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Full Length Article

Surface characterization and cathodoluminescence degradation of ZnO thin films

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ABSTRACT

ZnO thin films were successfully synthesized by the sol-gel method using the spin coater technique. The films were annealed at 600 °C in air for two hours and in Ar/H_2(5%) flow for 30 and 60 min, respectively. Structural analysis, surface morphology and characterization, as well as optical analysis (photoluminescence and cathodeluminescence (CL)) were done on the samples and discussed in detail. CL degradation during prolonged electron irradiation on the films was also determined. A preferential orientation of the *c*-axis perpendicular to the surface was observed from X-ray diffraction data showing the peak from the (002) plane for the films annealed in both the air and in the H_2 flow. The film annealed in air exhibited a broad visible emission as well as a strong ultraviolet emission. A single-green emission peak around 511 nm was obtained from the film that was annealed in Ar/H_2 flow for 60 min. The CL study revealed that the intensity of the green emission (511 nm) was very stable during electron bombardment for electron doses of more than 160 C/cm^2.

1. Introduction

Over the last fifty years, research on metal oxide semiconductors has generated significant interest because of their potential applications in optical, electrical and in electronic devices. ZnO has emerged as a II–VI group compound semiconductor with fascinating properties. The direct wide bandgap (3.37 eV) and the large exciton binding energy (60 meV) [1] of ZnO made it suitable and stable for such application conditions. Furthermore, ZnO has inherent defects which are responsible for its luminescence properties (visible emission from 400 nm to ~750 nm) [2–4]. The growing interests in ZnO thin films has been considered as a promising route to increase and improve its efficiency, excellent crystallinity and morphology which provides good optical and electrical properties [5,6].

Various techniques have been used to fabricate ZnO thin films such as radio frequency magnetron sputtering [7], pulsed laser deposition [8], chemical vapour deposition [9] and spray pyrolysis [10]. Amongst these techniques, the sol–gel process is on the forefront in both research and industrial fabrication because of its easiness, low cost and the best of all, the sol-gel process is able to provide homogeneous film at the molecular level, excellent control of the film composition and lower crystallization temperature. These are due to the mixing of liquid precursors [11]. Post-annealing treatments [12] and annealing in reducing atmosphere [13] are some of the laboratory routes to control the film stoichiometry and to enhance the film structure and morphology in order to obtain the desired properties.

The stability of ZnO phosphors under electron beam irradiation has been a subject of concern in the past few years. ZnO:Zn phosphor which emits a green emission centered at 511 nm showed substantial initial cathodeluminescence degradation [14] which was the drawback for the phosphor to be used in low voltage cathodoluminescence applications as well as optoelectronics.

In this work, sol-gel ZnO films were successfully deposited by using the spin coating technique. The structural, morphological and optical properties were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), cathodoluminescence (CL) and photoluminescence spectroscopy (PL) with a 325 nm He-Cd laser. CL degradation of the green emission was studied in a vacuum base pressure and an oxygen partial pressure atmosphere.

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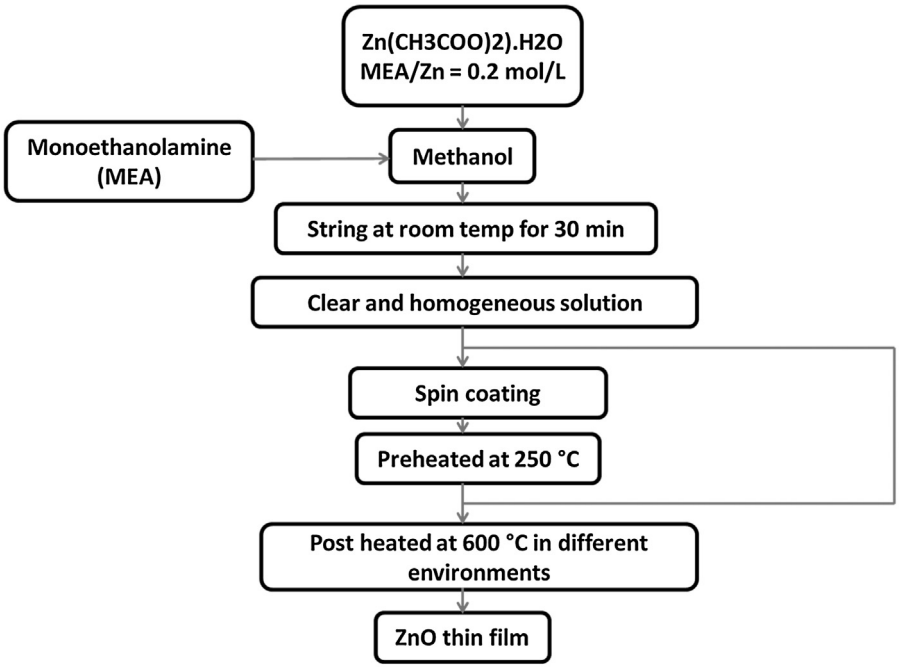

Fig. 1. Schematic diagram representing the ZnO thin film preparation method.

2. Experimental procedure

2.1. Sample preparation

Sol-gel ZnO thin films were prepared by using the spin coating technique, Fig. 1. Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, Alfa Aesar, purity 99.95%) was used as a starting material. Monoethanolamine and methanol were used as a stabilizer and solvent, respectively. A concentration of 0.2 mol/L zinc precursor solution was prepared by dissolving the zinc acetate dihydrate in the methanol. Monoethanolamine was dissolved in the solution. The molar ratio of the MEA:Zn was fixed at 1:1 for all the samples. The final solution was obtained by stirring the mixture for 30 min at room temperature using a magnetic stirrer. The final solution was kept for 48 h at room temperature ranging between 25 and 32 °C. Si (100) substrates were used for the film fabrication. The Si substrates were cleaned ultrasonically for 15 min using acetone to remove the organic contaminations, and then rinsed with ethanol and deionized water, and were then dried by N_2 gas. The solution was dropped onto the Si substrates, which were rotated at 2500 rev/min for 30 s by a spin coater. After deposition, the films were preheated in the air over a hot plate at the temperature of 250 °C for 10 min to evaporate the solvent and remove the organic residuals. The procedures from coating to preheating were repeated 7 times until the desired thickness was obtained. The films were annealed in air at 600 °C for 2 h using a tube furnace. After annealing at 600 °C a mixture of H_2:Ar gas was introduced into the tube furnace. A ratio of 5:95 H_2:Ar gas was used during the annealing of the films with the flow rate of 10 sccm. The H_2:Ar flow annealing was done for 30 or 60 min.

2.2. Characterization technique

For XRD a Bruker diffractometer (40 kV, 40 mA) with CuKα X-rays (1.5406 Å) was utilized for the structure and phase analysis. The 2θ scan range was from 15° to 100° in steps of 0.0178°. A JEOL JSM-7800F SEM was used to examine the sample particle morphology. An AFM model Shimadzu SPM – 9600 was used to assess the surface topography. The surface profile was obtained with the commercial software that forms part of the AFM system. PL spectra were collected by a photomultiplier tube detector at room temperature. The films were excited with a He-Cd laser with a wavelength of 325 nm. A PHI, model 545, Auger electron spectroscope (AES) was employed for the chemical composition and cathodoluminescence degradation study of the film. The experiments were carried out in a vacuum base pressure of 3.5×10^{-8} Torr and an O_2 partial pressure of 3.5×10^{-7} Torr. The film was bombarded by an electron beam with a current density of 1.27 mA cm^{-2}, beam current of 10 μA and acceleration voltage of 2 kV. The Auger peak-to-peak heights (APPH) and CL data were collected simultaneously using the same electron beam. An Ocean Optics PC2000 spectrometer and OOI base 32 computer software were used for the CL data collection. For the degradation studies, the films were subjected to electron beam irradiation for more than 24 h.

3. Results and discussion

XRD patterns of the sol-gel ZnO films are shown in Fig. 2. The as-prepared films were amorphous with weak peaks at about 33.6° that are marked with an asterisk which originated from the (200) forbidden reflection of the Si substrate. The annealed films exhibited strong diffraction peaks of the ZnO (002) plane at 34.3° as well as weak peaks indexed to (100) and (101) planes at 31.6° and 36.1° respectively. The high relative intensity of the (002) reflection compared to powder sample data indicated a preferential c-axis orientation perpendicular to the substrate surface, which is a common physical phenomenon exhibited by ZnO thin films crystallized by post-annealing treatment due to the low surface energy of the (002) plane [1]. The well-known Scherrer equation was utilized to estimate the crystallite size by using the full with at half maxima (FWHM) of the 002 peak after the contribution of the XRD machine was removed. The crystallite sizes were found to be 47 nm, 44 nm and 38 nm for the films annealed in air and H_2 flow for 30 min or 60 min, respectively. The crystallite size was observed to decrease when the ZnO films were exposed to the H_2 atmosphere. This may

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