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A template-free CVD route to synthesize hierarchical porous ZnO films

Xiangyang Duan [a], Guangde Chen [a], Lu'an Guo [a], Youzhang Zhu [b, c], Honggang Ye [a], Yelong Wu [a, *]

[a] Department of Applied Physics and the MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Xi'an Jiaotong University, Xi'an, 710049, PR China
[b] School of Electronics and Information Engineering, Xi'an Jiaotong University, Xi'an, 710049, PR China
[c] Department of Physics, Xi'an Research Institute of High Technology, Xi'an, Shaanxi, 710025, PR China

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ABSTRACT

Unique porous ZnO films were successfully synthesized on Si substrates without any catalysts or templates using chemical vapor deposition method. Unlike earlier reports, they are hierarchical porous, containing both macropores and mesopores. The zinc oxide seed layer and the weight ratio of source materials were found to be the major factors that would facilitate the synthesis of these hierarchical porous films. We found that all the macropores were surrounded by grain boundaries. As presented in the SEM images, the newborn ZnO atoms would prefer to adsorb nearby the grain boundaries and nucleate there in the growth stage. A schematic diagram based on the aforesaid phenomenon was proposed to explain the synthesis of the hierarchical porous ZnO film. An unusual strong emission peak located at 420 nm was observed in the photoluminescence spectrum. It was suggested that the emission peak was attributed to the special hierarchical porous structure, especially the grain boundaries in the nanowalls of these films.

1. Introduction

Zinc oxide is considered to be a promising material for high performance photonics applications because of its direct wide band gap (Eg ~ 3.3 eV at 300 K) and large exciton binding energy (~ 60 meV) [1,2]. However, the properties of ZnO are strongly dependent on the crystallite size and morphology. This promotes a lot of work on different nano-structures of ZnO with a large variety of growth methods, such as nanodots, nanoparticles, nanorods, nanowires, nanotubes and nanofilms [3–9]. Porous ZnO film appears to be an especially appealing one, due to its large specific surface area, large pores volume, chemical and photochemical stability, shape selectivity, and rich surface chemistry [10]. There are several techniques to produce porous films, however, an inevitable challenge in the synthesis process is the using of template. How to synthesize a large area and uniform template, and how to remove the template from the substrate completely are still unsolved [11]. Although some groups have improved the growth method to fabricate nanoplates, nanosheets and aggregated nanoparticles without template, the uniform and well-crystallized porous films have not been obtained [12–15]. In particular, hierarchical porous structures have rarely been reported.

* Corresponding author.
E-mail address: yelongwu@mail.xjtu.edu.cn (Y. Wu).

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In this work, we report the synthesis, structure characterization, growth mechanism and luminescence of hierarchical porous ZnO film grown by chemical vapor deposition method (CVD) without templates or catalysts. Structural characterization of the thin film was analyzed by X-ray diffraction patterns (XRD) and Scanning Electron Microscopy (SEM). Different from previous reported porous ZnO films that only contained one kind of pores, ours were found to contain both mesopores and macropores [16,17]. Further investigation showed that the grain boundaries that existed in the nanowalls and connected the macropores played an essential role in the growth of this unique porous ZnO film. A unique strong near ultraviolet emission peak at 420 nm was observed in the PhotoLuminescence (PL) spectrum.

2. Experimental

2.1. Experimental procedure

In our experiment, we chose silicon wafer as the substrate and cut it into desired dimensions (approximately 1 cm × 2.5 cm). Firstly, we dipped the substrate into acetone solution and cleaned it with ultrasonic washer for 20 min, then blow-dried it by a steam of nitrogen. After that, we cleaned the substrate in ethanol solution using the same method. Prior to the CVD process, a seed layer was prepared on the surface of the Si substrate. We put a drop of ethanol solution (contains 0.02 $mol \cdot L^{-1}$ Zinc Acetate dihydrate) onto the clean substrate, then blew dry the substrate with a steam of nitrogen. This coating step was repeated for three to five times to get an appropriate thickness of zinc acetate film. Subsequently, we heated the zinc acetate film to 120 °C and maintained for 30 min. After the above steps, we would yield a ZnO seed layer on the Si substrate. 0.5 g ZnO (99.9%) and 0.2 g graphite powder (99.9%), as the source materials, were placed in the center of a railboat. The Si substrate, which now had been cleaned and covered with a ZnO seed layer, was mounted on the railboat (5 mm above the source materials). Subsequently, we put the railboat in the center of a horizontal tube furnace. Then the temperature of the tube furnace was ramped to 950 °C within 25 min and maintained for 2 h. The whole heating process was under a constant flow of argon at 100 standard cubic centimeters per minute (sccm) and oxygen at 5 sccm. The tube furnace was maintained under ordinary pressure.

Considering that the oxygen is insufficient, we predict that the primary carbothermal reduction reactions can be described by the following three chemical equations:

$$ZnO_{(s)} + C_{(s)} \rightarrow Zn_{(g)} + CO_{(g)} \tag{1}$$

$$ZnO_{(s)} + CO_{(g)} \rightarrow Zn_{(g)} + CO_{2(g)} \tag{2}$$

$$2Zn_{(g)} + O_{2(g)} \rightarrow 2ZnO_{(s)} \tag{3}$$

where (s) means solid, (g) gas. Apparently, Eqs. (1) and (3) should be the dominant reactions in the tube furnace. With the increase of temperature in the tube furnace, graphite can reduce ZnO into Zn and CO_2 (or CO as well). Then Zn vapor could be blown to the substrate, oxygenated by oxygen and continually absorbed on the ZnO seed layer.

2.2. Characterization

The crystal structure was analyzed by XRD using Bruker Advance D8 with Cu $K_{\alpha 1}$ radiation, $\lambda = 1.5406$ Å. The microstructure of the porous film was characterized by Field Emission Scanning Electron Microscopy (FESEM, JEOL-7800F). The PL spectrum was measured by a steady state and transient state fluorescence spectrometer (Photon Technology International, QM 40) using a Xe lamp with an excitation wavelength of 325 nm.

3. Results and discussion

3.1. Analyst of hierarchical porous ZnO film

The crystalline structure of this ZnO film characterized by X-ray diffraction is shown in Fig. 1. The black plot is the XRD of the sample. All the diffraction peaks can be indexed as hexagonal wurtzite-type ZnO structure (compared with the standard PDF card, JCPDS no.75–0576, see the red line). No apparent impurity peak can be found in the figure indicating a pure crystal of ZnO. Compared with the standard X-ray diffraction data of bulk ZnO, the relative intensity of (002) peak is greatly higher than the other peaks, indicating that the ZnO porous film orients toward the ⟨002⟩direction preferentially. The high intensity and shallow half peak width show that the hierarchical porous film is well crystallized.

Fig. 2 shows the typical SEM images of the as prepared ZnO porous film. The most interesting thing is that the low magnification SEM image clearly shows us a large area thin porous film with innumerable macropores, see Fig. 2(a). The average diameter of the macropores is about several micrometers (approximately 1 ~ 5 μm). The macropores are constructed by a series of nanowalls, the average diameter of which is approximately several tens nanometers. They are so well connected