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Electroluminescence from ZnO nanowires homojunction LED grown on Si substrate by simple chemical vapor deposition

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ABSTRACT

ZnO nanowires homojunction LED with phosphorus-doped p-ZnO nanowires/n-ZnO nanowires structure was fabricated on Si substrate by simple chemical vapor deposition. The scanning electron microscope show well-aligned undoped ZnO nanowires and phosphorus doped ZnO nanowires with uniform diameter, length, and density were grown perpendicularly on Si substrate. The phosphorus related acceptor emissions were observed from photoluminescence spectra of phosphorus-doped ZnO nanowires at 20 K. Moreover, the current–voltage measurement of ZnO nanowires homojunction LED showed a good rectifying behavior with a turn-on voltage was about 3.8 V and a reverse breakdown voltage was about 6 V. Distinct electroluminescence with ultraviolet and visible emissions was detected from this device at room temperature.

1. Introduction

ZnO has attracted widely attention for its wide band gap of 3.37 eV and relatively large exction binding energy of 60 meV at room temperature (RT). It has been regarded as one of the most promising material candidates for ultraviolet (UV), light emitting diodes (LEDs), laser devices (LDs) and photodetectors [1,2]. In recent years, one-dimensional (1D) ZnO nanostructures such as nanorods [3], nanowires [4,5] and nanotubes [6] have attached much attention. Compared with bulk and thin films, ZnO nanostructures have more advantages, such as single crystalline and high optical quality [7,8]. However for the real application of ZnO nanostructures based optoelectronic devices, it is necessary to obtained both n-type and p-type ZnO nanostructures. Unfortunately, ZnO is intrinsically n-type materials, therefore most efforts have been focused attention to obtain p-type ZnO materials. Many acceptor dopants, such as N [4], P [5,9], As [10], and Sb [11], have been tried. Among them, phosphorus-doped ZnO exhibited a high carrier concentration, reasonable mobility and low resistivity [12,13]. Recently, electroluminescence from ZnO nanostructures p–n homojunction was obtained by few groups [3,14,15]. Such as Fang et al. prepared phosphorus-doped ZnO nanorod p–n homojunction LED by hydrothermal method [3]. Zhang et al. prepared controlled arsenic-doped ZnO nanowire homojunctions by post-annealing ZnO nanowires grown on GaAs substrates [14]. However, there are few reports on the ZnO nanowires homojunction LED by simple chemical vapor deposition (CVD) [16].

In this Letter, phosphorus-doped p-ZnO nanowires/n-ZnO nanowires structure homojunction LED was successfully fabricated on low-resistivity n-Si (111) substrate by chemical vapor deposition (CVD) method without catalyst and template. The surface morphology, structural and optical properties of phosphorus-doped p-ZnO nanowires and undoped ZnO nanowires were investigated by field-emission scanning electron microscope (FE-SEM), X-ray diffraction (XRD) and photoluminescence (PL). Furthermore, the ZnO nanowires homojunction showed a good rectifying behavior and both the ultraviolet (UV) and visible electroluminescence (EL) emissions form ZnO homojunction were observed at room temperature. The results suggest that ZnO nanowires homojunction LED can be realized by simple chemical vapor deposition (CVD).

2. Experiment

2.1. Growth of phosphorus-doped ZnO nanowires and undoped ZnO nanowires

The phosphorus-doped ZnO nanowires were prepared via simple chemical vapor deposition (CVD) method. The low-resistivity n-Si (111) ($3 \times 10^{-3}\ \Omega\,cm$) were used as the substrates and cleaned using a standard wafer cleaning procedure. High-purity metallic Zn powders (99.999%), P_2O_5 powders (99.99%) and oxygen gas were used as Zn, phosphorus and oxygen sources, respectively. Well-mixed powders of Zn and P_2O_5 were put in a quartz boat and

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placed in the center of the tube furnace. The Si substrate was set to downstream of the source at a distance of 3 cm. A mixture of Ar and oxygen were introduced into the quartz tube at a flow rate of 200 and 80 sccm, respectively. During the reaction process, the whole system was kept at 550 °C for 30 min and then the substrates cooled down to room temperature with the protection of Ar. For comparison, undoped ZnO nanowires were also grown following the same procedure without adding P_2O_5.

2.2. Preparation of ZnO nanowires homojunction LED

The ZnO nanowires homojunction were prepared by growing the phosphorus-doped ZnO nanowires on the undoped n-type ZnO nanowires under the same condition as mentioned above. The device structure is simply schematically shown in Figure 1. Transparent conductive Indium Tin Oxide (ITO) films were closely pressed to the phosphorus-doped ZnO nanowires as the top contact electrodes and the full-back-side Al electrode was attached to the n-Si substrate by the thermal evaporation method. As a result, the ZnO nanowires homjunction LED was fabricated.

3. Results and discussion

The morphologies of the undoped ZnO nanowires and phosphorus-doped ZnO nanowires were measured by FE-SEM, as shown in Figure 2a. High-density well-aligned undoped ZnO nanowires were perpendicularly pointing out of the substrate. The nanowires have a uniform length of about 1 μm with average diameter of about 120 nm. Figure 2b shows the FE-SEM images of the phosphorus-doped nanowires. The typical diameter and length are about 100 nm and 1 μm, respectively. Furthermore, compared with undoped ZnO nanowires, the preferential orientation and uniform density of phosphorus doping ZnO nanowires are impaired due to the phosphorus doping into ZnO nanowires.

The crystal structure of the undoped ZnO nanowires and phosphorus-doped ZnO nanowires were analyzed by XRD measurements, as shown in Figure 3. For undoped ZnO nanowires, only (002) diffraction peaks of wurtzite ZnO located at 34.5° can be observed, which indicates the highly preferred crystal orientation along the c-axis of ZnO in this sample. However, an additional (101) diffraction peak appears for phosphorus doping ZnO nanowires. This result suggests that P incorporation into the ZnO crystal lattices might have impaired the crystallinity, which is in agreement with the FE-SEM analysis.

To confirm the phosphorus doping in the ZnO crystal lattices, the low-temperature PL measurements of undoped and phosphorus-doped ZnO nanowires were carried out at 20 K, as shown in Figure 4a. The PL spectrum of undoped ZnO nanowires shows a strong near-band-edge (NBE) emission located at 3.368 eV, which is assigned to the transition of neutral-donor-bound exciton (D^0X) [7]. For the phosphorus-doped ZnO nanowires, the D^0X completely vanish and three new acceptor-related emission peaks emerge. The peak at 3.360 eV accords well with the neutral acceptor-bound

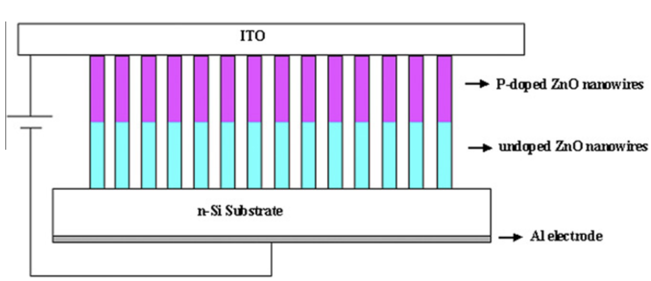

Figure 1. Schematic diagram of the ZnO nanowires based light-emitting device.

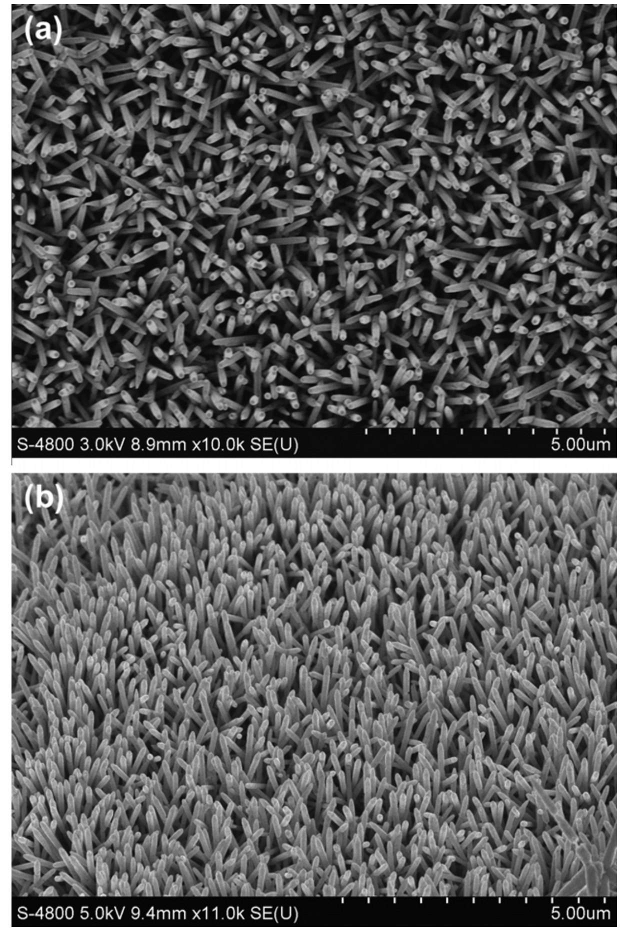

Figure 2. FE-SEM image of ZnO nanowires: (a) undoped, (b) phosphorus-doped.

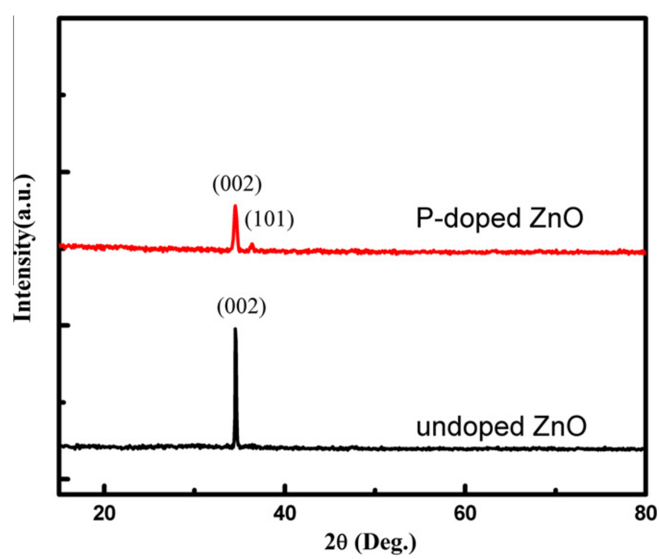

Figure 3. The XRD pattern of undoped ZnO nanowires and phosphorus-doped ZnO nanowires.

exciton (A^0X) emission in ZnO, this peak is also observed in phosphorus-doped ZnO films and nanowires [17,18]. Besides, the peak at 3.236 eV show a small blue shifts during the temperature increase as shown in Figure 4b, which are typical features of donor–acceptor pair (DAP) emission [19,20]. Therefore, the 3.236 eV peak is

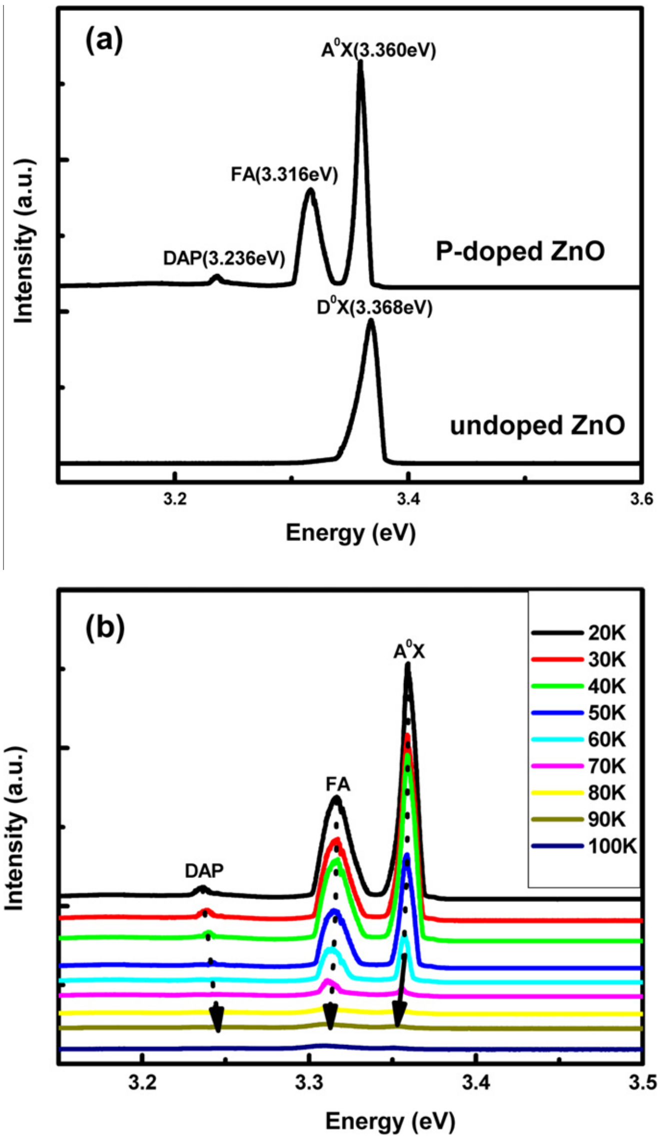

Figure 4. (a) The low-temperature PL spectra of undoped ZnO nanowires and phosphorus-doped ZnO nanowires at 20 K. (b) The temperature-dependence PL spectra of phosphorus-doped ZnO nanowires.

attributed to the DAP emission, and the 3.316 eV peak to free electron to the acceptor transition (FA) [21,22]. The existence of the three emissions suggests that some phosphorus-related acceptors exist in the phosphorus-doped ZnO nanowires.

The binding energy of the acceptor E_A can be estimated by the following formula:

$$E_A = E_{gap} - E_{FA} + \frac{k_B T}{2}$$

where the intrinsic band gap of ZnO $E_{gap} = 3.437$ eV [23,24], $E_{FA} = 3.316$ eV at 20 K, KB is the Boltzmann constant, and T is the temperature. The acceptor binding energy of E_A can be calculated to be about 121 meV, this value is consistent with the values reported in phosphorus-doped ZnO films [12,13].

To further prove that phosphorus-doped ZnO nanowires may present p-type conductivity. We fabricated a ZnO nanowires p–n homojunction. When the voltage applied on the two sides of the sample, the current–voltage (I–V) characteristics were measured by a semiconductor diode parameter analyzer at room temperature. Figure 5 shows the corresponding current–voltage (I–V) curve. It can be seen that a typical and clear rectifying behavior is exhibited. The turn-on voltage was about 3.8 V under forward bias voltage and reverse breakdown voltage of 6 V. These results further demonstrate the effective p-type conductivity of phosphorus-doped ZnO nanowires.

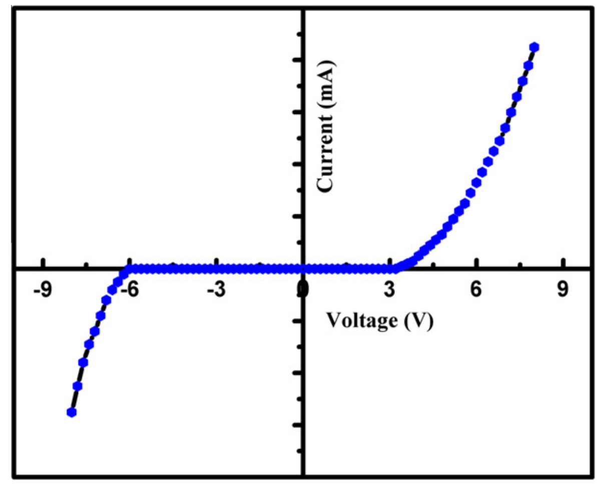

Figure 5. Current–voltage (I–V) curve of the ZnO p–n homojunction light-emitting device.

The EL measurement from the ZnO nanowires p–n homojunction was performed at room temperature by a CCD detector (HR320). Figure 6 shows the EL spectrum from the device at injection currents of 40 mA at room temperature. The EL emission is so obvious that it could be clearly seen by naked eye in the dark and the photograph is shown in the inset of Figure 6. The corresponding EL spectrum exhibits two independent bands that are a near-band-edge emission (NBE) on 3.18 eV and a deep-level (DL) emission on 2.39 eV. The origination of the NBE associated with the exciton related emission and the DL emission band is due to the defect related radiated recombination [25]. The DL emission was dominant and the NBE emission relatively weak in the spectrum that may be ascribed to the low radiative recombination efficiency and self-absorption effect by the DL traps in ZnO [26–28].

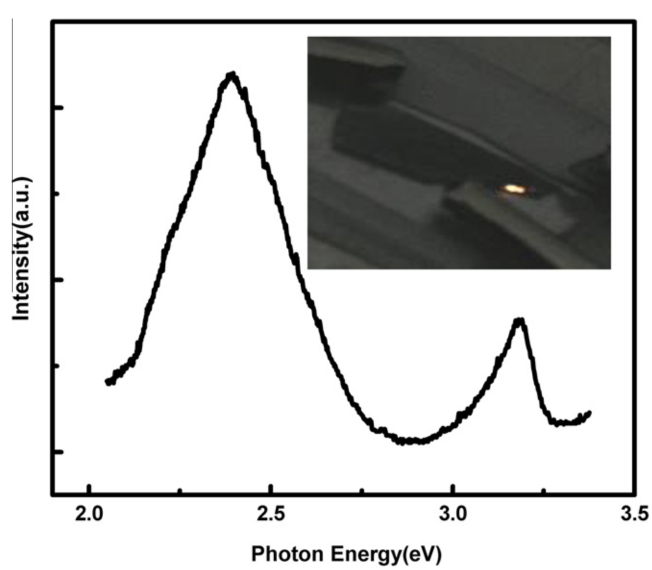

Figure 6. EL spectrum of ZnO homojunction light emitting diode at 40 mA in the room temperature. The inset is photograph of EL form ZnO p–n homojunction light-emitting device under forward current of 40 mA in the room temperature.

4. Conclusions

In conclusion, phosphorus-doped ZnO nanowires/n-ZnO nanowires homojunctions were synthesized by simple chemical vapor deposition method. The low temperature PL spectra measurements have confirmed phosphorus doped in the ZnO crystal lattice. With construction of ZnO nanowires homojunctions, the *I*–*V* characteristics showed a good rectifying behavior with a turn-on voltage of about 3.8 V and a breakdown reverse voltage of about 6 V. Furthermore, the electroluminescence spectrum was obtained on the ZnO nanowires homojunctions at room temperature with a weak ultraviolet emission peak at 3.18 eV and a broad visible band centered at 2.39 eV. The method may open a relative cheap and efficient way for fabricating the ZnO nanowires based light emitting diodes.

Acknowledgements

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