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The photoluminescence properties of ZnO whiskers

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Abstract

The ZnO whiskers were successfully fabricated by a simple thermal oxidation method. The morphologies of the samples were examined using a scanning electron microscope (SEM). The average length of the whiskers is about 0.7 μm with a diameter of about 100 nm. Intense ultraviolet photoluminescence was observed at room temperature. By studying the PL properties of ZnO whiskers at low temperature, a competitive process between the recombination of delocalized excitons and localized exciton emission is observed. The probable mechanism is discussed.

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1. Introduction

ZnO is known to have a wide range of technological applications, such as transparent conducting electrodes in solar cells, flat panel displays, surface acoustic wave devices, and chemical sensors. Since 1997, ZnO has been paid considerable attention because it can be used to produce light emitting devices in the ultra-violet region, and it is considered to be the next generation in LED materials [1–4].

Among all kinds of whiskers, ZnO whiskers are the only one with tetrapod shape [5,6]. They possess good overall properties, such as semiconductivity, wear resistance, vibration insulation, and microwave absorption. They can be widely applied as both functional and structural materials, because of their peculiar shape and single crystalline character. There are few methods invented to control the oxidizing speed of zinc to ZnO, so that the whiskers can be generated slowly.

In this letter, a simple thermal oxidation method was employed to synthesize the ZnO whiskers. The morphologies and the photoluminescence (PL) properties of the ZnO were measured.

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2. Experimental procedure

The reaction to form ZnO whiskers was carried out in a conventional tube furnace with a horizontal quartz glass tube. First the furnace was heated up to 800°C. Then the metal zinc grains (6 N) within a quartz boat were loaded into the center of the quartz tube under an O_2 (5 N) ambient with the flow of about 50 cm^3/min. The tube was heated to 1000°C with the rate of 5°C/min. After that the quartz tube was kept constant at 1000°C for 60 min. Finally, the quartz boat was pulled out from the tube furnace, when the temperature was cooled naturally to 700°C. A white and fluffy product was obtained. For the PL spectra, the excitation source was a continuous wave He–Cd laser with a wavelength of 325 nm and a power of 50 mW. The luminescence signals were detected by an UV Microlaser Raman spectrometer made in France. A CCD camera with a choice of high resolution or wide spectral range was used to detect the emission spectra.

3. Results and discussion

Fig. 1 shows SEM photos of ZnO whiskers. It can be seen that the most whiskers are tetrapodal (Figs. 1(a) and (b)). The average length of the whiskers is 0.7 m with the diameter of 100 nm. In addition to whiskers there are some flakes and lotus root-like ZnO grains (Figs. 1(c) and (d)).

The PL spectrum of the ZnO whiskers at room temperature is shown in Fig. 2. There are two emission peaks in the spectrum: one is located at 394.5 nm in the ultraviolet region; the other is located at 510 nm in the visible region. The ultraviolet band corresponds to the near band gap excitonic emission [7]. The green emission has been attributed to the presence of singly ionized oxygen vacancies. The emission is caused by the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy [7].

Fig. 3 shows the photoluminescence spectra of ZnO whiskers over a wide temperature range (82–327 K). At 82 K, there are two main peaks in the

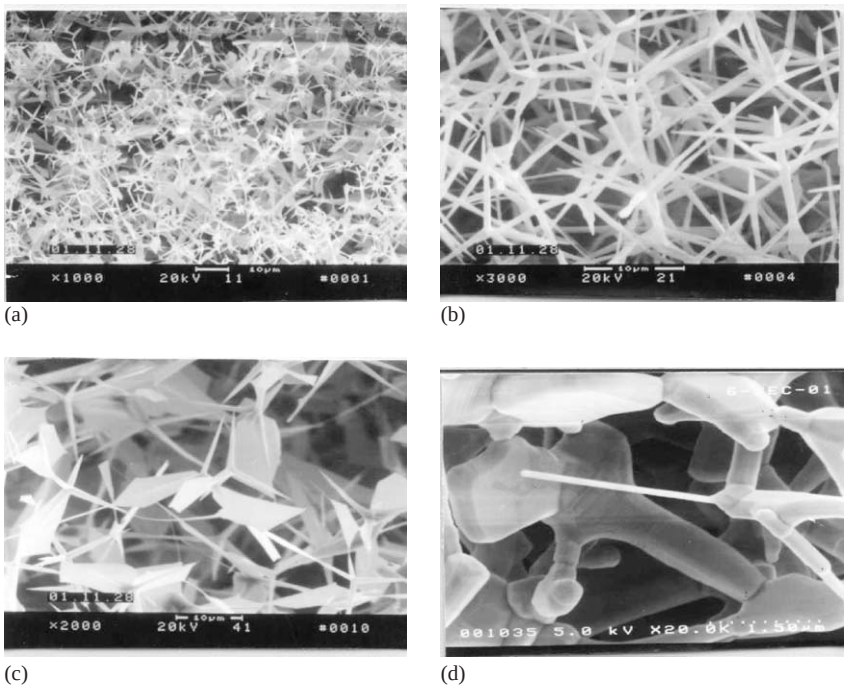

Fig. 1. SEM images of ZnO whiskers.

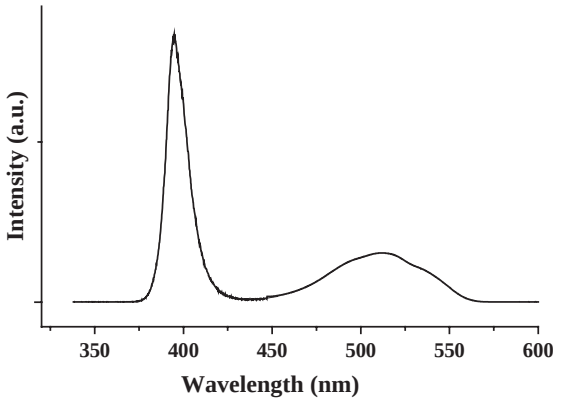

Fig. 2. The PL spectrum of ZnO whiskers excited by He–Cd laser at room temperature.

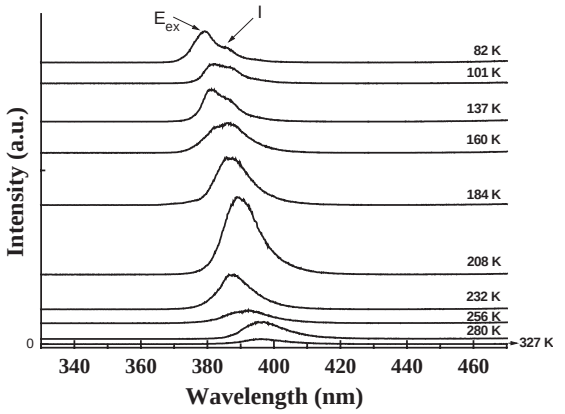

Fig. 3. The PL spectra of ZnO whiskers over a wide temperature range.

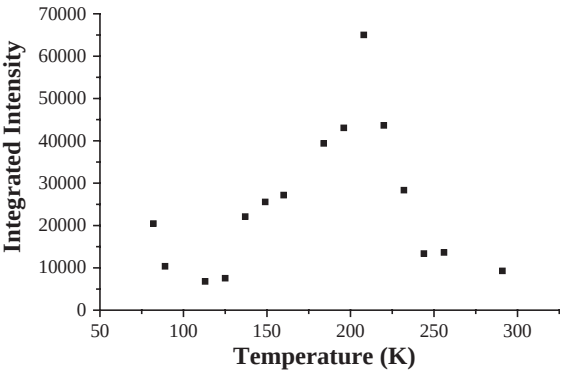

Fig. 4. The integrated intensities of free exciton emission as a function of the temperature.

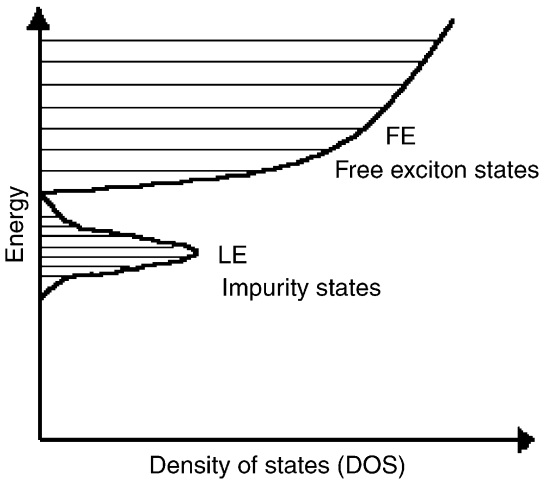

Fig. 5. Schematic diagram of energy and density of states (DOS) of LE and FE, which is used to show the localized characteristic of LE and delocalized characteristic of FE.

spectra denoted by E_{ex} and I, which have been assigned to free exciton emission and excitons bound to neutral donors or acceptors [8]. With increasing temperature, the emission peaks shift to the low energy side. The I band becomes weak and ultimately disappears at 184 K in the spectra. The emission associated with free excitons could still be seen at high temperature.

The integrated intensity of E_{ex} band as the function of the temperature is shown in Fig. 4, which is quite different compared to ZnO thin films fabricated by either sol–gel deposition method or the molecular beam epitaxy (MBE) [2,8]. At the beginning, the intensity of the free exciton emission decreases when the temperature increases. But when the temperature is raised to 125 K, the integrated intensity of E_{ex} band increases sharply, and reaches its maximum value at 220 K. Above 220 K the emission intensity decreases again with temperature.

An exciton localization and delocalization effect is considered to explain the above phenomenon [9,10]. A simple sketch is shown in Fig. 5, in which FE is a high energy delocalized state or free

excitonic state with a large density of states. Here, LE is an impurity-related band in the ZnO whiskers, and it has a lower density of states compared to the FE band. At low temperature a part of the photogenerated carriers are localized at the impurity-related states and form bound excitons. With increasing temperature some non-radiative recombination channels are activated by thermalization, which causes the integrated intensity to decrease. But when the temperature reaches a certain point ($\sim$125 K), the bound excitons located at the localization states transform to the delocalization states due to thermalization. Thus the emission intensity caused by the recombination of delocalized excitons increases, and LE is quenched very fast.

4. Conclusions

In summary, ZnO whiskers were synthesized successfully by a simple method. Most of the whiskers have tetrapod shapes, but there are also some samples with flakes and lotus root-like shapes. At room temperature an intense ultraviolet emission is obtained. By studying the PL properties of ZnO whiskers at low temperature, a competitive process between the recombination of delocalized excitons and localized excitons is observed. The probable mechanism is discussed.

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