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Characterization and optical properties of ZnO tetrapod nanorods synthesized by two-step method

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Uniform ZnO tetrapod nanorods were produced by the thermal evaporation zinc powder at 900□on zinc thin films deposited by Pulse Laser Deposition (PLD). The morphology and microstructure of the nanotetrapods were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The zinc thin films on the sapphire substrates prepared by PLD will make the ZnO tetrapod nanorods grown uniformly with a high crystal quality and thick arms. The room-temperature photoluminescence spectrum (PL) was carried out, besides UV and green emission, a blue band centred at 460nm was recorded and analyzed in this work.

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1. Introduction

In recent years, the study of the low-dimensional self-assembled nanostructures has attracted much attention because of the significant advancements in their synthesis [1-3]. Among the nanomaterials, zinc oxide (ZnO) has been recognized as a promising semiconductor material owing to its wide bandgap (3.37 eV) and a large exciton binding energy (60 meV) [4]. ZnO shows various morphologies on the nanoscale. Nanobelts [5], nanowires [6-7], nanoneedles [8], nanosheets [9] and tetrapods [1, 10] have been reported in some literatures. The tetrapod ZnO nanorods are one of the interesting morphologies due to their unique size and morphology which displays promising properties in field emission [11-13], infrared adsorption [14], microwave adsorption [15], sensor [16-17], etc. Since Yoshinaka [18] reported on the preparation of tetrapod ZnO nanorods, various methods have been developed to synthesize them, such as metal organic chemical vapor deposition (MOCVD) [19] , hydrothermal methods [20], oxide-assisted growth method [21], thermal evaporation [12] and so on. Up till now, the thermal evaporation we used as a simple and effective method has been utilized widely. However, many difficult issues about the tetrapod ZnO are still disputed, such as the improvement of uniform size and high crystal quality , the control growth of different sizes and the growth mechanism.

In this work, we prepared the zinc thin films using PLD system. The characteristics of the vacuum ambience and the rapid deposition speed can prevent the zinc thin films from being oxygenated and polluted during the deposition process. Then, using the simple thermal evaporation method, the high-quality and large-scale ZnO tetrapod nanorods are synthesized on the zinc thin films. It demonstrates that the zinc thin films conduce to produce the uniform ZnO tetrapods with thick arms, which can provide a significant opportunity to control the ZnO tetrapods growth with large diameter of arms.

2. Experimental

The ZnO tetrapod nanorods were synthesized by two steps. Firstly, we deposited the zinc thin films on the sapphire (0001) substrates using PLD-(III) system. The incident laser beam is from Nd:YAG laser with 1064 nm wavelength. The pulse duration is 10 ns and the repetition rate is 10 Hz. Its energy density is 20 J/cm^2 in this work. We deposited the zinc thin films at 100°C for 30 min, and maintained the argon pressure at 0.1 torr during the experiment. The thickness of deposited zinc thin films was 100 nm approximately. Secondly, the prepared zinc thin films by PLD and the high purity metallic Zn powder (99.99 %) were placed on a quartz boat and annealed in the conventional horizontal tube furnace (L4513II-2/QWZ). During the growth process, the temperature was maintained at 900°C for 30min. The two sides of the horizontal tube furnace were open, so the ZnO tetrapods were grown in the air. The product after these two steps is named Sample 1. In the same time, to study the effect of the zinc thin film on the growth of the ZnO tetrapods, we also put the sapphire substrates without the zinc thin film into the conventional horizontal tube furnace in the second step. The obtained product is named Sample 2.

The crystalline structure was examined by X-ray diffraction (XRD, A Rigaku D/max-rB X-ray diffraction meter with Cu K α -line). The morphologies and microstructures were characterized by scanning electron microscopy (SEM, Hitachi S-570), transmission electron microscopy (TEM , Hitachi H-800) and high resolution transmission electron microscopy (HRTEM, JEOL JEM2100, 200 kV). The photoluminescence spectrum (PL) of the sample was carried out at room-temperature by Edinburgh Instruments FLS920 steady-state fluorescence spectrometer (U. K.) using the Xe lamp with a wavelength of 280 nm as the excitation source.

3. Results and discussion

3.1. XRD

Fig. 1 shows the XRD stereo patterns of Sample 1 and Sample 2. The diffraction patterns are quite similar for the two samples. The peaks can be indexed as the hexagonal wurtzite structure of ZnO with the lattice parameters of a=0.3249 nm and c=0.5206 nm. No characteristic peaks of the impurities are observed in any samples. Obviously, all the peaks of Sample 1 are much sharper and stronger than those of Sample 2, which indicate that Sample 1 has a high crystal quality.

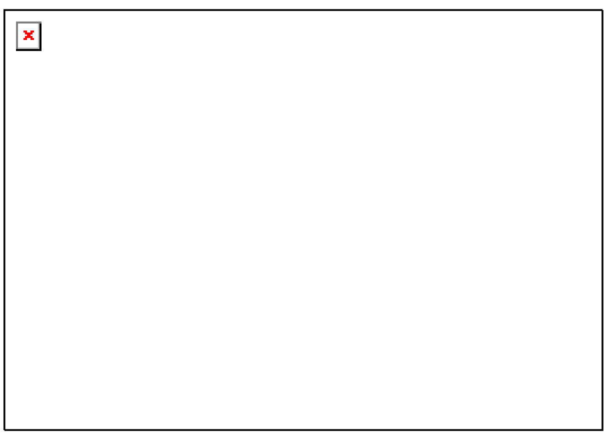

Fig. 1 The XRD stereo patterns of the ZnO tetrapod nanorods

The XRD results of Sample 1 and Sample 2 implicates that the zinc thin films on the sapphire substrates prepared by PLD will make the ZnO tetrapod nanorods grown with a high crystal quality.

3.2. SEM

A typical SEM image of Sample 1 is shown in Fig. 2(a). It demonstrates that ZnO tetrapod nanorods with uniform sizes were formed. The length of these arms is 1.5 – 2 μm and the average diameter is about 200 nm. The arms are prisms with a hexagonal cross section and have smooth surfaces. Some nucleus can be observed at the center of the ZnO tetrapods. Fig. 2(b) shows the SEM image of Sample 2, we also obtained the ZnO tetrapod nanorods. Compared with Sample 1, no nucleus can be seen, the average diameter of the ZnO tetrapod nanorods for Sample 2 is smaller obviously and many other structures immingle in it.

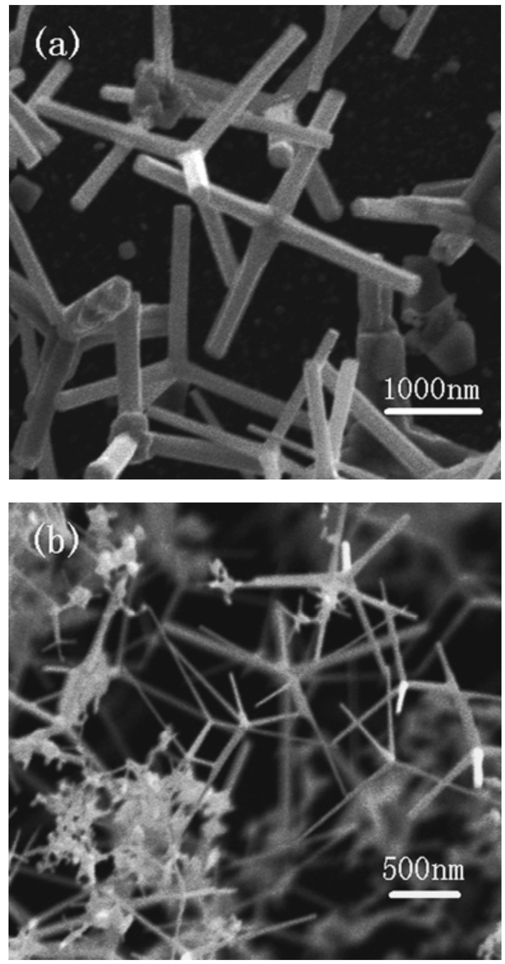

Fig. 2 The SEM images of the ZnO tetrapod nanorods: (a) Sample 1 grown with zinc thin film; (b) Sample 2 grown without zinc thin film.

From the mentioned above, we can infer that the zinc thin films have a great influence on the growth of the ZnO tetrapod nanorods. Under the same experimental conditions, the thick ZnO tetrapods can be acquired using the prepared zinc thin films.

3.3. TEM And HRTEM

Fig. 3(a) shows the TEM image of one arm in Sample 1. At the tip of the arm, an area has been selected to perform the HRTEM study, and it's image is shown in Fig. 3(b). From the image, a lattice spacing of the selected area is measured as 0.26 nm, which corresponds to the [0002] plane of the wurtzite ZnO [1]. This indicates that each arm grows preferentially along the [0001] direction. The parallel and uniform [0002] planes illuminate that Sample 1 is the hexagonal wurtzite structure of the ZnO with a high crystal quality, which is consisted with the XRD result.

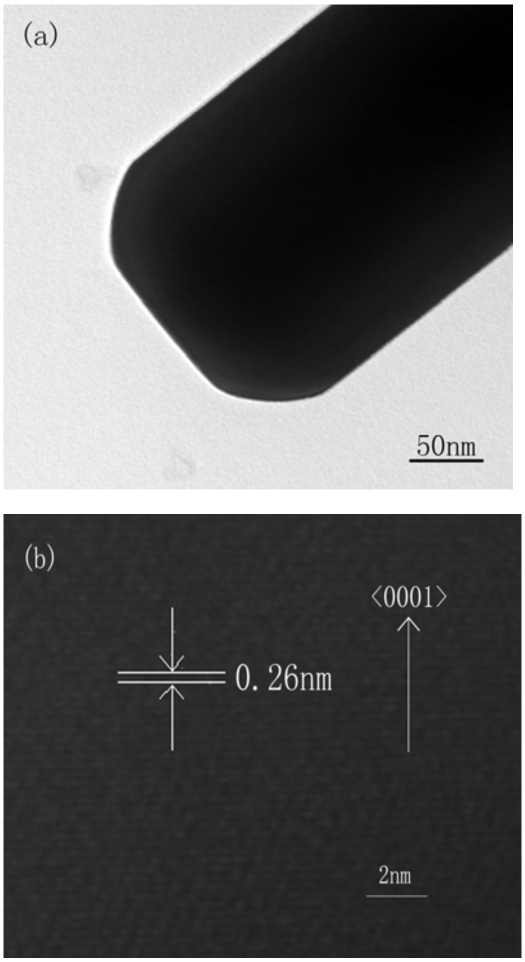

Fig. 3 (a) high magnification TEM image of the single ZnO rod of Sample 1, (b) the corresponding HRTEM images.

3.4. Optical Properties

As a good candidate in the application of the photoluminescence, the optical properties of the ZnO has been attracted much attention. In this paper, the Photoluminescence (PL) spectrum of ZnO tetrapod nanorods at room temperature was measured for Sample 1 and shown in Fig. 4. One shoulder peak centered at 397nm (UV) and two strong green emission bands centered at 520 nm and 555 nm can be found. It is well known that the UV emission which is originated by the band-edge transition or the exciton transition is the characteristic emission of the ZnO. The green emission is most likely related to the structural defects such as the singly ionized oxygen vacancies and the interstitials of the ZnO [22]. Therefore, the relatively strong green emission may indicate the existence of a high concentration of oxygen vacancies within the nanotetrapods. In our experiment, no directional air current flows through the furnace, the products grew in the atmosphere with the insufficient oxygen. Therefore, oxygen vacancies for Sample 1 are formed easily during the growth process.

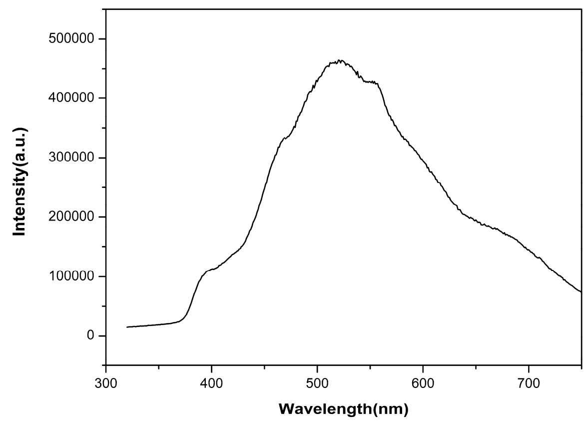

Fig. 4 The room temperature PL spectrum of the ZnO tetrapod nanorods of Sample 1.

Besides the two-band fluorescence mentioned above, a blue band centred at 468nm is recorded in this work. This peak was also found in the ZnO nanorods arrays [23]. It is generally accepted that the blue emission might be due to the existence of oxygen-depleted interface traps in ZnOx [24].

4. Growth mechanism analysis

In our experiment, the zinc thin films on the sapphire substrates and the zinc powder are annealed in the horizontal tube furnace simultaneous at 900 ℃. The zinc vapor which is from evaporating the zinc powder in the air will be oxygenated partially and changed into ZnO_x (x<1). In fact, the blended steam of the Zn and the ZnO_x existed in the furnace. For Sample 1, the zinc source comes from two parts: one is the vapor of the zinc powder and the other is the zinc thin films produced by PLD. When the zinc thin film is annealed, the zinc atoms on the substrates obtain the enough energy and move to the minimum energy position of the substrate. They aggregate together and form the Zn liquid droplets. These droplets are oxygenated easily, so there are a lot of liquid droplets of the Zn and the ZnOx mixture on the surface of the substrate. These mixed droplets can absorb the blended steam of the Zn and the ZnO_x coming from the zinc powder vapor effectively during the nucleus growth process. Obviously, the zinc thin films have a great effects on the growth process.

Because the exist of the Zn liquid droplets is the catalyst, we believe that the vapor-liquid-solid (VLS) growth mechanism [25] plays an important role in the growth process of Sample 1. Iwanaga et al [26] proposed an octa-twin growth model for the ZnO tetrapod nanocrystals, and it has been generally accepted. We consider that the octa-twin only exists in the beginning of the crystal growth process. ZnO is a polar hexagonal and highly anisotropic crystal, which implies that its growth direction is along the c-axis. Therefore, the four arms grow out from the four +c planes of the octa-twin along the [0001] direction. During the growth process, the gas phase molecules of the Zn and the ZnO_x deposit at the root of arms and move to the top of the arms which make the arms grow long. In Fig. 1(a), some big nucleus still can be seen in the centers of the ZnO tetrapods, which proves our ideas powerfully. The vaporing speed of the limited zinc powder is rapid. Therefore, the saturated vapor pressure in the furnace descends with the growth time increasing. In the same time, the deposition speed of the Zn and the ZnOx at the roots becomes slow till stops. With the growth process, the ZnO nucleus will became smaller gradually and disappear, they will evolve into the junction of the ZnO tetrapods. We call this evolvement process "dispersal". Fig. 5 shows the schematic model of the junction of ZnO tetrapod nanorods whose nucleus has dispersed. In this work, the growth time is 30 min, which is so short for the big nucleus that the nucleus didn't disperse, as shown in Fig. 1(a). While for the some small ones, the nucleus have been dispersed into the four arms in 30 min. As shown in Fig. 6, one arm of the ZnO tetrapod nanorods was covered and in the back of the image. From this image, the interfaces between each of the arms can be seen, no nucleus is observed. There are still some remains of the dispersed nucleus can be found as marked with the arrow. This is consisted with the schematic model in Fig. 5.

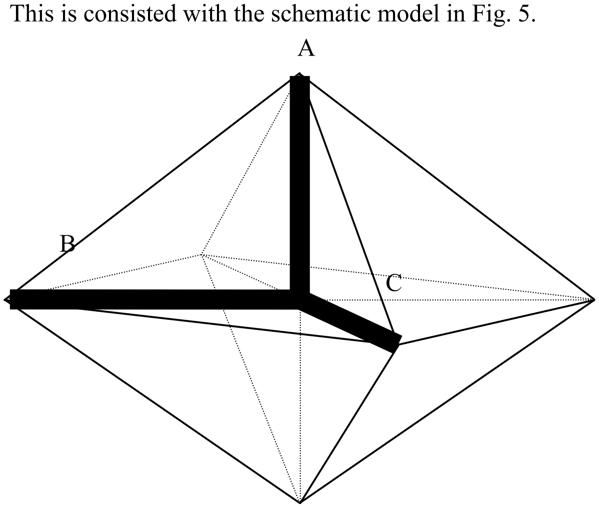

Fig. 5 The schematic model of the junction of ZnO tetrapod nanorods.

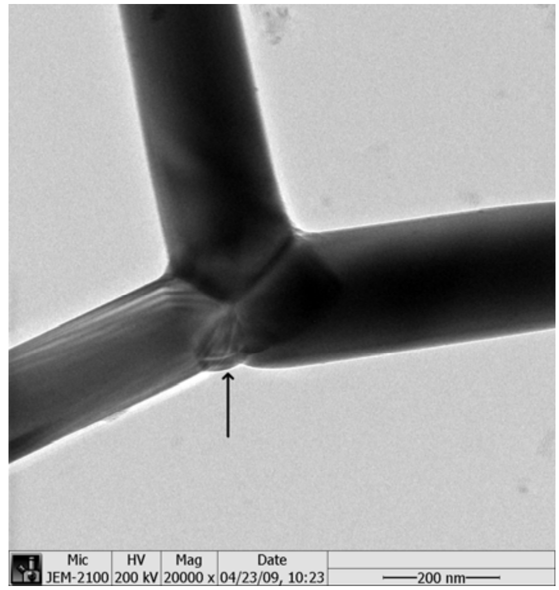

Fig. 6 The low magnification TEM image of the junction of the ZnO tetrapod nanorod in Sample 1 whose one arm is covered and in the back of the image.

All of the mention above confirms that the saturated vapor of the Zn and the ZnOx will deposit at the root and the nucleus will disperse into the four arms in the end of the growth process in further. As for Sample 2, the zinc source is only from the blended steam of Zn and ZnOx from vapor of the zinc powder. The vapor deposits on the substrate directly, gathers and forms the nucleus. Then, the ZnO tetrapods are grown. Therefore, we consider that the vapor-solid (VS) growth mechanism is the main function [27]. The insufficiency of zinc material makes for the average diameter small.

5. Conclusion

To sum up, the high-yield and uniform ZnO tetrapod nanorods have been synthesized by two-step method. The zinc thin films on the substrates prepared by PLD will make the ZnO tetrapod nanorods grown uniformly with a high crystal quality and the thick arms. During the growth process, gas phase molecules of the Zn and the ZnOx deposit at the root of arms. The octa-twin will disperse into arms in the end stage of the growth process of the ZnO tetrapods. Three emissions are obtained, they are a UV emission, two green emission and a blue band in Photoluminescence spectrum.

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