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Applied Surface Science 252 (2006) 2853–2857
applied surface science
www.elsevier.com/locate/apsusc

Synthesis of bamboo-leaf-shaped ZnO nanostructures by oxidation of Zn/SiO_2 composite films deposited with radio frequency magnetron co-sputtering

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Received 16 July 2004; received in revised form 25 April 2005; accepted 25 April 2005
Available online 25 May 2005

Abstract

Bamboo-leaf-shaped ZnO nanostructures were synthesized by oxidation of metal Zn/SiO_2 matrix composite thin films deposited on Si(1 1 1) substrates with radio frequency magnetron co-sputtering. The synthesized bamboo-leaf-shaped ZnO are single crystalline in nature with widths ranging from 30 to 60 nm and lengths of up to 5–10 μm, room temperature photoluminescence spectrum of the nanostructures shows a strong and sharp UV emission band at 372 nm and a weak and broad green emission band at about 520 nm which indicates relatively excellent crystallization and optical quality of the ZnO nanostructures synthesized by this novel method.

PACS: 71.55.Gs; 81.15.−z; 68.65.−k

Keywords: Magnetron co-sputtering; Oxidation; ZnO nanostructures; Optical property

1. Introduction

Zinc oxide (ZnO), a direct and wide band-gap (3.37 eV) semiconductor with large exciton binding energy of 60 meV at room temperature, has been considered as a promising high efficient short-wavelength light-emitting material operating at room temperature [1,2]. One-dimensional nanomaterials have attracted considerable interest in recent years because of the continual demand for reduction in device size and their striking magnetic, optical, electronic and chemical properties, which strongly differ from those of the corresponding bulk materials. Due to their excellent crystalline quality, chemical stability, thermal stability and wide band-gap, one-dimensional ZnO nanomater-

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doi:10.1016/j.apsusc.2005.04.029

ials have been a matter of concern recently. Various methods including thermal evaporation [3,4], vapor phase transport process [5,6], metalorganic chemical vapor deposition (MOCVD) [7,8], etc., have been attempted to fabricate one-dimensional ZnO nanomaterials. Due to the promising application in nanoscale optoelectronic devices, it is important to be able to synthesize these nanomaterials in singlecrystalline form and study their optical property.

In this system, we chose a novel method to fabricate one-dimensional bamboo-leaf-shaped ZnO nanostructures in singlecrystalline form by oxidation of metal Zn/SiO_2 matrix composite thin films deposited on Si(1 1 1) substrates with radio frequency (RF) magnetron co-sputtering. In particular, metal zinc separated out from SiO_2 matrix and was oxidized into ZnO on the surface of SiO_2 insulator layer on Si substrates, which is of great importance in achieving Si on insulator (SOI) structures and for the long-range goal of three-dimensional integrated circuits. The preparation of ZnO nanostructural layer/SiO_2/Si offers very attractive potential to harmonically incorporate ZnO optoelectronic devices in silicon-based very-large-scale integrated circuits.

2. Experiment

The Zn/SiO_2 composite thin films were deposited on Si(1 1 1) substrates in JCK-500A RF magnetron sputtering system with 6×10^{-4} Pa basic pressure by sputtering a composite target, which was composed of a high-purity (99.999%) SiO_2 of 80 mm in diameter containing several chips of high-purity metal zinc (Fig. 1). The distance between the target and the substrate was 80 mm. Si substrates were cleaned by standard cleaning procedures. The sputtering pressure was typically 1.1 Pa (0.1 Pa O_2 in Ar). Pre-sputtering was carried out for 5 min with pure Ar. The RF sputtering power was 150 W and sputtering time was 20 min. Substrates were held on the water-cooled upper electrode, which maintained the substrates' temperature close to the room temperature. Subsequently, the as-deposited films were placed on a quartz carrier and annealed in an open tube furnace in pure O_2 atmosphere with a flow rate of 600 ml/min at 650 °C for 40 min.

The products was characterized using X-ray diffraction (XRD, Rigaku D/max-rB Cu Kα), scanning electron microscopy (SEM, HITACHI H-8010) and high-resolution transmission electron microscopy (HRTEM) images which were obtained with a Philips Tecnai-20U-TWIN electron microscopy system operated at 200 keV. Photoluminescence (PL) was carried out on an FLS920 PL spectrophotometer and the excited wavelength was at 310 nm and a 420 nm filter was used. All measurements were carried out at room temperature.

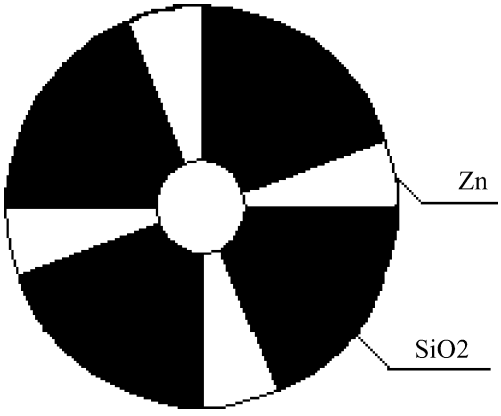

Fig. 1. Sketch map of the Zn/SiO_2 composite target.

3. Results and discussion

Fig. 2 shows the X-ray diffraction patterns of the as-deposited sample (a) and the sample annealed in O_2 at 650 °C for 40 min (b), respectively. The diffraction peaks in panel (a) located at $2\theta = 36.3°$, 38.9°, 43.1°and 54.2° correspond to ZnO(1 0 1), Zn(0 1 0), Zn(1 0 1) and Zn(0 1 2) planes, respectively, which reveals that the as-deposited layer is mainly composed of polycrystal metal zinc. However, a small quantity of ZnO has already formed in the sputtering process. It is generally accepted that ZnO is difficult to be formed in a collision between a sputtered Zn atom and an oxygen atom in the gas phase without a third partner to carry away the binding energy. More likely, the source of the ZnO is, we think, the sputtering of this species from the oxidized Zn target, which might act as the precursor for the post-growth of ZnO nanostructures during the annealing process. Due to its lower crystalline temperature, ZnO can be partly crystallized on substrates without purposive pyrogenation. The peaks which locate at $2\theta = 31.6°$, 34.3°, 36.2°, 47.4° and 56.5 °