

Facile fabrication of nano-scale ZnO p-n junction and its blue electroluminescence

XUELI DU^{a,b*}, YUE SUN^a, QIAN WANG^a, NAN MA^a, ZHIHAO YUAN^{a,c}

^a*School of Materials Science & Engineering, Tianjin University of Technology, Tianjin 300384, China*

^b*Tianjin Key Lab for Photoelectric Materials & Devices, Tianjin 300384, China*

^c*Key Laboratory of Display Materials & Photoelectric Devices (Tianjin University of Technology), Ministry of Education, Tianjin 300384, China*

The arrayed ZnO p-n nano-junctions were fabricated with n-type ZnO nano-granular film (with the particle size about 30 nm) and p-type ZnO nano-rods (with the diameter around 100 nm) through a simple chemical synthesis method without special devices and complex doping processing. I-V curve of the p-n nano-junction shows an obvious rectifying behavior with a threshold voltage of about 3.0 V, which presents typical electrical property of a diode. Electroluminescence shows deep-level related blue band (456nm) emission at room temperature.

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1. Introduction

Because of significant advantages such as wide band gap, high saturated electron velocity and high critical electric field, the semiconductors, such as silicon carbide (SiC), gallium nitride (GaN) and zinc oxide (ZnO), are considered to be excellent candidates for electronic devices in high power, high frequency, high temperature and anti-radiation applications. For these applications, GaN has been developed to industrial uses, such as high emission intensity light-emitting diodes (LEDs) and blue laser. However, the high cost and complex process of fabrication constrain the extensive application for GaN [1, 2].

ZnO has attracted considerable interest for its direct wide band gap (3.37 eV) and regarded as one of the most promising candidates for the next generation of optoelectronic applications such as short-wavelength LEDs, laser devices (LDs) and ultraviolet (UV) photodiodes. It has advantages relative to GaN because of its availability in bulk, single-crystal form and its larger exciton binding energy (~60 meV, cf. ~25 meV for GaN), which makes the stimulated emission possible under room temperature [3-6]. In addition, the advantages of abundance in nature, easy preparation and ultraviolet (UV) emission make ZnO more competitive than the current GaN-based light emitting device. However, realization of stable and reproducible p-type ZnO has long been the bottleneck of ZnO optoelectronic devices. Researchers have managed to dope p-type ZnO with group-V elements through various growth methods, such as molecular beam

epitaxy (MBE), pulse laser deposition (PLD), magnetron sputtering and metal organic chemical vapour deposition (MOCVD). Though certain progress has been made in p-type ZnO and even ZnO-based homojunction light emitting devices, how to prepare p-type ZnO with a simple and low cost method still a remained challenge [7-10].

In recent years, chemical synthesis in solution for preparation of n-type and / or p-type ZnO is receiving attention due to advantages of low temperature, low cost and simple process [11-13]. In this paper, a simple chemical synthesis method was used for preparation of ZnO p-n junction.

2. Experiments

2.1 Fabrication of ZnO nano dot-rod array

0.5 mol / L zinc acetate ($Zn(Ac)_2$) and ethanolamine (C_2H_7NO) were first dissolved in a isopropyl alcohol ($(CH_3)_2CH_2OH$) solution at room temperature. The resultant solution was stirred at 60 °C for 30 min to yield a clear and homogeneous solution, which served as a seed coating solution. Then, a cleaned conductive FTO glass substrate was spin-coated with the solution, and dried in air for 15 min. Finally, the as-coated substrate was heated in an electrical furnace at 350 °C for 30 min and cooled in air, produced the ZnO nano-granular films. The ZnO coated substrates as seeds were suspended in an aqueous solution of 0.025 mol / L zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine ($C_6H_{12}N_4$) and homoepitaxially

grown ZnO nano-rods at 60 °C for 2 h. As a result, the ZnO nano-scale dot-rod array was constructed, as shown in Fig. 1. If the dot and rod are n-type and p-type conductivity, they will construct a perfect ZnO p-n homojunction.

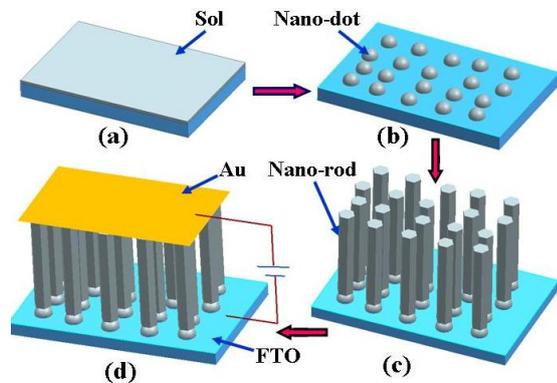


Fig. 1 Schematic illustration for preparing of ZnO nano-scale dot-rod array: (a) sol coated on the substrate; (b) formation of nano-granular films after heating; (c) growth of ZnO nanorods in aqueous; (d) Schematic diagram of the ZnO homojunction for I-V curve and EL measurements

2.2 Samples characterization

X-ray diffraction (XRD, Rigaku, D/max- III 2C, Cu K α , $\lambda=0.15418$ nm, 40 KV, 150 mA) was used to identify the phases of nano-granular films and nano-rods. The microstructures of nano-granular films and nano-rods were observed by field emission scanning electron microscopy (FESEM, JEOL, JSM-6700F). Hall effective displacement transducer (Accent, HL5550PC) was used to detect semiconductor properties (including conductivity type, carrier concentration and Hall mobility) of ZnO nano-granular films and nano-rods. The electroluminescence (EL) and photoluminescence (PL) behavior of ZnO nano-scale dot-rod array was analyzed with fluorescence spectrophotometer (Hitachi F-4500).

3. Results and discussion

Fig. 2 exhibits the XRD patterns of ZnO nano-granular film heat-treated at 350 °C (a) and ZnO nano-rods grown homoepitaxially in aqueous solution at 60 °C (b). All characteristic peaks of ZnO nano-granular film and ZnO nano-rods can be indexed to hexagonal wurtzite structure and (002) diffraction peaks are greatly enhanced with c-axis perpendicular to the substrates. It is noted that the full width at half maximum (FWHM) of ZnO (002) diffraction peaks of ZnO nano-granular film and ZnO nano-rods are 0.414° and 0.225°, which indicates the better crystallinity and c-axis orientation for the later.

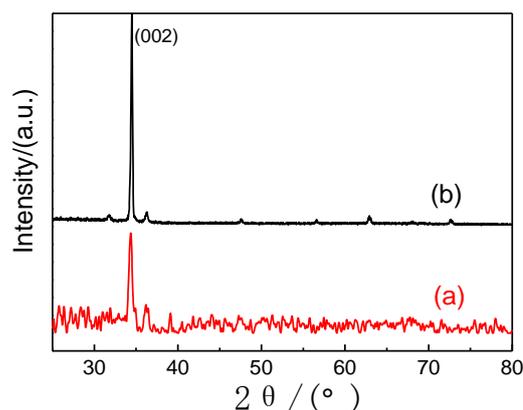


Fig. 2. XRD patterns of ZnO nano-granular film (a) and nano-rods (b)

The field emission scanning electron microscopy (SEM) images of ZnO nano-granular film (a) and ZnO nanorods (b) are shown in Fig. 3. It can be seen that the surface of ZnO nano-granular film is smooth and continuous and the particle size is about 20~30 nm. The nano-rods are perpendicular to the substrate illustrate a preferred orientation along c-axis, which is consistent with the XRD analysis result and the diameter of the ZnO nano-rods is about 100 nm.

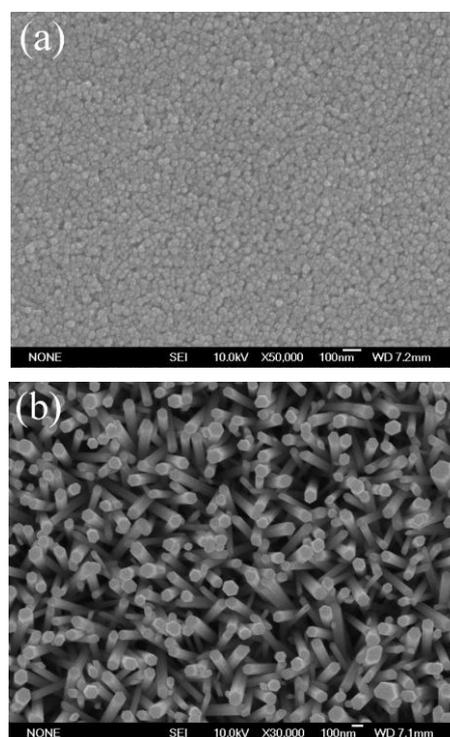


Fig. 3 SEM images of ZnO nano-granular film (a) and nano-rods (b).

The electrical properties of ZnO nano-granular film and ZnO nano-rods measured with Hall effect displacement transducer are shown in Table 1. As grown ZnO is normally n-type because of intrinsic donor defects such as oxygen vacancies and zinc interstitials, or unintended hydrogen, p-type doping of ZnO has been more difficult, possibly due to self-compensation by easily formed donor defects. In this work, the ZnO nano-granular film and ZnO nano-rods were all undoped, but they show a completely different conductivity, the ZnO nano-granular film is n-type conductivity with carrier concentration of $-7.29 \times 10^{13} \text{ cm}^{-3}$ and the ZnO nano-rods show p-type conductivity with carrier concentration of $+2.65 \times 10^{16} \text{ cm}^{-3}$. ZnO n-type nano-granular film and homoepitaxially grown ZnO nano-rod constitute a perfect homostructural ZnO p-n junction. Coincidentally, Y. F. Hsu et al [11] got undoped p-type ZnO nano-rods by a hydrothermal method, the p-type ZnO nano-rods exhibit a good stability (the carrier concentration almost no reduction in 3 weeks). The undoped p-type ZnO nano-rods might be attributed to the zinc vacancy formed during ZnO nano-rods growing in aqueous solution of Zinc nitrate at 60 °C, the accurate mechanism needs to be clarified.

Table 1 Electrical properties of ZnO nano-granular film and nano-rods.

Sample	Mobility/ $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	Carrier concentration n/ cm^{-3}	Conductivity Type
ZnO nano-granular film	9.59	-7.29×10^{13}	n
ZnO nano-rods	5.43×10^{-2}	$+2.65 \times 10^{16}$	p

The room temperature I-V characteristic of the homostructural ZnO p-n junction is shown in Figure 4. The dependence of current on voltage curve demonstrates a clear rectifying behavior of a p-n junction. The forward turn-on voltage is 3.0V and the corresponding current is about 0.1 mA, which may be result from the lower carrier concentration of ZnO nano-granular film and high contact resistivity between the electrode and the ZnO nano-rods.

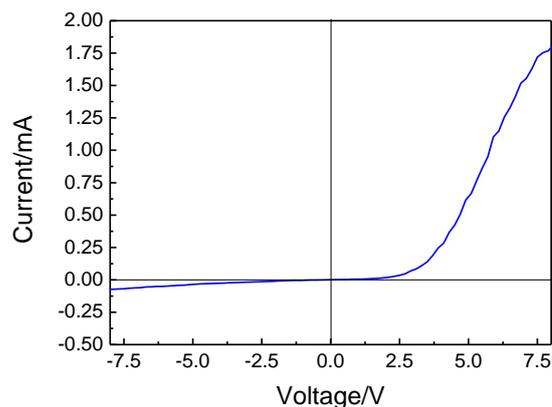


Fig. 4 I-V curve of ZnO p-n homojunction

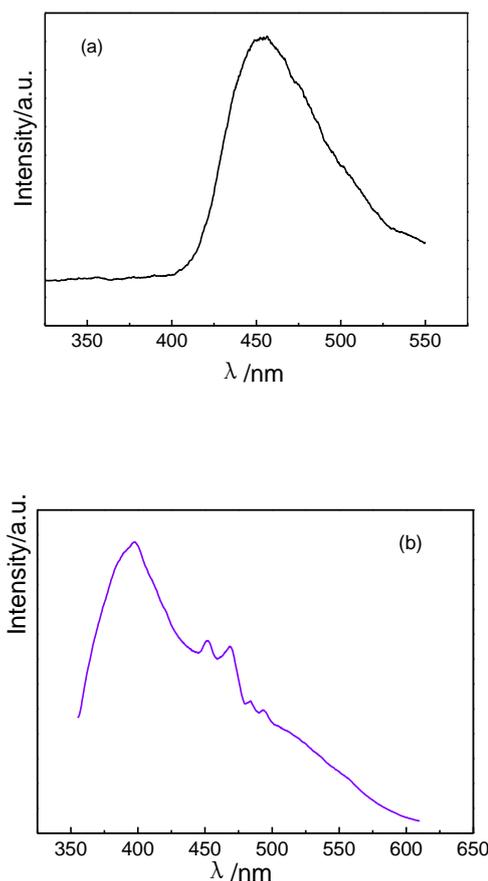


Fig.5. EL (a) and PL (b) spectrum of ZnO p-n homojunction

The EL spectrum of ZnO p-n junction at room temperature is shown in Figure 5(a), the spectrum exhibits a wide band emission centered at 456 nm. To further investigate the origin of the EL emission, PL measurement at room temperature was carried out on the ZnO p-n junction, as illustrated in Figure 5(b). It can be found that the near-band-edge emission at 390 nm is accompanied by four rather weak, deep-level emissions, the emission centered at around 450 nm, which is closely link with the EL emissions of 456 nm. The near-band-edge emission is usually ascribed to the exciton related emission, and the deep-level emission results from the oxygen vacancies or zinc interstitials. Thus, comparing with the PL spectrum, the EL emission peak centered at 456 nm is commonly assigned to intrinsic defects and associated with defect-related recombination [10, 14]. The near-band-edge emission band is not observed from EL spectrum of ZnO p-n junction might be due to the strongly UV absorbing of ZnO nano-rods.

4. Conclusions

The undoped n-type ZnO nano-granular films chemically synthesized in Zinc acetate solution and p-type ZnO nanorods homoepitaxially grown from aqueous solution of Zinc nitrate at 60 °C constructed a perfect homostructural ZnO p-n junction. The carrier concentration of n-type ZnO nano-granular film and p-type ZnO nano-rods are $-7.29 \times 10^{13} \text{ cm}^{-3}$ and $+2.65 \times 10^{16} \text{ cm}^{-3}$ respectively. The homostructural ZnO p-n junction shows an obvious rectifying behavior and the forward turn-on voltage and the corresponding current, are 3.0V and about 0.1 mA, respectively. The blue emission at 456 nm is occurred in EL spectrum of ZnO p-n junction, which associated with defect-related recombination. The usual ZnO near-band-edge emission band is not observed from the EL spectrum. The results shown in this paper provide some convincing evidence that ZnO-based light-emitting devices could be realized at rather low cost.

Acknowledgments

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*Corresponding author: d7288@126.com