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Structural and optical properties of ZnO and Al-doped ZnO microrods obtained by spray pyrolysis method using different solvents

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ABSTRACT

ZnO and Al-doped ZnO microrods were obtained by spray pyrolysis method using different solvents such as methanol and propanol. The effect of the type of solvent in the starting solution on the structural, morphological and optical properties of the samples was investigated. X-ray diffraction patterns showed that the undoped and Al-doped ZnO microrods exhibited hexagonal crystal structure with a preferred orientation along (002) direction. Surface morphology of the samples obtained by scanning electron microscopy revealed that undoped and Al-doped ZnO microrods grew as quasi-aligned hexagonal shaped microrods with diameters varying between 0.7 and 1.3 μm irrespective of solvents used. Optical studies indicated that microrods had a low transmittance (≅30%) and the band gap increased from 3.24 to 3.26 eV upon Al doping. Photoluminescence measurements indicated the existence of two emission bands in the spectra: one sharp ultraviolet luminescence at ~383 nm and one broad visible emission ranging from 420 to 580 nm.

1. Introduction

Considering the ever-decreasing dimensions of electronic devices, producing self-assembled micro- and nano-structured materials systems is becoming increasingly important for commercial applications. There is also significant academic interest in nano systems, as their properties can be remarkably different from those of the bulk materials due to quantum-size effects. Much attention has been paid

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recently to the nanostructured materials such as ZnO and GaN due to their ability to exhibit near-ultraviolet (UV) emission. ZnO is especially interesting due to its direct band gap of about 3.37 eV and its large exciton binding energy (60 meV). ZnO is a low cost material with various industrial applications in manufacturing gas sensors, varistors, Schottky diodes, solar cells, piezoelectric devices, etc. [1–4]. Therefore, fabrication of ZnO nano-microrods in highly oriented, aligned and ordered arrays is of critical importance for the development of novel devices.

Several methods have been developed for the synthesis of oriented arrays of ZnO nano-microrods. Umar et al. [5] synthesized a large quantity of perfectly hexagonal-shaped ZnO rods via a simple thermal evaporation method using metallic zinc powder and oxygen gas. Previously we investigated ZnO micro-rods grown by spray pyrolysis method at 550 °C on the glass substrate [6]. Li et al. [7] synthesized well-aligned ZnO rods grown by a low-temperature hydrothermal method on sapphire substrates at 600 °C. In this work, the grain size of the ZnO rods was changed by adjusting an aqueous solution with some methylamine. Micro-rods of ZnO grown by simple oxidation of zinc metal grains at 1000 °C were reported by Zhao et al. [8]. Most of the reported studies for the ZnO nano-micro rods were produced at high growth temperature. Although ZnO rods are of single-crystalline nature, they have poor optical properties such as low transmittance, broad and dominated green emission. It is known that the strong deep-level emission in the photoluminescence spectrum is related to the presence of structure defects and impurities in the structures.

Zhao et al. [9] fabricated ZnO nano-rods on the ZnO coated seed substrate by solution chemical method followed by annealing at comparatively low temperature of 300 °C. They observed with the increasing precursor concentration [$Zn(NO_3)_2$ and NaOH] in this system, the average diameter and length of ZnO nanorods increased, leading to decreasing of optical transmittance. Ting et al. [10] demonstrated that the solution-growth technique was used to produce high-quality and dense ZnO nanorods and the transmittance of the ZnO nanorods grown at 75 °C is higher than that of grown at 95 °C. They attributed that this decrease of transmittance could be related to two factors. One was the thicker ZnO nanorod thin films having larger hexagonal grain size and larger surface roughness. The other was the higher absorption effect for thicker films.

It is known that pure zinc oxide is an insulator while its conductivity and transparency could be enhanced by adding Group III metal dopants, such as Al, B, In and Ga and Group VII dopants like F [11]. Al-doped ZnO has several advantages over indium tin oxide when it is used as the transparent conducting oxide film in photovoltaic applications. Both Al and Zn are of low cost, non-toxic elements with abundant supply. In addition, ZnO:Al films can tolerate reducing chemical environment, such as hydrogen plasma [12]. Al-doped ZnO thin films also can lead to a tunable band gap. ZnO:Al thin films with high *c*-axis orientated crystalline structure along (002) plane are potential device applications in broadband UV photodetectors with high tunable wavelength resolution [13]. ZnO:Al thin films with *c*-axis orientated crystalline structure are fabricated by RF magnetron sputtering [14], pulsed laser deposition [15], sol–gel [16] and spray pyrolysis [17], etc. Among these, the spray pyrolysis is especially suitable, since it has proved to be a simple and inexpensive method, particularly useful for large area applications. It is possible to alter the mechanical, electrical, optical and magnetic properties of ZnO nanostructures by doping with selective elements. In this work, undoped and Al-doped ZnO thin films were deposited by the spray pyrolysis method using alcohol solvent (methanol and propanol) instead of commonly used spray pyrolysis with water solvent. Methanol leads to a major beneficial effect on the properties of the ZnO film [18]. In this study, we used Alq_3 (tris(quinolin-8-olato) aluminum(III)) for Al doping into ZnO thin films instead of commonly used aluminum chloride. The structural, morphological and optical properties of the samples were investigated to establish a correlation between the process parameters and the film properties.

2. Experimental

Undoped and Al-doped ZnO microrods were obtained by spray pyrolysis in air atmosphere. The experimental set up and the other experimental details are explained elsewhere [19]. The initial stock solution was prepared from zinc chloride ($ZnCl_2$) at 0.1 M concentration in methanol and propanol solvents. The doping was achieved by the addition of Alq_3 (tris(quinolin-8-olato) aluminum(III)) solved in