ARTICLE IN PRESS

Available online at www.sciencedirect.com

ScienceDirect

Ceramics International ∎ (∎∎∎∎) ∎∎∎–∎∎∎

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effects of the pre-annealing temperature on structural and optical properties of sol–gel deposited aluminium doped zinc oxide

Ian Y.Y. Bu

Department of Microelectronics Engineering, National Kaohsiung Marine University, 81157 Nanzih District, Kaohsiung City, Taiwan, Republic of China

Received 25 January 2014; received in revised form 5 April 2014; accepted 5 April 2014

Abstract

Highly transparent aluminium doped zinc oxide (AZO) thin films were deposited by the sol–gel deposition technique. The effects of various pre-sintering temperatures on the film's structural, optical and electrical properties were investigated using scanning electron microscopy, X-ray diffraction spectroscopy, photoluminescence emission measurements, UV–vis spectroscopy and electrical characterization. It was found that the pre-sintering temperature greatly affected the film's structural properties and resulted in an almost 100% increase in grain size within the investigated experimental window. Photoluminescence emission and photovoltaic measurements confirmed that the best optoelectronic properties of AZO thin films can be achieved with a pre-sintering temperature of 400 °C.

Keywords: A. Sintering; Annealing; Aluminium doped zinc oxide; Optical; Sol–gel

1. Introduction

Zinc oxide (ZnO) is a semiconductor material, with a hexagonal wurtzite structure, that possesses a direct wide band gap (E_g=3.37 eV) and large exciton binding energy (60 meV) [1–4]. Nanostructured ZnO has been proposed as a potential material for use in various optoelectronic device applications, such as solar cells[5], light emitting diodes [6], waveguides [7,8] and lasers [9]. In addition, ZnO is piezoelectric and moisture sensitive, and its use has also been explored in nanogenerators [10] and humidity sensors [11]. In addition to its unique properties, ZnO possesses a distinct processing advantage over other nanomaterials, as it can adapt many different geometries (nanorods [2], nanowires [12,13], nanoflowers [14], and so on).

As-deposited ZnO tends to exhibit an n-type conduction behaviour due to its structural defects [15]. This pronounced n-type behaviour can be further enhanced through the addition of dopants; such as Al [16], In [17], and B [18]. Owing to its low production-cost, non-toxicity and high optical transparency, Al doped ZnO (AZO) is one of the materials touted to replace the indium tin oxide (ITO) commonly used in solar cells [19,20]. Although it is possible to deposit high quality AZO through thermal oxidation [21], such a method suffers from the drawbacks of low material yield and expensive vacuum set-up. On the other hand, the sol–gel based deposition method is of interest, as it offers precise composition control, simple set-up and high material utilization [15,22,23]. A typical sol–gel preparation procedure for AZO utilizes zinc containing compounds in solvents, with Al as the dopant [24]. During the sol–gel synthesis, the AZO films undergo two heating processes at different temperatures. First, the films are pre-annealed at around 250–300 °C to remove the solvents [25]. This process is followed by the second thermal annealing procedure at 500–600 °C to crystallize the film [15]. Indeed, as will be shown in this paper, pre-annealing is important not only in removing organic compounds, but also in governing the subsequent orientation and grain size of the crystallites. The temperature of the pre-annealing step is generally set at above the boiling point of the solvent and chelating agents in order to ensure complete removal of the organic compounds [26,27]. Previous studies have shown that properties of the sol–gel deposited ZnO films are highly influenced by sol concentration [28], choice of stabilizers [27,29], pH [23], aging

http://dx.doi.org/10.1016/j.ceramint.2014.04.030
0272-8842/

period [30] and post annealing temperature [31]. However, there have been a limited number of studies on the effects of pre-annealing temperature on the subsequent properties of AZO thin films.

In this study, AZO thin films were deposited on Corning glass substrates by a sol–gel technique. Samples were prepared by pre-heating at different temperatures (300–550 °C). The effects of the pre-annealing temperature on the structural and optical properties of the AZO films are investigated by scanning electron microscopy X-ray-diffraction, photoluminescence emission and electrical measurements.

2. Experimental

AZO thin films were prepared by sol–gel process. Al doping was achieved by adding 2 at% of Al into the ZnO precursor solution using $AlCl_3$ (hexahydrate). The Al dopant concentration was selected from the previously reported optimized conditions [32,33]. The films were coated on pre-cleaned Corning glass substrates using a spin coater set at 3000 rpm. The films were then pre-annealed at 300, 400, 500 and 550 °C and post annealed at 550 °C. This coating/drying/post annealing cycle was repeated five times to obtain the desired thickness (around 250 nm).

The surface morphology and structural properties of the sol–gel synthesized AZO thin films were investigated by using an FEI Quanta 400 F environmental scanning electron microscope (SEM). The chemical composition of the deposited thin films was determined by an energy dispersive spectroscope (EDS) within the SEM chamber. A Siemens D5000 X-ray Diffractometer with Cu Kα radiation was used to determine the crystalline orientation and grain size of the thin films. Hall effect measurements in the Van der Pauw configuration were used to determine the electrical conductivity type, resistivity and mobility. Optical transmittance was measured by an UV–vis NIR (Hitachi U-4100). The quality of the deposited AZO thin films was evaluated by the photoluminescence (PL) emission using a 325 nm He/Cd laser (Jasco Model FP-6000). Dark and illuminated current–voltage (*i*–*v*) characteristics were measured using a Keithley 2400 source-measure unit, with illumination (100 mW/cm^2) provided by a solar simulator (Science-tech.).

3. Results and discussions

Fig. 1(a)–(d) shows the SEM images of AZO thin films, pre-sintered at various temperatures and post annealed at 550 °C. It can be seen that the surface morphology of the films is strongly influenced by the pre-sintering temperature. The surface morphology of films deposited at pre-sintering temperature of 300 °C consists of small crystallites with an average diameter of around 50 nm. As the pre-sintering temperature increases, the grain size becomes larger and the diameter rises up to around

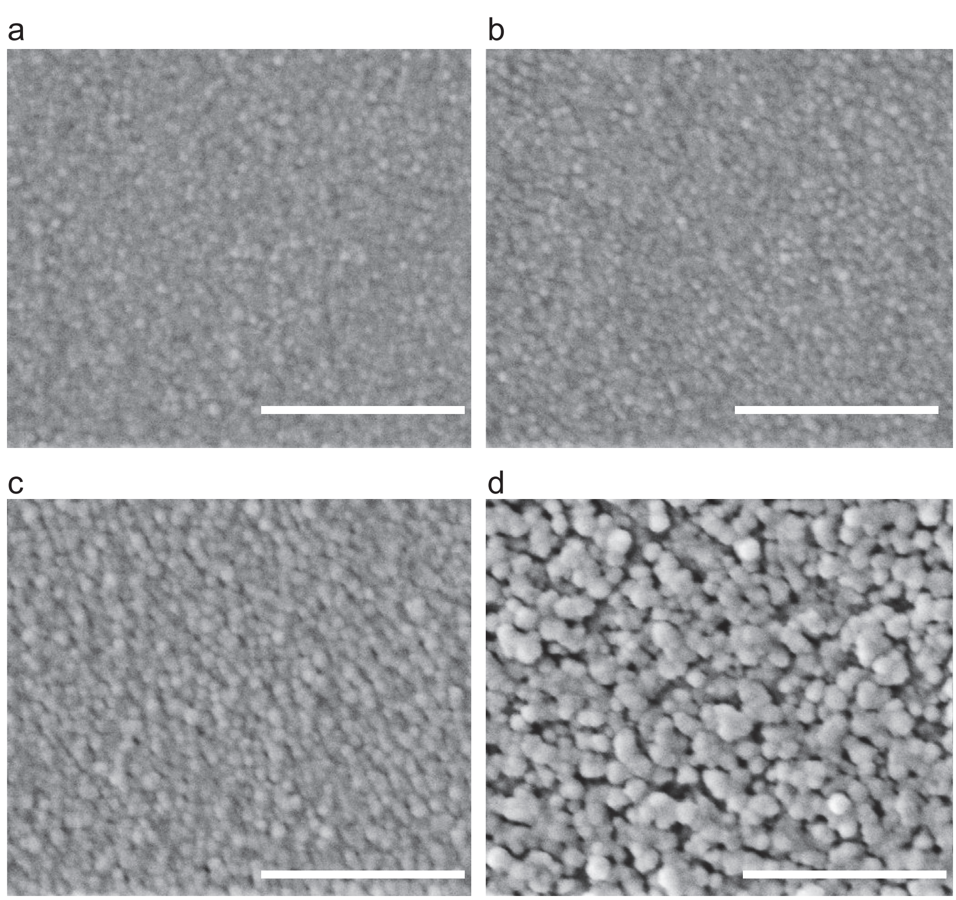

Fig. 1. SEM image of sol–gel derived AZO with pre-sintering temperatures of (a) 300 °C, (b) 400 °C, (C) 500 °C and (d) 550 °C (scale bar 1 μm).

Please cite this article as: I.Y.Y. Bu, Effects of the pre-annealing temperature on structural and optical properties of sol–gel deposited aluminium doped zinc oxide, Ceramics International (2014), http://dx.doi.org/10.1016/j.ceramint.2014.04.030