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Sol–gel production of aluminium doped zinc oxide using aluminium nitrate

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ABSTRACT

Sol–gel synthesis of aluminium doped zinc oxide was performed via a spin coating process through a precursor solution that consisted of zinc acetate, aluminium nitrate and ammonia. The effects of sintering temperature on the optoelectronic properties of the derived films were investigated through scanning electron microscopy, X-ray diffraction, photoluminescence, UV–vis spectroscopy and Hall effect measurements. It was found that as the process temperature increases the film changes from a grain-like morphology towards a nanowire structure. This trend is also evident in the presented XRD data. Optical measurements revealed the derived films to be highly transparent with an optical transparency ~92%.

1. Introduction

Recently, metal oxide semiconductor materials have attracted considerable attention due to their potential applications in next generation optoelectronic devices [1]. Among these materials, zinc oxide (ZnO) is one of the most intensively studied, due to its high electron mobility, piezoelectric properties, large band gap (3.37 eV) and large exciton binding energy (60 meV) [2]. Consequently, applications of ZnO have been proposed with regard to transparent conductive oxide [3], light emitting diodes [4], humidity sensors [5]and piezoelectric nanogenerators [6].

In terms of deposition, ZnO can be synthesized through both solution [7] and vacuum-based processes [8]. Vacuum-based processes include chemical vapour deposition (CVD) [9], sputtering, laser ablation [10] and spray pyrolysis [11]. Although high-quality ZnO can be deposited via vacuum-based deposition methods, these techniques often require complicated and expensive equipment. Alternatively, one can use solution-based deposition methods, such as chemical bath deposition [12], sol–gel process [13], electrodeposition [14] and a hydrothermal process [15], in order to deposit ZnO. These solution-based processes offer superior control of geometry, and involve only simple equipment. Among the different chemical based techniques sol–gel possesses are particularly attractive due to the advantages of precise control of chemical composition and efficient material utilization [16].

Generally, as-deposited ZnO is n-type, due to the incorporation of impurities during the synthesis process [17]. The conductivity of ZnO can be further increased by the addition of Al [18] and Ga [19]. Due to the material abundance and high optical transparency, Al doped ZnO (AZO) has been proposed to replace indium tin oxide as transparent conductive film. Previous studies have shown that physical properties of the sol–gel deposited AZO thin films are highly influenced by dopant concentration [13], selection of stabilizers [20] and post-sintering temperature [21]. However, there have been a limited number of studies on the effects of dopant source on the subsequent properties of AZO thin films. In this study, the effects of

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sol–gel synthesis temperature on the production of AZO using aluminium nitrate are investigated. The resultant ZnO films were thoroughly investigated through scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, photoluminescence spectroscopy, Raman spectroscopy and electrical measurements.

2. Experimental

Corning glass (Eagle 2000) substrates were cleaned using baths of acetone, isopropanol and D.I. water within an ultrasonicator. All the chemicals used in this study were of analytical grade and used without further purification. AZO thin films were deposited on pre-cleaned glass substrates by spin coating the derived sol. Firstly, zinc acetate dehydrate was mixed into isopropanol to form 0.7 M of precursor solution. Then 2 ml of monoethanolamine (MEA) was then added as a chelating agent to prevent precipitation during the mixing stage of the process. Doping was achieved through addition of 1 wt% of aluminium nitrate nonhydrate. The solution was mixed for 1 h at 60 °C and left to age for 48 h. Sol–gel deposition was performed through a spin coating at 3000 rpm and a two-step annealing process at 250 °C and 400–550 °C. Each spin-sintering cycle yielded around 50 nm of film thickness and was repeated five times to form 250 nm of AZO.

The crystalline orientation of the films was studied using an X-ray diffractometer (Philips, Model: PW1830) with Cu Kα radiation with an angular step of 0.01°. The XRD scan was taken between 2 theta between 20° and 80°. The structural properties of sol–gel derived AZO thin films were characterized using an FEI Quanta 400 F environmental scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). Photoluminescence emission and Raman spectroscopy measurements were obtained through the use of a Dongwoo Macro Raman spectrometer. The optical transmittance of the derived samples was obtained using UV–vis–NIR spectroscopy (JASCO). Hall effects measurements were taken with an Ecopia HMS-3000 Hall effect measurement system. As a demonstration, pn junctions were formed through spin coating of AZO onto p-type silicon substrates. In order to ensure Ohmic contacts to the fabricated device Zn/Al were evaporated onto the surface through a pre-fabricated mask to form electrodes. Current density–voltage (J–V) characteristics were measured using a Keithley 2400 source measure unit.

3. Discussions

The surface morphology of the deposited AZO thin films was evaluated using SEM. Fig. 1a–d shows the SEM images of the sol–gel synthesized AZO thin films sintered at 400 °C, 450 °C, 500 °C and 550 °C. It can be observed from the SEM images that the sol–gel derived AZO thin film was composed of uniform particles with diameters varying from 20 to 60 nm. The microstructures of the thin films were found to be highly dependent on the post-sintering temperature and transformed from small particles into larger interconnected grains as the temperature was increased from 400 °C to 550 °C. Fig. 1a shows that AZO thin films annealed at 400 and 450 °C (Fig. 1b) consisted of nano-particles with average grain sizes of around 10–20 nm. For the AZO thin films annealed at 500 °C (Fig. 1c), the grain size increased to around 40 nm in diameter, with clearly observed pores between the nano-particles. In the case of AZO thin films annealed at 550 °C the grain size increased up to 60 nm with the pores closed. During the sol–gel synthesis of AZO the thin films underwent two stages of heating: 1) a pre-sintering process at around 250 °C and 2) a post-sintering process at 400–550 °C. At the pre-sintering stage, most of the organic compounds were eliminated from the precursor coated substrates. The post-sintering process supplied the required energy for crystallite nucleation. The formation of pores between the crystallites is due to the elimination of organic matters from the precursor solution. Fig. 1e) shows the representative EDS compositional analysis of the AZO thin film deposited at 550 °C. As expected Zn, O, Al and N were detected, with a near equal at% of Zn:O. The present study involves precursors prepared under an excessive ammonia condition that results in the formation of ammonia complexes and aluminium hydroxide, as shown in the following equation:

$$\mathrm{Al(NO3)3(aq)+NH_4OH(aq)(aqueous\ NH_3)---> Al(OH)_3\ (s)+NH_4NO_3(aq)} \quad (1)$$

The orientations of the deposited AZO thin films as a function of sintering temperature were determined using XRD. Fig. 2a shows the XRD peaks as a function of annealing temperature. All the deposited AZO thin films were polycrystalline with a hexagonal wurtzite structure and a *c*-axis (002) orientation. Such a *c*-axis orientation is a common feature of ZnO derivative thin films deposited using the sol–gel deposition technique. Distinct XRD peaks at 31.99°, 34.49°, 36.38° and 56.79° correspond to the (100), (002), (101) and (110) orientations. As can be observed from Fig. 2a, AZO thin films post-sintered at 500 °C exhibited the highest diffraction intensity and hence crystallinity. Furthermore, it can be deduced from Fig. 2a that as post-sintering temperature increased up to 500 °C the intensity of the (002), (100) and (101) diffraction peaks also increased. A further increase in the post-sintering temperature to 550 °C resulted in a decrease in the intensity of the (002) peak. The XRD data corresponds well with the SEM image shown in Fig. 1, where grains size is shown to increase as a function of temperature. Specifically, Fig. 1c and d shows that as the sintering temperature was raised to 500 °C, this resulted in a grain-like morphology due to growth in the (100) and (101) orientations. The full-width half-maximum (FWHM) is a useful value to evaluate film properties and can be extracted from the XRD pattern. It can be observed from Fig. 2a that there is a simultaneous decrease in the peak intensity at the (002) orientation with an increase in the (110) orientation. This suggests that films grown at 550 °C increased growth at the (110) orientation and thus leading to decreased growth in the (002) orientation. It is known that films tend to grow with the plane with the lowest surface energy. Fujimura et al. [22] observed that the surface energy