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The surface defect-related electroluminescence from the ZnO microwire

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Abstract

Surface defect-related electroluminescence (EL) was realized from a single ZnO microwire-based metal–semiconductor–metal structure on a glass substrate. ZnO microwires were successfully fabricated using a simple chemical vapour deposition approach. Schottky contacts were detected between Au electrodes and the ZnO microwire. The EL spectrum showed a broad emission band covering the visible range from 400 to 700 nm. The possible EL emission mechanism is discussed in detail in this paper.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

ZnO, a wide direct band gap semiconductor (3.37 eV), has a large exciton binding energy of 60 meV, which makes the excitons thermally stable at room temperature (RT) because the value is much larger than the thermal energy of 26 meV [1]. Due to these properties, ZnO is considered as a promising material with wide applications in short-wavelength optoelectronic devices, such as ultraviolet (UV) and white light-emitting diodes (LEDs), photodetectors, UV laser diodes (LDs) and so on. In recent years, different types of LEDs have been reported, for instance p–n heterojunctions [2–8], p–n homojunctions [9, 10], metal–insulator–semiconductor (MIS) junctions [11–13], etc.

Although there have been many reports about ZnO p–n homojunction LEDs, it has still been very difficult to obtain stable and high-quality p-ZnO, due to the low dopant solubility, the deep acceptor energy level and the self-compensation from native point defects in ZnO [14]. For this reason, ZnO p–n heterojunctions were developed using various p-type materials such as GaN [2, 3], Si [4], AlGaN [5], SiC [6] and NiO [7]. Furthermore, ZnO-based MIS LEDs were also fabricated using SiO_2, MgZnO and i-ZnO as insulator layers. By now, for most of the ZnO-based LEDs, ZnO thin films and nanostructures have been used to construct the devices [15, 16]. However, single ZnO microwire-based MSM structure LED has not yet been reported.

In this paper, ZnO microwires were fabricated by a traditional vapour transport deposition method. The as-grown ZnO microwires were single crystalline with a length of about 1 cm, which enables us to make the device easily by the conventional methods. Until now, there have been few reports about ZnO microstructure-based LEDs. A metal–semiconductor–metal (MSM) structure was designed based on a single ZnO microwire using Au as electrodes, and the EL properties and emission mechanism of the device were studied.

2. Experimental details

The ZnO microwires were synthesized via a traditional chemical vapour deposition method in a horizontal tube furnace. A mixture of ZnO, graphite and GaAs powders with a definite weight ratio of 1 : 1 : 0.01 was loaded in an alumina boat serving as the reactant source material. Before being loaded into the furnace chamber, around 100 nm thick ZnO

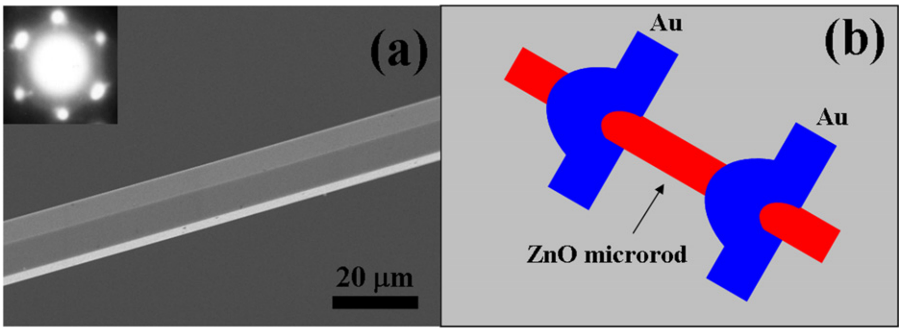

Figure 1. (*a*) The SEM image of a single ZnO microwire on glass substrate. The inset shows the SAED image of the ZnO microwire. (*b*) The schematic diagram of the single ZnO microwire-based MSM structure on glass substrate.

film was first deposited on the Si (1 0 0) substrate surface via an electron beam evaporation method at 400 °C. Then, the as-grown ZnO film/Si substrate was loaded above the source material with a vertical distance of 4 mm. During the synthesis process, a constant flow of Ar (99.99%) (100 standard cubic centimetres per minute) was introduced into the tube furnace as the protecting gas. The furnace was heated to 990 °C at a speed of 24 °C min^{-1}. After maintaining at 990 °C for 30 min, the furnace was cooled down to room temperature naturally. White wire-like structures were clearly observed on the surface of the substrate and the boat both by the naked eye. By the analysis of x-ray photoelectron spectroscopy, only Zn and O elements were detected, but no As signal was examined, which meant the as-grown sample was pure ZnO mircrowire.

The morphology of the ZnO microwires was characterized by field-emission scanning electron microscopy (FESEM) (model: Hitachi S-4800) operated at 5 kV. The current–voltage (I–V) characteristic of this device was measured using a Hall measurement system (LakeShore 7707). The EL spectra of the diode were performed at RT in a F4500 spectrometer. The RT photoluminescence (PL) measurements were performed using a He–Cd laser line of excitation wavelength 325 nm and a micro-Raman spectrometer in a backscattering geometry configuration to detect the emission spectra (model: LABRAM-UV Jobin Yvon), which can focus on an area of diameter 10 μm and adjust the depth of the laser focus. The low-temperature (LT) EL spectra of this diode were detected by a SPEX1404 double grating spectrometer.

3. Results and discussion

A typical SEM image of the as-grown single ZnO microwire is shown in figure 1(*a*). The average diameter of the ZnO microwires is about 15 μm with length of up to 1 cm. The inset of figure 1(*a*) shows the pattern of the selected area electron diffraction (SAED) measurement for a cross section of the microwire. The clear dot SAED pattern means the microwires are single crystals with wurtzite structure. To make a MSM device, two Au electrodes were deposited on a single ZnO microwire with a distance of 2 mm by the thermal evaporation method as schematically shown in figure 1(*b*).

Figure 2 shows the RT I–V characteristics of the ZnO microwire device. The I–V curve presents a nonlinear shape, which indicates the formation of Schottky contacts between the Au electrodes and the ZnO microwire. Similar electrical characteristics can also be detected between zinc oxide nanowires and Au electrodes as reported in the literature [17]. With a bias voltage being applied, a yellow–white EL emission could be observed from the whole ZnO microwire by the naked eye, and the turn-on voltage of the EL was 5 V.

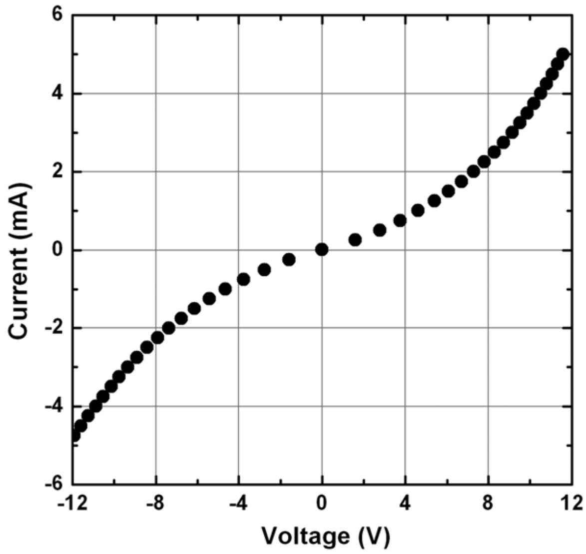

Figure 2. The room temperature current–voltage characteristics of the single ZnO microwire-based light-emitting device.

Figures 3(*a*) and (*b*) show the RT EL spectra of the device under different voltages, respectively. Under 5 V bias, as shown in figure 3(*a*), the EL spectrum exhibits a broad visible emission band centred at about 520 nm and covers the whole visible region from 400 to 700 nm. The inset of figure 3(*a*) shows the corresponding photograph image of light emission taken by a charge-coupled device (CCD) camera from the device operated at the same bias. A weak dark red emission is clearly observed across the microwire. With increasing applied voltage, the EL emission intensity increases quickly. The EL emission intensity is almost 20 times than that under a bias of 5 V when the applied voltage is increased to 8 V, which is shown in figure 3(*b*). Furthermore, the EL emission peak position red-shifts to 540 nm, which may be due to the increase in the intensity of the longer wavelength component in the EL process. And a bright yellow–white EL emission is observed close to the cathode for the device, and the photograph image is also shown in the inset of figure 3(*b*).

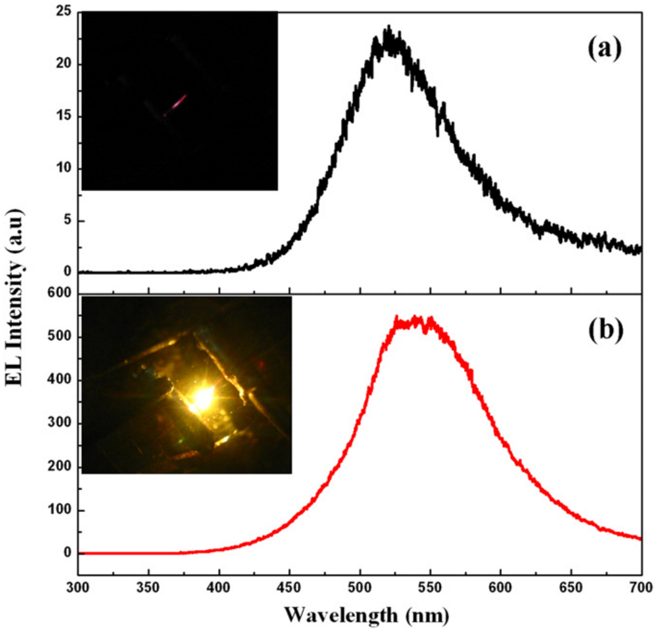

Figure 3. The room temperature EL spectra at different bias (*a*) 5 V and (*b*) 8 V. The inset shows the CCD camera images taken at the corresponding voltages.

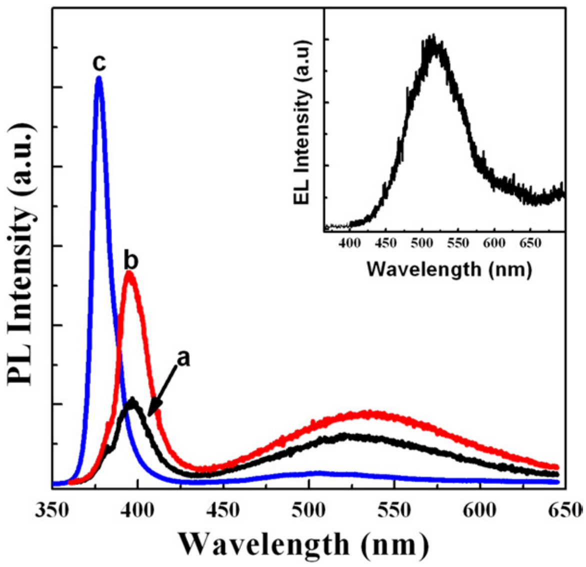

Figure 4. The room temperature PL spectrum of the single ZnO microwire with different depths under the surface: (a) the laser focus on the surface, (b) a little deeper under the surface, (c) deep in the microwire. The inset shows the low-temperature EL measurement performed under 8 V at 10 K.

In order to explore the origin of the EL emission and the recombination mechanism for the device, PL and the LT EL measurements were performed. The RT PL spectra of the single ZnO microwire with different depths of the laser focus are shown in figure 4. When the laser focus is just on the ZnO microwire surface, an UV emission band located at 396 nm and a broad visible emission located at 522 nm could be detected with almost the same intensity. Usually, the UV emission is attributed to the near band edge emission in ZnO. And the deep-level emission is ascribed to different defects such as surface defects, oxygen vacancies (V_O), zinc interstitials (Zn_i) or antisite defect O substitutional Zn (O_{Zn}) in ZnO [18]. When the laser focus is a little deeper under the surface the intensity of the UV emission increases more quickly than that of the visible emission band. On adjusting the laser focus deeper into the microwire, the PL emission spectrum is composed of a very strong and dominant ultraviolet emission located at 387 nm and a rather weak and broad visible emission centred at 504 nm. According to previous reports, the depth of the surface defect region could extend to tens of nanometres below the surface [19, 20], and based on the above PL data, it is assumed that a large number of defects are present mainly close to the microwire surface region and there are fewer defects inside the microwire.

By the analysis of the EL spectra and the PL spectra, the origin of the EL emission could be attributed to the surface defects. But the EL emission mechanism is still a puzzle. Until now, different models have been proposed to explain the electrically driven light emission from a single-component structure, including a bipolar EL mechanism, a unipolar impact excitation process by hot carriers and a thermal light emission due to Joule heating. To further understand the mechanism of the EL emission, a LT EL measurement is performed under 8 V, as shown in the inset of figure 4. The EL emission spectrum is obtained at 10 K showing the same shape as that at room temperature. Since we could obtain the LT EL emission, the Joule heating mechanism is not suitable to explain the emission mechanism. For the bipolar EL mechanism, the electrons and holes are injected simultaneously into the emitting material. Then the EL emission occurs through the radiative electron–hole recombination. Because the undoped ZnO usually shows n-type conductivity due to native defects, the recombination of the directly injected electrons and holes is also not proper to explain the EL emission in our experiment. Therefore, a model based on the inelastic scattering of tunnelling electrons is proposed for the EL emission from the ZnO microwire MSM diode [21, 22]. According to this model, the electrons drifted into the cathode can tunnel through the single barrier between the Au electrode and the ZnO microwire. The electrons tunnelling through the barrier have sufficient energy to scatter inelastically and excite the electron–hole pairs within the ZnO microwire. The generated electrons relax to the deep-level defects in ZnO rapidly, which results in the fact that the EL emission is dominated by the visible band.

4. Summary

In conclusion, single crystalline ZnO microwires were synthesized via a simple vapour phase transport process. A MSM device structure was fabricated using Au as the electrodes. By applying a bias voltage, a bright yellow–white emission could be observed in the whole ZnO microwire. The visible EL emission ranging from 400 to 700 nm was ascribed to the surface defect-related emission in ZnO. And the EL emission mechanism was assumed based on the inelastic scattering of the tunnelling electrons.

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