Cryst. Res. Technol. **43**, No. 12, 1314 – 1317 (2008) / **DOI** 10.1002/crat.200800157

Synthesis and optical properties of ZnO nanorods

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Received 4 May 2008, accepted 9 June 2008

Key words ZnO nanorods, chemical synthesis, optical properties.
PACS 78.55.Et

ZnO nanorods were prepared on the silicon (100) substrates using the chemical solution deposition method (CBD) without catalyst under a low temperature (90°C). The cool water was used to dissolve the mixture of zinc nitrate hexahydrate ($Zn\ (NO_3)_2{\cdot}6H_2O$) and methenamine ($C_6H_{12}N_4$) in order to decrease the size of ZnO nanorods. From the X-ray diffraction (XRD) results, it can be seen that the growth orientation of the as-prepared ZnO nanorods was (002). Scanning electron microscopy (SEM) results illustrated that the nanorods had a hexagonal wurzite structure and average diameter of about 120nm. The average diameter of nanorods prepared by the cool water process was much smaller than that by the room-temperature (RT) water process we always used. Photoluminescence (PL) measurements were also carried out. The result showed that a blue shift in UV emission band appeared in the PL spectrum of the sample grown with cool water process, which was mainly due to the reduction of tensile strain when the diameter of the ZnO nanorods decreased.

1 Introduction

In recent years, ZnO nanostructure semiconductor materials have attracted much attention due to their great potential in aspects of fundamental studies and applications. For fundamental studies, it is a good candidate to investigate the effects of dimension and size on the physical properties due to its flexible shape. For applications, ZnO is an exceptionally important functional material for pigments, rubber additives, gas sensors, varistors, and optical devices due to its direct band gap of 3.37eV [1,2]. And as well as it is also expected to be a promising candidate for room-temperature UV laser utilization [3,4] due to large exciton binding energy of 60meV which could lead to lasing action based on exciton recombination even above room temperature [5,6]. Up to now, many approaches have been developed to synthesize 1D-ZnO nanorods, such as metal organic vapor phase epitaxy, pulsed laser ablation, metal organic chemical vapor deposition, electrodeposition and hydrothermal method [7-11]. Compared with those methods, chemical solution deposition method can be controlled easily, and no sophisticated equipments are required. In addition, the experiment can be carried out under low temperature. Therefore, in this paper, two series of ZnO nanorods with different growth conditions are prepared by the method of CBD, wherein no catalysts are involved. Then their structure, morphologies and optical properties are studied.

2 Experimental

ZnO nanorods were grown on the Si (100) substrates by the CBD method. Precursor solutions were prepared by dissolving the zinc nitrate hexahydrate [$Zn\ (NO_3)_2{\cdot}6H_2O$, 99.9% purity] and methenamine ($C_6H_{12}N_4$, 99.9%

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purity) in the cool deionized water. The concentration of zinc and amine were fixed at 0.1M. In contrast with the cool water process, we prepared another sample whose precursor solutions were dissolved in the RT deionized water.

The Si (100) substrates were cleaned with the mixture of Hydrofluoric Acid and H_2O (keeping 1:1 ratio by volume), deionized water, respectively. Then, the Si substrates were immersed in the precursor solution and tilted against the wall of beaker, which was put into an oven for several hours without any stirring at 90°C. Subsequently, the thin films were thoroughly cooled to room temperature, washed with deionized water and dried in air. XRD (MAC Science, MXP18, Japan), SEM (Hitachi, S-570) and PL (He-Cd Laser, 325nm) were used to characterize the crystal structure, surface morphologies and optical properties of ZnO nanorods.

3 Results and discussion

Figure 1 shows the XRD patterns of the ZnO nanorods deposited on the Si substrates with different processes. All the peaks of the XRD patterns can be indexed to ZnO with the hexagonal wurtzite structure. No diffraction peaks are detected from any other products. Strongest intensity of the diffraction peak corresponding to (002) plane indicates that all the samples grow along c-axis.

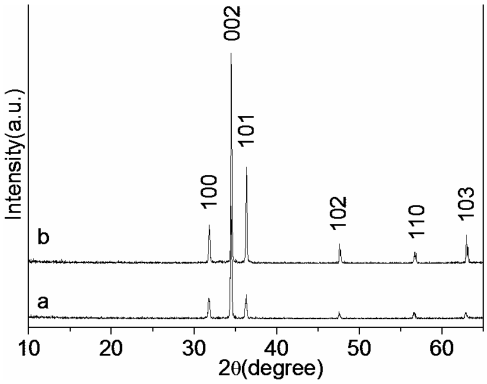

Fig. 1 XRD patterns of ZnO nanorods on Si substrates when the molar concentration of zinc nitrate is 0.1M and the reaction time is 12h, (a) cool water process; (b) RT water process.

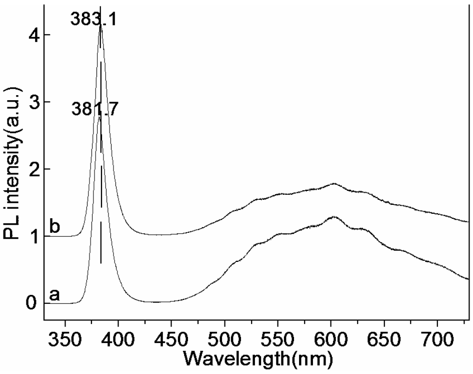

Fig. 3 PL spectra of ZnO nanorods on Si substrates when the molar concentration of zinc nitrate is 0.1M and the reaction time is 12h, (a) cool water process; (b) RT water process.

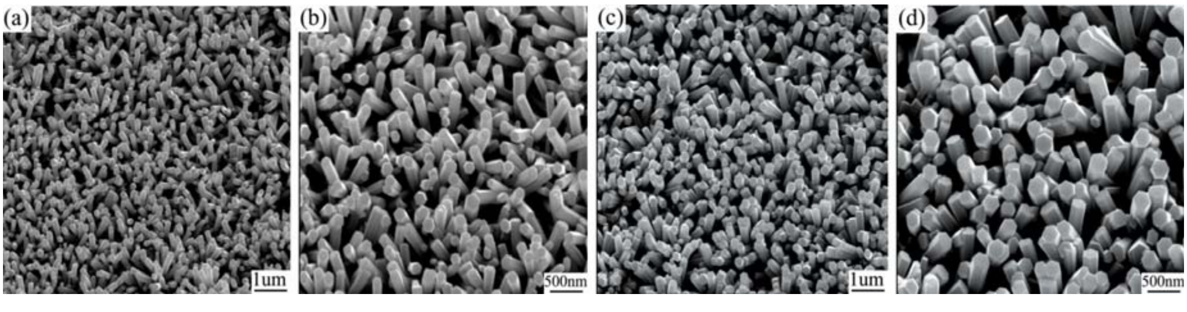

Fig. 2 SEM images of ZnO nanorods on the Si substrates when the molar concentration of zinc nitrate is 0.1M and the reaction time is 12h, (a, b) cool water process; (c, d) RT water process.

Figure 2 shows the SEM images of ZnO nanorod arrays grown on the Si substrates with different processes. Compared with the two images (Fig. 2 (a) and Fig. 2 (c)), the diameter is smaller when the cool water process was used. The high magnification picture shows that the hexagonal ZnO nanorods with the diameter of 120 nm formed over the entire Si substrate using the cool water process, which can be clearly seen in figure 2 (b). Meanwhile, as shown in figure 2 (d), the ZnO nanorods with hexagonal structure have an average diameter of 240 nm. The result indicates that the cool water process is actually beneficial to decrease the diameter of the nanorods. The reason for different diameter of the ZnO nanorods obtained on the Si substrates should be related to the nucleation mechanism in the solution. The CBD method is based on the formation of solid phase from the solution, which involves two steps as nucleation and growth [12]. In the process of nucleation, the clusters of molecules formed undergo rapid decomposition and particles combine to grow up to a certain thickness of the film by heterogeneous reactions at the substrate surface. When the solution is heated, the precipitation on the down face forms the ZnO nuclei, thus ZnO nanorods grows from the nuclei on the substrate. In this experiment, we adopt the cool water to dissolve the mixture, which can drastically reduce the initial temperature of the solution. It can successfully suppress the ZnO nuclei to become large. As we known, the diameter of the ZnO nanorods is mainly restrained by the size of the nuclei. Therefore, we adopt the cool water process to control the size of ZnO nanorods efficiently. In addition, in figure 2, the nanorods have uniform orientation with different processes. It illustrates that the cool water process can not only reduce the diameter of nanorods but also can not affect the tendency of orientation of nanorods.

Figure 3 illustrates the room-temperature photoluminescence (PL) spectra of ZnO nanorods grown on the Si substrates with different processes. The two emission bands are observed in the entire photoluminescence spectrum for ZnO: one is an UV emission due to excitonic recombination [13,14] and the other is a wide emission band contained several emission peaks such as green, orange and red which is related to defects in the ZnO nanorods. Generally, the green emission was due to the point defects, such as oxygen vacancies or impurities [15]. The orange and red luminescence was attributed to the intrinsic defect in ZnO such as oxygen interstitials [16, 17], and perhaps had much to do with the structure of ZnO_2 [18]. In comparison with the PL spectrum of the sample grown with RT water process (Fig.3 (b)), the intensity of UV peak in the PL spectrum form the sample grown with cool water process decreased, and on the contrary the intensity of the green and orange emissions increased as shown in figure 3 (a). To ascertain by computation [19], the relative PL intensity ratio of ultraviolet emission (I_{UV}) to deep level emission (I_{DLE}) of ZnO nanorods grown by the cool water process is estimated to be about 2.2 and that of the RT water process is about 4.0. The intensity ratio of I_{UV}/I_{DLE} is related with the crystallization. ZnO nanorods would have much better crystallization according to the larger intensity ratio. In the cool water process, the solution usually need much more time to reach the optimal temperature (90°C), but ZnO nanorods have already grown during this increasing temperature period. Therefore, compared with the RT water process, more defects formed in the ZnO nanorods. In addition, the UV peak appearing at 381.7 nm wavelength in figure 3 (a) shows a slight blue shift in comparison with figure 3 (b) which UV peak appearing at 383.1 nm wavelength. The slight blue shift in UV emission from (b) to (a) is due to the tensile strain which turns reductive as the diameter of the ZnO nanorods decreases [20, 21].

4 Conclusion

In this paper, ZnO nanorods have been successfully prepared by a simple CBD method on the Si substrates. The effect of cool water process on the diameter of the ZnO nanorods is discussed. It indicates that the cool water process can effectively decrease the diameter of the nanorods. And it can not affect the tendency of orientation of nanorods. Photoluminescence measurements show that the slight blue shift in UV emission is mainly due to the reduction of tensile strain when the diameter of the ZnO nanorods decreases.

Acknowledgements We would like to thank financial support of the National Nature Science Foundation of China (Grant Nos. 60778040), the Ministry of Science and Technology of China (863) (Item No. 2007AA032400448), the Science and Technology program of “11th five-Year” of Education for Jilin province (No.20070162) and the Science and Technology bureau of Key Program for Ministry of Education (Item No. 207025).

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