Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Synthesis of ZnO nanoporous structure materials by two-step thermal oxidation of Zn film

Qiang Xu[a,b,*], Rongdun Hong[b], Xiaping Chen[b], Jiaju Wei[c], Zhengyun Wu[b,**]

[a] Department of Nuclear Science and Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 211106, China
[b] Department of Physics, Xiamen University, Xiamen 361005, China
[c] Purple Mountain Observatory, Chinese Academy of Sciences, Nanjing 211106, China

ARTICLE INFO

Keywords:
Thermal oxidation
Zn film
ZnO nanoporous
Optical properties

ABSTRACT

We describe the synthesis of ZnO nanostructures materials on quartz substrates by a simple two-step thermal oxidation process. Firstly, a thin layer of metallic Zn films are oxidized in nitrogen atmosphere at 350 ℃, and then the samples annealed at high temperature (from 600 to 800 ℃) to improve the crystal quality. The properties of the materials are characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy and UV–Visible spectroscopy at room temperature. The results show that nano porous structure materials have been formed after the samples annealed at high temperature. Since the small grain size and grain boundary induced effect of conduction band bending, the optical band gap shifts to low energy.

1. Introduction

Various structures of ZnO materials (including bulk, thin film, nanostructures) have been synthesized via different deposition methods, such as Molecular Beam Epitaxy (MBE), Metal organic Chemical Vapor Deposition (MOCVD), Radio-frequency magnetron sputtering, hydrothermal method, thermal oxidization and so on [1–5]. All these different material structures have been greatly applied in light-emitting diodes, transparent conductive oxides, gas sensor, photodetector and scintillator [6–10]. All of these applications are associated with the unique material properties of wide band gap (3.34 eV), large exciton binding energy (60 meV), and environment friendly (non-toxic). Moreover, nanostructure materials have been attracted more attention than thin film materials, due to its large surface to volume ratio, which will greatly enhance the performance of devices. Recently, one-dimensional, two-dimensional, and three-dimensional nanostructure (nanowires, nanorods, nanotubes, nanoflowers, etc.) materials have been obtained by different deposition methods [1,2,4]. Most synthesis nanostructure material methods are focusing on research in materials with small active area. As a popular deposition method, sputtering has been considered as one of the most effective methods to grow large scale, uniform thin film materials. Therefore, it is an excellent approach to depositing large scale and uniform nanostructure materials.

Several groups have investigated the mechanism of oxidization metallic Zn film and have achieved various ZnO nanostructure materials [11,12]. Dikici synthesized the ZnO nanostructures on the electroplated Zn layer and studied the affection of the surface morphologies of ZnO nanostructures by different oxidation temperatures [13]. Fan et al. obtained ZnO dendritic nanowires on faceted surface by using a two-step low temperature and catalyst free process [14]. Previously, our group has studied the growth mechanism of spontaneously oxidation of metallic Zn film on p-type silicon substrate and has obtained diverse morphologies of hierarchical ZnO nanostructures materials with gold as catalyst [15]. We also synthesized ZnO nanocave structure by using two-step thermal oxidation Zn film, which greatly enhanced the band-gap emission [16]. However, the study of large scale and uniform ZnO nanostructures materials by oxidation method is still limited by the existence of catalyst. Therefore, we have developed a thermal oxidation process without catalyst to synthesis large scale and uniform ZnO nanoporous materials.

2. Experimental

1 cm × 1 cm quartz substrates were ultrasonicated with acetone and ethanol for 15 min, respectively. The substrates were then rinsed with deionized water for three times, dried with nitrogen gas. Then films with thickness of 1.5 μm layer of Zn were deposited on quartz substrates by using a direct current sputtering system with a base pressure of 8×10^{-4} Pa at room temperature, the metal Zn targeted with the purity of 99.99%. In order to oxidize Zn films, the samples

* Corresponding author at: Department of Nuclear Science and Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 211106, China.
** Corresponding author.
E-mail addresses: xuqiangxmu@nuaa.edu.cn (Q. Xu), zhywu@xmu.edu.cn (Z. Wu).

http://dx.doi.org/10.1016/j.ceramint.2017.09.014
Received 28 July 2017; Received in revised form 1 September 2017; Accepted 1 September 2017

were placed in quartz furnace flowed with nitrogen mixed air gas (Nitrogen: air = 90:10) and keep the furnace temperature at 350 ℃ for 1 h. Finally, to improve crystal quality of ZnO materials, the samples were carried out in nitrogen furnace, and annealed at various temperatures from 600 to 800 ℃ for 1 h.

The structural properties, surface morphology and optical properties were carefully investigated with various characterization techniques. The structural properties were investigated by XRD (Panalytical X'pert PRO powder, Cu Kα = 0.15406 nm), and Raman spectroscopy (Renishaw UV-1000). The surface morphology was observed by FESEM (LEO 1530). The optical properties were studied by UV–Visible spectrophotometer (Varian Cary 5000). All measurements were carried out at room temperature.

In this study, we investigated ZnO nanoporous materials by a two-step thermal oxidation method. Firstly, a thin layer of metallic Zn films deposited on quartz was oxidized in 350 ℃ nitrogen atmosphere for 1 h. And then, to improve the quality, the samples subsequently annealed in nitrogen ambient for 1 h at 600 ℃, 700 ℃ and 800 ℃. Lastly, the crystalline structure, surface morphology, and optical properties are carefully investigated by X-ray diffractometer (XRD), Raman spectrometer, field emission scanning electron microscopy (FESEM) and UV–Visible spectrometer.

3. Results and discussion

The XRD pattern of thermal oxidation of Zn films at 350 ℃ and thermal annealing at 600, 700 and 800 ℃ are given in Fig. 1. According to JCPDS36-1451 card, five crystal planes of the hexagonal wurtzite structure of ZnO (100), (002), (101), (102) and (110) have been observed with different diffraction peaks, which located at 31.68°, 34.33°, 36.17°, 47.56° and 56.57°, respectively (labeled as black rectangle). Also, the other three peaks located at 38.90°, 43.12° and 54.2° are associated with phase of Zn (100), (101) and (102) (labeled as red triangle). For the sample oxidized in the temperature of 350 ℃ nitrogen atmosphere, the peaks ascribed to both ZnO and metal Zn were observed, which means that part of metal Zn was oxidized. After the samples annealed in nitrogen atmosphere at high temperature (600, 700, and 800 ℃), the Zn (100), (101) and (102) peaks disappeared and ZnO (100), (002), (101) peaks were greatly stronger and sharper, which indicated that the quality of the films increased and presented a polycrystalline hexagonal wurtzite crystal structure. Moreover, the strong similarity in the intensity of ZnO diffraction peaks, also demonstrated that the samples were with porous structures, which without preferred orientation.

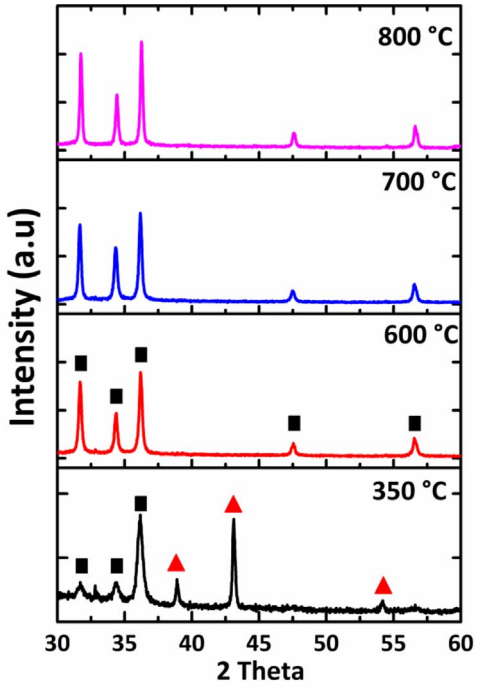

Fig. 1. XRD pattern of Zn film oxidized in a dried nitrogen atmosphere for 1 h at 350 ℃, and annealed at 600, 700, 800 ℃ for 1 h, respectively. The black rectangle stands for the crystal planes of ZnO; the red triangle stands for the crystal planes of Zn. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The average grain size of all samples could be deduced from the full width at half maximum (FWHM) of the (002) peak by employing Scherrer's equation [17]: $d = 0.9\lambda/\beta \cos\theta$, where λ is the X-ray wavelength (0.154 nm, Cu K α source; β is the Bragg diffraction angle; θ is the FWHM of the (002) peak. The calculated average grain size is 15.33 nm, 31.53 nm, 32.13 nm and 37.81 nm for 350 ℃, 600 ℃, 700 ℃ and 800 ℃, respectively. The results indicate that the grain size increases with the increasing of annealing temperature and also demonstrate that high quality ZnO material will be obtained at high temperature.

Fig. 2 shows the cross-section and surface morphology SEM images of ZnO thermal oxidized at 350 ℃ (a, c), and thermal annealing at 600 ℃ (b, d), respectively. From the Fig. 2(a, c), the samples show a flaky structure while it thermal oxidized at 350 ℃, which also related to the Zn (100), (101) diffraction peaks of XRD data. After the samples thermal annealing at high temperature, flaky structure is disappeared and porous structure materials have been observed. It is to be noticed that the surface morphology is different from the result of our previous paper, in which the samples formed a nanocave structure material [16]. The different surface morphology is mainly caused by the layer of gold. With an increasing thermal annealing temperature, no obvious changes are observed for the surface morphology images, which is also related to the static of XRD pattern for the samples.

Since the ZnO is a wurtzite structure material, there are two formula units in a primitive cell. The Raman active zone modes expressed as follows [18]:

$$\Gamma = A_1 + 2E_2 + E_1 \quad (1)$$

Where A_1 and E_1 photon modes are polar phonons, splitting into two frequencies of the transverse optical (TO) and longitudinal optical (LO) phonons. Nonpolar E_2 modes have two symmetry frequencies E_2(high) and E_2(low). According to previous report [18,19], A_1 and E_1 are assigned to Raman and infrared active, respectively. The A_1(TO) and A_1(LO) mode peaks are located at 379 and 575 cm^{-1}, respectively. E_1(TO) and E_1(*LO*) peaks are correlated with the peaks position at 410 and 591 cm^{-1}, respectively. Nonpolar E_2(high) and E_2(low) modes are Raman active only, which located at 439 and 102 cm^{-1}, respectively.

The Raman spectra of the ZnO nanoporous films are recorded by using Renishaw UV-1000 spectrometer, as shown in Fig. 3. The spectrum is excited by a wavelength of 532 nm laser with a diameter of 1 μm laser spot at room temperature. For all spectra, two peaks located at 330 and 430 cm^{-1} have been observed, which are assigned to multiple phonon processes and E_2(high) mode, respectively. After the samples annealed, additional two peaks 379 (assigned to A_1(TO)) and 575 cm^{-1} (assigned to A_1(LO)) have been observed, which is due to the improvement of quality. A noticeable phenomenon is that compared to theoretical results, the E_2(high) mode is shifted by 9 cm^{-1}, which is mainly ascribed to the spatial confinement of nanocrystal grain boundary and the defect [20].

The optical properties of ZnO nanoporous materials annealed for 1 h at various temperatures, as shown in Fig. 4. The transmittance of the samples is about 80% in visible region from 400 nm to 800 nm, and the waveforms are from the interface between the substrate and ZnO material. A sharp clearly absorption cut-off edge has been observed around the wavelength of 380 nm, indicating that ZnO is a direct bandgap material. The absorption cut-off edge shifts to a longer wavelength with the increasing of annealed temperature. The optical bandgap of the