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Photoluminescence of ZnO nano-tetrapods

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Abstract. The ZnO nano-tetrapods have been prepared by the evaporation of metallic Zn powder at the temperature range of 700°C- 950°C in air. The influence of experimental conditions, such as the evaporation temperature and the substrate temperature, on the morphology, the size and the photoluminescence (PL) was investigated. The XRD pattern showed that the nano–tetrapods were ZnO with hexagonal structure. The branch size of the tetrapods was about two hundreds nanometers. The photoluminescence spectrum measured at room temperature consists of two bands, a narrow band at 380 nm (UV band) and a wide band around 500 nm (green band (GB)). The intensity of each band, the ratio of the peak intensity of UV band to the GB band and the GB band position depend on the experiment conditions. However, the peak position of the UV band was not changed.

1. Introduction

Zinc oxide is one of the most efficient wide band-gap phosphor materials so it is attracting more attention in the field of optoelectronics and photonic devices. It has a large exciton binding energy (60 meV) which allows UV lasing action to occur even at room temperature [1]. In ZnO, oxygen vacancies exhibit an efficient green emission. ZnO is also one of gas-sensing materials due to advantageous features, such as high sensitivity to ambient conditions, low cost and simplicity in fabrication [2]. Recently, the growth and elucidation of the properties of well-defined nanoscale materials are critical to efforts directed towards understanding the fundamental physics of nanostructures, creating nanostructured materials, and developing new nanotechnologies [3]. In this regard, one-dimentional ZnO, such as nanowires, nanotubes, nanorods have great potential to address basic issues in applications.

In this report we present the influence of the preparation conditions on the photoluminescence of ZnO nano-tetrapods prepared by evaporation method.

2. Experimental

ZnO nano-tetrapods have been prepared by simple evaporation method. The evaporation precursor was Zn powders. The system consists of a horizontal tube furnace and a quartz tube (Fig.1). The Zn powder was placed at the sealed end of the tube. The first Si substrate was placed 1.0 cm far from the Zn source. The place of the Zn source is in the centrum of the furnace. The system was performed in air. The

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evaporation temperature (the temperature of the Zn source) was changed from 700°C to 950°C and hold for 2–60 min. After the evaporation, white fluffy products formed on the Si substrates.

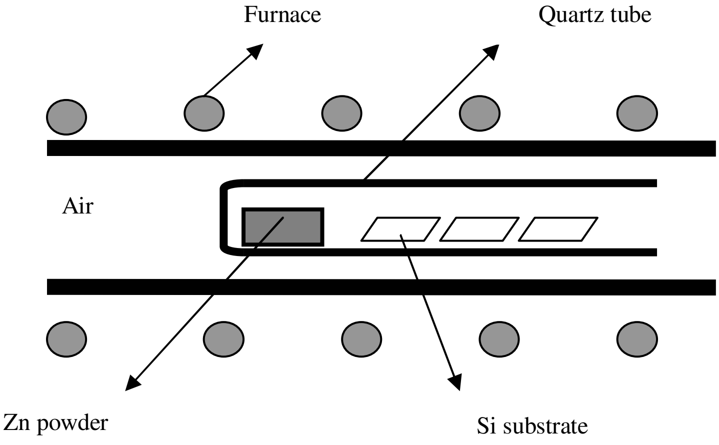


Fig.1. The evaporation system.

The synthesized products were characterized using scanning electron microscopy (SEM, JEOL-JSM 5410 LV), X-ray diffraction (XRD-D5005). The photoluminescence (PL) and excitation photoluminescence (PLE) measurements were carried out on the FL3-22 spectrophotometer with a 450 W Xe lamp.

3. Results and discussion

The XRD pattern shown in Fig. 2 indicated that the products deposited on the substrate are ZnO crystals with hexagonal wurtzite structure and there is no Zn peak.

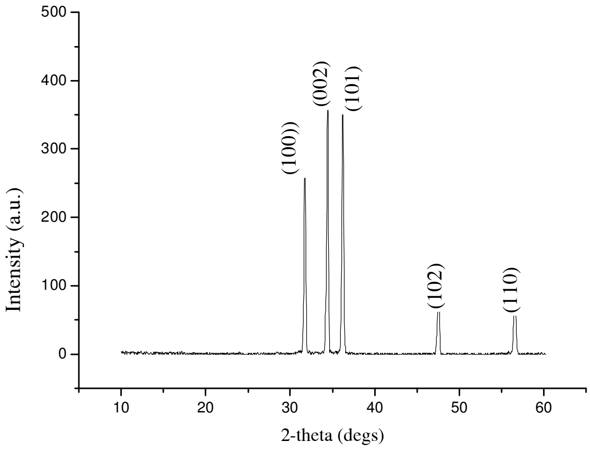
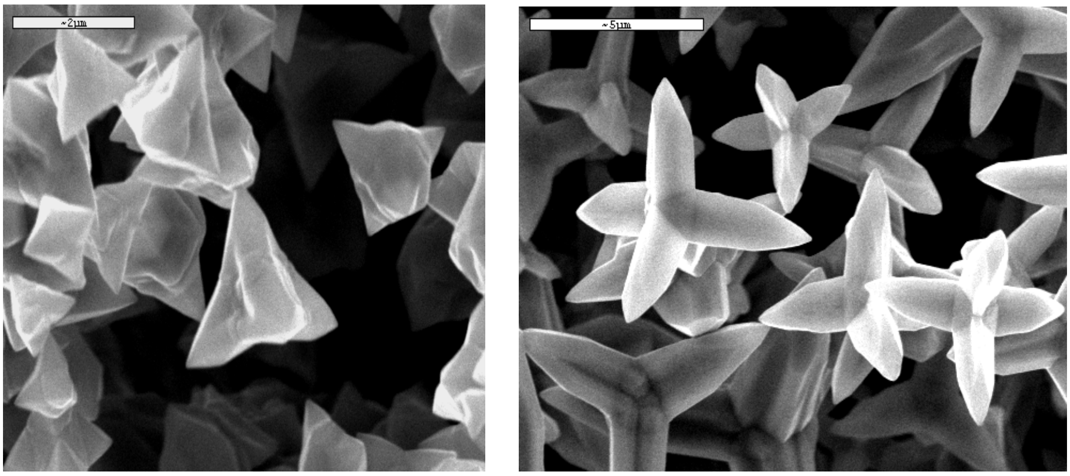


Fig. 2. XRD pattern of ZnO nanotetrapods.

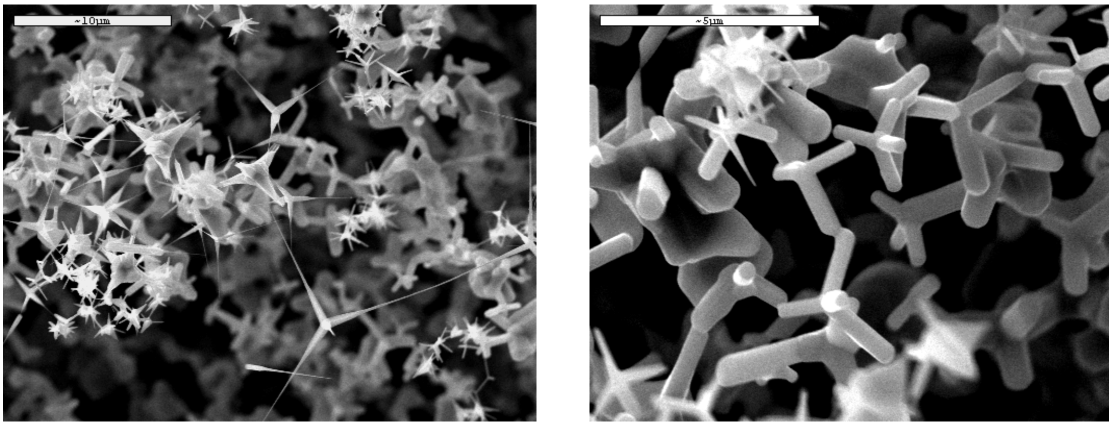
The morphology of as-prepared products was characterized by SEM. The results showed that the morphology of all products was tetrapods and depends on the evaporation temperature, the substrate temperature (exactly, the substrate temperature zone) and the evaporation time. In this study the evaporation time was 60 min. Fig. 3 shows the SEM images of the tetrapods when the evaporation temperatures were 700°C and 800°C. It is seen from Fig. 3 (a) that at 700°C, the tetrapods started to form but the lengths were short. At 800°C the lengths were longer (Fig.3 (b)).



a) b)

Fig. 3. SEM images of ZnO nano-tetrapods evaporated at (a) 700°C and (b) 800°C.

When the evaporation temperature was 900°C, the products have two types depending on the substrate temperature. We denote the products with higher substrate temperature (next to the Zn source and far from the open end of the tube (Fig.1) by sample **A** and the products with lower substrate temperature zone (far from the Zn source, next to the open end) by sample **B**. The results showed that **A** has bigger size with a tip shape and **B** has a rod shape with a smaller size (about 200 nm).



a) b)

Fig. 4. SEM images of ZnO nano-tetrapods evaporated at 950 °C: (a) sample **A**, (b) sample **B**.

This behavior was also for the evaporation temperature of 950°C. In Fig. 4 are SEM images of the sample evaporated at 950°C. From the SEM images it is expected that our synthesis was based on the thermal evaporation of Zn powders without the presence of catalyst, therefore the ZnO tetrapods were formed by oxidation of evaporated zinc vapor in gas phase. This growth was governed by a vapor-solid (VS) process [4]

For investigation of the optical properties of ZnO nano-tetrapods, the PL and PLE spectra were measured at room temperature. Fig. 5 shows the PL spectra for ZnO nano-tetrapods evaporated at 900°C. The excitation wavelength is 335 nm. It is seen that the PL spectra consist of a strong, narrow peak in a near UV region (380nm) (UV band) and a broad peak of 495 nm in the visible region (green band (GB)). The UV emission peak is due to the exciton recombination and the broad peak at 495 nm is attributed to defect levels in the band- gap, e.g. the radiative recombination of a photogenerated hole with an electron trapped by the oxygen vacancy [5].

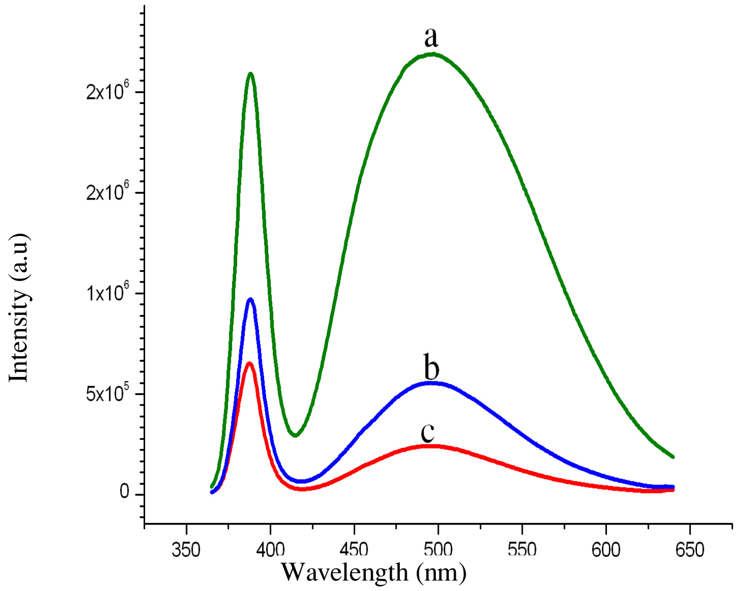


Fig. 5. PL spectra of ZnO nano-tetrapods evaporated at 900 °C, under 335 nm excitation. The substrate temperature zone is about (a) 800 °C, (b) 700 °C, (c) 600 °C.

It is seen from Fig. 5 that, the lower substrate temperature is, the lower PL intensities for both bands are, but the ratio of the peak intensities of UV band to that of the green band (UV/GB) increases, e.g. 1/1, 2/1 and 3/1 for a, b and c, respectively. Besides, the peak positions of the two bands were unchanged when the substrate temperature was changed. The decrease of PL peak intensities with the substrate temperature in Fig. 5 is probably concerned with the crystallization of ZnO tetrapods. When the substrate temperature increases, the higher crystallization of nano-tetrapods occurs and this leads to the increase of the PL intensity. The increase of the ratio UV/GB is due to the increase of the oxygen concentration of the substrates closer to the open end of the quartz tube, e.g. the decrease of oxygen vacancies results in the decrease of the GB intensity.

In Fig. 6 and 7 are PL spectra of ZnO nano-tetrapods deposited at two fixed substrate temperature (samples **A** and **B**) and were evaporated at 700 °C and 800 °C. A comparison of PL spectra in Fig. 5, 6 and 7 illustrates that, beside the similar behavior, such as the ratio UV/GB of the sample **A** is smaller than that of **B**, the difference between them is the red shift of green band when the substrate temperature decreases (e.g. when the substrate is more far from the Zn source and closer to the open end of the quartz tube). The change of the ratio UV/GB can be explained like above.

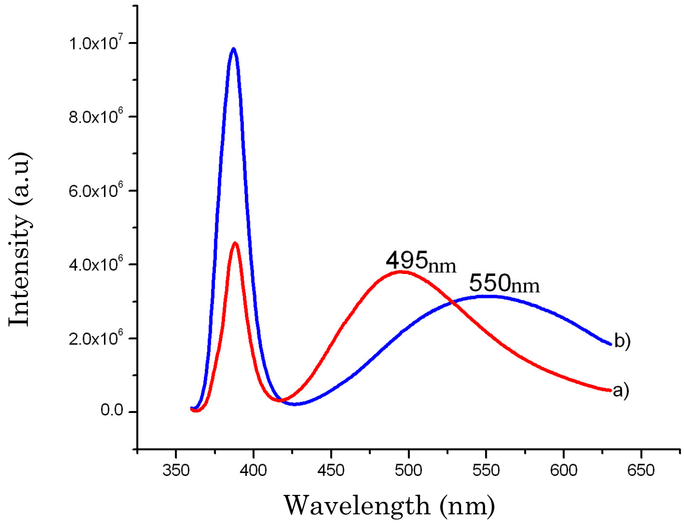


Fig. 6. PL spectra of ZnO nano-tetrapods evaporated at 800 °C: (a) Sample **A**, (b) sample **B**.

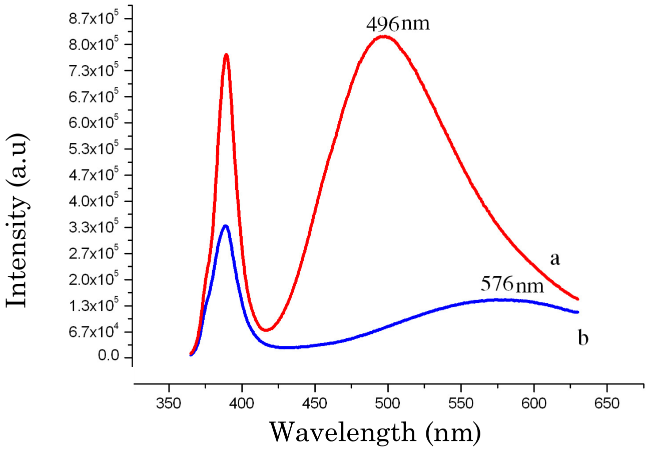


Fig.7. PL spectra of ZnO nano-tetrapods evaporated at 700 °C: (a) Sample **A**, (b) sample **B**.

The red shift of the green band can be explained as follows: After several reports [5, 6] the green band (500 nm) is attributed to the oxygen vacancies and the yellow band (about 600 nm) is due to zinc vacancies. As mentioned above, the samples **A** are next the Zn source and far from the open end of the quartz tube so it has a lack of oxygen (rich Zn). It is opposite with sample **B**, which was producted at the place far from the Zn source and next the open end of the quartz tube. So these products have enough of oxygen but lack of zinc.

It is seen from Fig. 5, 6 and 7 that the GB of 576 nm (evaporation temperature is 700^{o}C), 550 nm (evaporation temperature is 800^{o}C) and 500 nm (evaporation temperature is 900 ^{o}C) were from the products deposited at the same place in the furnace. This means that the higher evaporation temperature is, the more blue shift of green band is. It is due to the more Zn vapor can be evaporated when the evaporation temperature is higher. This leads to most Zn for the products of ZnO tetrapods evaporated at 900^{o}C, when the defect is mainly oxygen vacancies. The GB is the superimposition of two bands resulting from oxygen vacancies and zinc vacancies.

A comparison of our PL spectrum with other studies showed that the peak positions of 495 nm and around 570 nm of our study are similar to the PL of ZnO nano-tetrapods nanorods reported by [7-9].

4. Conclusions

ZnO nano-tetrapods were successfully synthesized by the thermal evaporation of Zn powders without a catalyst. The morphology of the tetrapods depends on the substrate temperature. The size of the tetrapods was about 200 nm. The photoluminescence spectrum has two bands, a UV band at 380 nm and a green band around 560 nm depending on the evaporation and the substrate temperature. The green band is the superimposition of two bands, related with oxygen and zinc vacancies, respectively.

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