e N_D} \right)^{1/2} \quad (1)$$

where ϵ_{ZnO} is the static dielectric constant of ZnO, V_{bi} is the boundary electric potential, e is the electron charge, and N_D represents the charge density of the depletion layer.¹⁵ This formula reveals that the boundary electric potential and the carrier concentration directly affect the thickness of the depletion layer. At room temperature, surface adsorption will increase the boundary electric potential of the ZnO NRs, while the photogenerated carrier concentration is lower, so the thickness of the depletion layer of the ZnO NRs is larger, and the V_O defects are dominated by V_O^{++} , resulting in strong P3 emission. As the temperature increases, the carrier concentration rises rapidly since the intrinsic excitation of ZnO increases, which narrows the depletion layer.^{15,21,26} Then, the V_O^{++} decrease while the V_O^+ increase, and the P2 emission gradually increases, eventually exceeding P3 at 773 K. Limited by the thermal resistance of the device, we were unable to measure PL spectra at higher temperatures, and no further enhancement of the P1 emission band could be observed.

For comparison with the PL spectra, the Gaussian fitting of the EL spectra is presented in Fig. 7: the E3 (yellow, ~ 580 nm) and E4 (red, ~ 670 nm) emission bands appeared at 15 V; the E2 (green, ~ 520 nm) emission band appeared at 25 V; the E2 emission band gradually increased with increasing voltage, exceeding E3 at 35 V; eventually, at bias voltage to 90 V, a strong E1 (blue, ~ 462 nm) emission band resulted. Similar to the PL mechanism, in the EL measurements, when the bias voltage was small, the injected carrier concentration was low and the depletion layer of the ZnO NRs was wide or it was even completely depleted.²⁶ In this condition, the V_O defects are mainly in the V_O^{++} state, and the whole device emits yellow light (~ 580 nm) visible to the naked eye; as the bias voltage is increased, the injected carrier concentration gradually increases and the depletion layer shrinks. So the V_O^{++} decrease, the V_O^+ increase, and the green emission (~ 580 nm) band appears, so the device emits bright white light; when the bias voltage is larger, the depletion layer is further narrowed, and due to the higher concentration of injected carriers, the V_O^+ capture electrons and transform into V_O^X . A blue emission (~ 450 nm) band appears, resulting in brighter white light. Comparing the EL and PL spectra reveals four emission bands (blue, green, yellow, and red) whose variation can be attributed to V_O , which is greatly influenced by the variation of the carrier concentration.^{15,26} Compared with the EL spectra, the emission bands in the PL spectra

Fig. 3. (a) Temperature-dependent PL spectra of ZnO NRA and room-temperature PL spectra of *p*-GaN. (b) PL spectra under liquid-nitrogen conditions (inset shows temperature-dependent peak position of PL spectra; dark area indicates the ~ 25 -nm blue-shift of the peak position). (c) Gaussian fitting results for PL spectra at different temperatures (Color figure online).

Fig. 4. Schematic energy band diagram of ZnO NRs.

exhibit some peak shift due to the different form of electronic transport. it is interesting to note that both P4 and E4 exhibit a red-shift of 0.4 eV, further indicating that the source of the red light is the transitional complex between Zn_i and V_o^{++} (Fig. 4). As shown by the temperature-dependent PL (Fig. 3a and b) and bias-dependent EL (Fig. 2g) spectra, both the temperature and bias effect can lead to a blue-shift in the luminescence spectra, and temperature could indeed make a certain contribution to the EL peak shift. However, note that the peak showed a relatively small blue-shift (~ 30 nm) from ~ 574 nm to ~ 544 nm in the temperature-

Fig. 5. Absorption model for ZnO NRA.

dependent PL measurements from 273 K to 773 K, while the room-temperature EL spectra exhibited a blue-shift of almost ~ 100 nm from ~ 620 nm to 520 nm at relatively low bias from 0 V to 35 V. This phenomenon indicates that the change in temperature is rather small to yield a blue-shift of more than 30 nm when the bias is less than 35 V. It can therefore be concluded that the bias effect rather than the temperature effect dominates the light emission in the EL.

Fig. 6. V_O defect distribution and transformation model of ZnO NRs.

Fig. 7. Gaussian fitting results of EL spectra under forward bias of 15 V, 20 V, 25 V, 30 V, 35 V, and 90 V.

CONCLUSIONS

A p -Ga N /i-MgO/ n -ZnO heterojunction LED device was fabricated. The test results showed that it emitted high-brightness white light. The device was analyzed by four-peak fitting of the EL spectra under different forward bias voltages and high-temperature PL spectra. The location of the blue, green, yellow, and red luminescence emission bands in the schematic energy band diagram and a mechanism for the blue-shift in the luminescence spectra are proposed. The results of this study suggest a feasible approach for defect research in one-dimensional ZnO NRs and provide a method for the preparation of white-light devices with adjustable chromaticity.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51872187, 60976036, 21805194, 61704111, and 11774241), National Key Research and Development Program of China (Grant No. 2017YFB0400304), Natural Science Foundation of Guangdong Province (Grant Nos. 2016A030313060 and 2017A030310524), Fundamental Research Project of Shenzhen (Grant Nos. JCYJ20180305124701756, JCYJ20180305071822 48925, and JCYJ20180508163404043), and Science and Technology Foundation of Shenzhen (JCY J2016-2019).

CONFLICT OF INTEREST

The authors declare no competing interests.

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