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RESEARCH ARTICLE

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Hydrothermal synthesis of 2D ordered macroporous ZnO films

Abstract The ZnO films with two-dimensional ordered macroporous structure were successfully fabricated through hydrothermal crystal growth of ZnO on the ZnO substrate covered with a monolayer of polystyrene (PS) spheres as template. The precursor solution of hydrothermal crystal growth of ZnO were prepared by equimolar solution of $Zn(NO_3)_2 \cdot 6H_2O$ and hexamethylenetramine (HMT). The confinement effect of the PS spheres template on the growth of ZnO nanorods and the influence of sodium citrate on the crystal growth of ZnO had been studied. The film surface morphology and the preferential growth of ZnO crystal were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. Also, the photoluminescence spectrum of ZnO films had been measured, and the corresponding mechanism was discussed.

Keywords ZnO, hydrothermal crystal growth, sol-gel, inverse opal structure

1 Introduction

Zinc oxide (ZnO), as an important direct band-gap semiconductor, has a wide band-gap of 3.37 eV and large free exciton binding energy of 60 meV at room temperature. Its free exciton binding energy is much larger than that of ZnSe (22 meV) or GaN (25 meV). Thus, it ensures the realization of excitonic emission at room temperature and generates near ultraviolet short wave which can be utilized for the fabrication of photoelectric devices such as light-emitting diode [1] and ultraviolet laser [2]. Other unique properties of ZnO such as piezoelectricity, optical absorption and emission [3,4] made ZnO be very useful in the applications of sensors [5], solar cells [6] and photonic crystals [7]. For this reason, ZnO has become one of hot topics in the research field of semiconductor materials. Besides, owing to quantum size effect, low-dimension materials of ZnO, such as nanorods, nanowires, nanobelts and nanotubes, show a series of new specialties and have been paid much attention.

Arrays of the low-dimension material of ZnO can confine the movement of exciton and enhance the transition intensity. Furthermore, the structure of hexagonal arrays of ZnO microrods can be regarded as natural laser resonance. Therefore, it has enormous application value in photoelectric devices, such as solar cells and piezoelectric materials, in virtue of its particular properties of optics and electrics. Two-dimensional arrays of ZnO materials are usually fabricated by micro/nano processing techniques and photolithographic techniques [8–10]. Photolithographic techniques have many disadvantages such as high cost, low processing efficiency and environment unfriendly. On the contrary, wet chemistry method is a low cost, environmental benign technique for fabricating ZnO microstructures.

The films of highly ordered micropattern have been reported by utilizing microsphere templating methods [11,12]. Recently, highly ordered arrays of ZnO nanorods/wires materials have been reported [13,14]. Fan et al. [15–17] and Wang et al. [18–20] reported the fabrication of the large scale ordered arrays of ZnO nanorods via vapor-liquid-solid (VLS) method, respectively. In this paper, a new method for synthesis of the ordered macroporous films on ZnO substrate was reported, where microsphere template was used as template in the ZnO hydrothermal growth process [21,22].

In this study, ZnO polycrystalline film was used as seeds for the subsequent hydrothermal growth process. Well-aligned dense arrays of ZnO nanorods were successfully obtained due to preferential nucleation of ZnO nanorods on the polycrystalline seed substrate. Furthermore, with the assistance of polystyrene (PS) spheres template, the hexagonal arrays of ZnO nanorods have been obtained due to the confinement of PS spheres on the growing process. More interesting, it was found that the growth morphology can be well controlled by adding sodium

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citrate in the hydrothermal growth process. The structural transition from nanorods arrays to compact and highly-ordered macroporous films was obtained in this experiment. The present study provides a new method for large scale epitaxial growth of ZnO ordered nanostructures, which has potential applications in improving luminescence efficiency and producing quantum devices.

2 Experimental

Firstly, hexamethylenetramine (HMT) was heated in the aqueous solution and decomposed into formaldehyde (HCHO) and ammonia gas (NH_3). Then, NH_3 gradually dissolved in water and formed ammonia ($NH_3{\cdot}H_2O$). Because of the ionization of $NH_3{\cdot}H_2O$, OH^- existed and showed the property of alkalescence. Zn^{2+} combined with OH^- forming $Zn(OH)_2$. Finally, $Zn(OH)_2$ was dehydrated and formed ZnO. The whole process can be represented by the following chemical reactions:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \qquad (1)$$

$$NH_3 + H_2O \rightarrow NH_3{\cdot}H_2O \qquad (2)$$

$$Zn^{2+} + 2NH_3{\cdot}H_2O \rightarrow Zn(OH)_2 + 2NH_4^+ \qquad (3)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \qquad (4)$$

In experiments, a piece of glass slide with the size of 3.8 cm × 1.2 cm was put into chromic acid solution washing for 24 h and then cleaned several times in de-ionized water. The glass slide was dried by nitrogen gas. The sol-gel solution of ZnO was made according to the method of Meulenkamp [23]. The seed polycrystalline ZnO substrate was prepared through homogeneously pulling the clean glass slide from the sol-gel solution. The pulling speed was set at 0.4 cm/min. Then, the ZnO seed substrate prepared was put into the muffle oven for annealing at 450°C in order to make it crystallize and remove the organic compounds and impurities. The monolayer of PS spheres template was prepared as follows: mixing the PS latex spheres (the diameter of the particles is 1 μm and the weight fraction is 5.5 wt %) with the ethanol solution (4:3 in volume ratio) sufficiently in an ultrasonic bath. A little amount of the mixed liquid was put out by the pipette and dripped into a beaker filled with de-ionized water. Due to influence of water surface tension, a monolayer of PS spheres formed on the surface of water. The multicolor light reflection from the surface can be observed clearly under the illumination of light. Then, the ZnO seed glass substrate prepared was inserted into the beaker and lifted out slowly the dispersed monolayer from the water. Before the hydrothermal synthesis, the glass slide covered with the PS spheres should be heated at the temperature of 90°C for 0.5 h, in order to strengthen the connection between the PS spheres and the substrate. The precursor solution of hydrothermal growth of ZnO was prepared by equi-molar solution of $Zn(NO_3)_2{\cdot}6H_2O$ and HMT. The precursor solution was put into a 45 ml glass bottle and dispersed it by ultrasonic cleaner, and then put it into an autoclave. The glass slide, which was used for hydrothermal growth process, was fixed vertically in the solution. The growth process was kept at a constant temperature for 2 h or 24 h according to the need. When the growth process was finished, the substrate plate was put out from the autoclave and washed in de-ionized water for several times, and then dried naturally in air.

3 Results and discussion

Combining the PS sphere template method and the hydrothermal growth technique, the nanorod arrays and highly-ordered macroporous ZnO films have been successfully fabricated. Because the growth space (the interstitial space among three PS spheres and the substrate) is only of nanometer-sized order in size, the key issue is how to control the crystal growth in such a tiny space. Controlling nucleation and growth rates for different crystalline planes play an important role in this process. All these key factors determined the morphology and quality of the as-prepared materials. In section 3.1, the experimental results of arrays of ZnO nanorods and ordered porous materials are described. In section 3.2, the key factors and corresponding mechanism in the fabricating process are discussed.

3.1 PS-spheres-template-assisted hydrothermal synthesis for arrays of ZnO nanorods and ordered porous materials

According to the experimental method, 15 ml precursor solution was prepared, and hydrothermal growth temperature was set at 90°C and growth time was 2 h. Fig. 1(a) shows a SEM image of ZnO nanorods grown from PS spheres covered substrate. It clearly illustrated that ZnO nanorods can grow from the interstitials among the PS spheres. Fig. 1(b) shows a large scale SEM image of ZnO nanorods arrays after removal of PS spheres from the substrate. Because of the confinement of the PS spheres template, the as-grown ZnO nanorods show ordered hexagonal symmetry, which proves that this method can be used for fabricating ordered arrays of ZnO nanorods. The inset of Fig. 1(b) is a high magnification SEM image of ZnO morphology beneath a PS sphere. It shows that tiny ZnO nanorods did grow from the seed substrate even if the growth place was fully covered by PS spheres, but can not grow up sufficiently. Moreover,

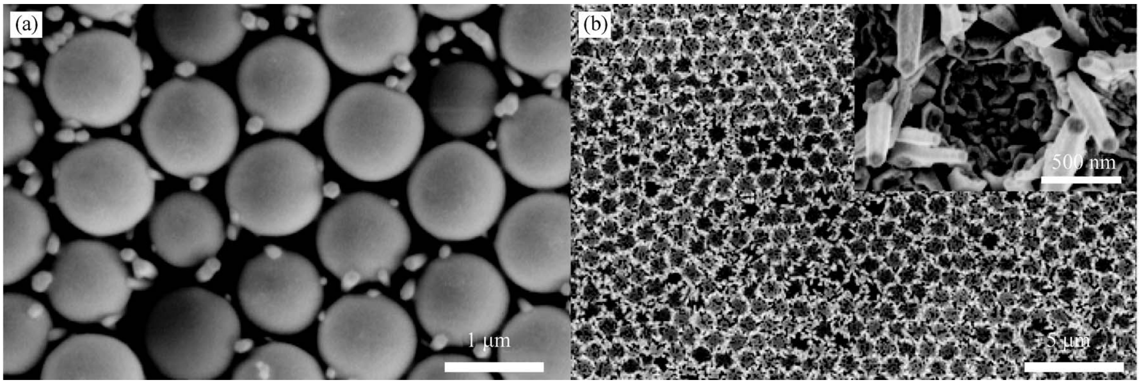

Fig. 1 (a) SEM image of ZnO nanorods with PS spheres assisted (PS spheres are not removed yet); (b) SEM image of ZnO nanorods with PS spheres assisted (PS spheres have been removed), the inset shows the corresponding enlarged local field

spherical growth outline surrounded by ZnO nanorods can be seen obviously. The experiments indicated that the existence of PS spheres has confinement effect on the growth of ZnO nanorods just beneath the PS spheres. Therefore, hexagonal arrays of ZnO nanorods are presented on the substrate. It is obvious that PS spheres template method can effectively control the growth morphology of ZnO nanorods. However, to get continuous and close-grained films with ordered pore structure, using the template method alone is not enough to control the growth procedure.

It is well known that ZnO is a polar crystal. Growth rates for various crystalline planes can be presented as follows: $V_{\langle 0001\rangle} > V_{\langle 01\overline{1}\overline{1}\rangle} > V_{\langle 01\overline{1}0\rangle} > V_{\langle 01\overline{1}1\rangle} > V_{\langle 000\overline{1}\rangle}$ [24]. The two surfaces for a ZnO crystal are named as Zn-terminated (0001) surface and O-terminated (000) surface. It has been demonstrated that adding sodium citrate into the growth solution can modulate the growth rates for different polar surfaces of ZnO crystal [25–27]. The growth morphology can be controlled through this modulating effect of sodium citrate. Hence, the continuous and close-grained ZnO with ordered porous structures are successfully fabricated through the confinement of PS spheres template in combination with the influence of sodium citrate on the growth rate for various ZnO crystal planes. According to the experimental method, 30 ml precursor solution was prepared, then 1.5 mg sodium citrate was added, and hydrothermal growth temperature was set at 60°C and growth time was 24 h. Removing the PS spheres when experiment completed, ZnO inverse opal structure can be obtained, as showed in Fig. 2. The effect of sodium citrate on the growth morphology can be well illustrated from the following experimental results: ZnO nanorods showed loose columnar-like arrays morphology without adding of sodium citrate, while uniform compact film of inverse opal structure can be obtained after removal of PS spheres template with adding of sodium citrate. The mechanism of adding effect of sodium citrate can be understood as follows: citrate ions in the growth solution can easily adsorb on the polar Zn-terminated (0001) planes and counteract the reaction between OH^- in solution and Zn^{2+} on (0001) surface, and thus slow down the growth rate in the $\langle 0001\rangle$ direction, in the meanwhile the crystal growth in other directions are not restrained. Therefore, the addition of sodium citrate suppressed the preferentially rapid growth of ZnO in $\langle 0001\rangle$ direction and uniformed the crystal growth. Thus, morphological transition from nanorod arrays to compact films was obtained in the experiments.

Figure 3 shows the XRD pattern for polycrystalline ZnO seed substrate and ZnO film after hydrothermal reaction. The film thickness of ZnO seed substrate is too thin to be detected by the XRD. Instead, only amorphous diffraction peak from the glass slide can be observed, as shown in Fig. 3(a). After the hydrothermal growth process, the film thickness increased to be about 500nm and the diffractions from the as-grown porous ZnO film can be well distinguished in Fig. 3(b). According to the Joint Committee on Powder Diffraction Standards (JCPDS Card No.: 36–1451), it can be deducted that this porous film has hexagonal wurtzite structure. The difference between the pattern of ours and ordinary XRD pattern is that the peak intensity of (002) plane is obviously high in

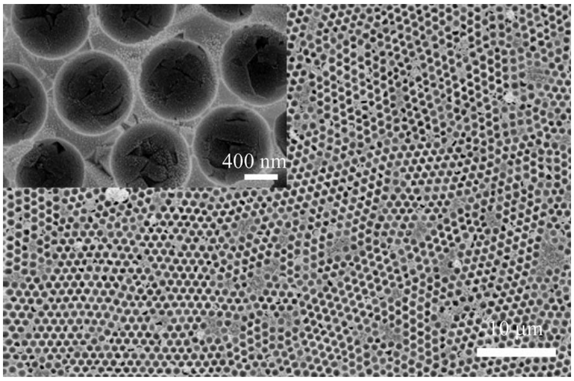

Fig. 2 SEM image of ZnO inverse opal fabricated via hydrothermal method with the addition of sodium citrate, the inset shows the corresponding enlarged local field

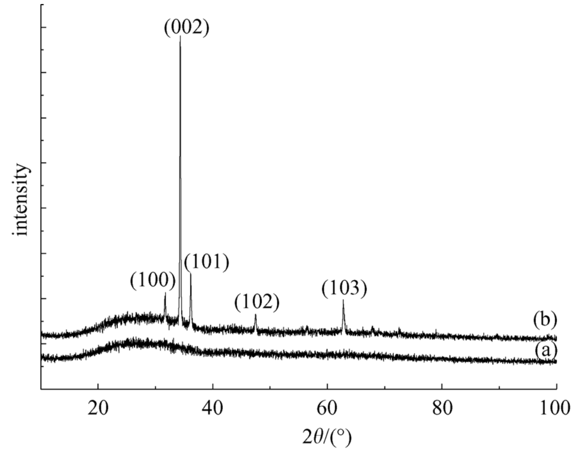

Fig. 3 (a) XRD pattern of ZnO films fabricated via sol-gel method; (b) XRD pattern of 2D periodically ordered macroporous ZnO films after hydrothermal reaction

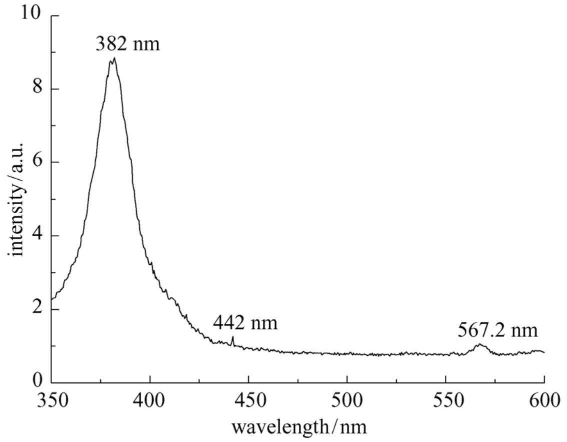

Fig. 4 Photoluminescence spectrum of 2D ordered macroporous ZnO films with excitation wavelength 325nm

Fig. 3(b), which indicates the preferential growth in the direction perpendicular to the surface of the porous films.

In order to investigate the optical property of the 2D ordered porous ZnO films, the photoluminescence spectrum of which has been measured, as shown in Fig. 4. The photoluminescence excitation photon wavelength is 325 nm (3.81 eV). The photoluminescence spectrum has three obvious luminescence bands, including a strong ultraviolet, a weak blue and a green emission band centered at about 382 nm (3.25 eV), 442 nm (2.81 eV) and 567.2 nm (2.19 eV), respectively. Because ZnO has a high free exciton binding energy of 60 meV, which is much larger than thermal ionization energy (26 meV), the excitonic emission at room temperature can be observed. And the photon energy of emission peak at about 382 nm (3.25 eV) is a little lower than the energy gap (3.37 eV) of ZnO at room temperature. Therefore, the peak could be assigned to the exciton recombination between conduction band electrons and valence band holes, namely band edge exciton transition [28,29]. The blue emission peak at about 442 nm may be due to the transition of electrons from conduction band to deep acceptor level (zinc vacancy or interstitial oxygen) or from shallow donor level (interstitial zinc or oxygen vacancy) to valence band [30–32]. It is generally accepted that the visible light emission is due to the deep level transition from oxygen vacancies [33,34]. However, the visible light emission peaks are not strong in Fig. 4, which indicates that the as-prepared films have relatively-high crystal integrity.

3.2 Effect of ZnO seed substrate and sodium citrate on the hydrothermal crystal growth of ZnO

The fabrication of porous ZnO films was affected by many factors, such as the nucleation on the polycrystalline seed substrate, the confinement of the PS template, and the addition of sodium citrate. To study the influence of the seed substrate, the hydrothermal growth experiments with and without assistance of the seed substrate were carried out. The SEM images in these two cases are shown in Fig. 5. Figure 5(a) shows that well-aligned ZnO nanorods in the growth without ZnO seed substrate can not be

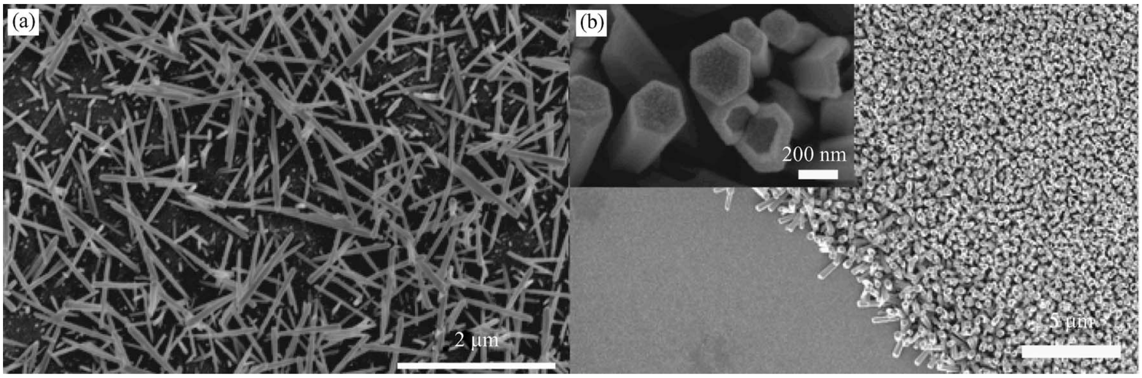

Fig. 5 (a) SEM image of ZnO nanorods fabricated via hydrothermal method without ZnO seeds layer; (b) SEM image of ZnO nanorods fabricated via hydrothermal method with ZnO seeds layer (margin of the seeds layer), the inset shows the corresponding enlarged local field

obtained. ZnO nanorods just deposit on the substrate randomly. On the contrary, Fig. 5(b) shows that ZnO nanorods have a dense distribution and well orientation. The ZnO nanorods, whose ends have regular hexagon shapes as shown in the inset of Fig. 5(b), are pillar-like and the diameter is about 200 nm. Although PS spheres template can be used to get ordered porous structure, the interstitial space among the PS spheres is so small that it hindered solute diffusion due to the influence of surface tension. The existence of seed substrate, in some extent, can facilitate the crystal growth in such a small space.

In order to analyze the effect of sodium citrate on the morphology of ZnO crystal growth, the hydrothermal growth process without PS spheres template on ZnO seed substrate was directed performed. The surface morphology of as-grown film is shown in Fig. 6. Instead of nanorods arrays, the compact ZnO film was obtained with addition of sodium citrate, even no PS spheres template was used in the experiments. It indicated that the addition of sodium citrate did affect the growth morphology. From the inset of Fig. 6, it can be clearly seen that the films are composed of small crowded micro-crystals. The reason is that, the ZnO seed substrate is a polycrystalline film. When sodium citrate is added, the growth predominance in $\langle 0001 \rangle$ direction can not significantly affect. Instead, the crystal growth developed along all crystal planes, which results in crowded micro-crystals morphology. The random growth other than orientated growth is due to the overlapping of various micro-crystals. It can be seen that sodium citrate plays an important role in the morphology control of hydrothermal crystal growth of ZnO.

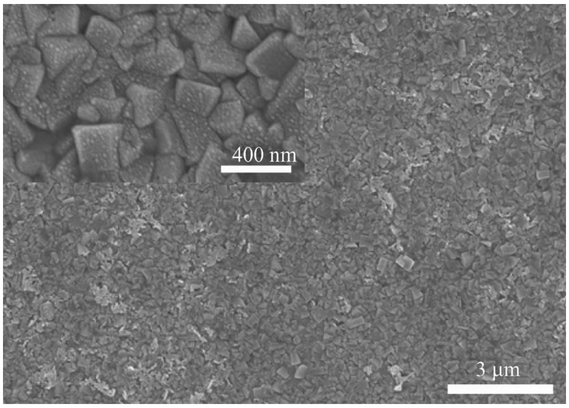

Fig. 6 SEM image of ZnO films fabricated via hydrothermal method on ZnO seeds layer with the addition of sodium citrate, the inset shows the corresponding enlarged local field

4 Conclusions

Highly-aligned arrays of ZnO nanorods have been successfully fabricated by using hydrothermal crystal growth method. And with the assistance of monolayer PS spheres template, the hexagonal arrays of ZnO nanorods was obtained. ZnO films with inverse opal structure have been synthesized by addition of sodium citrate. Results of SEM, XRD and photoluminescence spectrum indicated that the films are compact, orientational and have good quality of crystallization. By using PS spheres template to assist the hydrothermal crystal growth process, ZnO micro/nano structure with the controllable morphology has been successfully achieved. This simple and cost-effective wet chemistry method has a promising application in mico/nano processing technology.

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