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Effect of magnesium and fluorine dopants on properties of ZnO thin films

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Abstract

Effects of Mg and F codoping on properties of ZnO films were studied in this work. F and Mg codoped ZnO films with a fixed Mg concentration of 20 at% and 0–8 at% F concentration were deposited on microscope glass substrates by the ultrasonic spray pyrolysis. The morphology of all films showed a spherical grain shape, and F doping decreased roughness with the addition of F concentration as well as decreased grain size with doping higher than 4 at% of films. The XRD patterns of all films were identified as a polycrystalline hexagonal wurtzite structure of ZnO with (002) preferred orientation. The band gap of 0 at% F doping film was 3.69 eV, which decreased to a minimum with 2 at% F doping and increased again with higher than 2 at% F doping. F doping decreased resistivity to a minimum with addition until 4 at% F doping and then increased again with higher than 4 at% F doping.

Keywords: A. Films; C. Electrical properties; C. Optical properties; D. ZnO; E. Electrodes

1. Introduction

Transparent conducting oxide is a material that shows excellent electrical conductivity and high transparency in the visible and near infrared regions. So, this material is widely used as electrodes in many optoelectronic devices such as solar cells, liquid crystal displays organic light emitting diodes, electrochromic devices, etc. [1,2]. Most oxide based materials are *n*-type semiconductors and have been widely studied for example: indium oxide (In_2O_3) [3], indium tin oxide (ITO) [4], tin oxide (SnO_2) [5], fluorine tin oxide (FTO) [6], zinc oxide (ZnO) [7] and aluminum zinc oxide (AZO) [8].

ZnO is one of the most interesting oxide based materials for solar cell applications. ZnO has high stability, nontoxicity as well as low cost [7]. However, there are 2 limitations of ZnO when applied to solar cells, these limitations are low energy band gaps as well as low carrier concentrations [9,10]. Abundant research has tried to improve these limitations of ZnO films by using doping elements. Magnesium (Mg) is a dopant that can improve the band gap of ZnO films due to nature of MgO as it has a wide band gap of about 7.3 eV [11]. From the previous research, the band gap of undoped ZnO films were in the range 3.2–3.3 eV [9,12–14] and could be improved to more than 3.3 eV with little Mg doping [9,12–14] and to more than 4.0 eV with heavy Mg doping (≥ 30 at%) [9]. In addition, the substitutional doping of ZnO films with metal, in group III metals (Al, B, Ga, In) has been widely reported as these metals can give improved electrical conductivity [13]. However, the problem with doping of these metals is the diffusion of the electrical active metal dopant into the film which can lead to a reduction in device performance [15–17]. This diffusion effect is less significant in ZnO films doped with Fluorine (F) [15–17]. Moreover, F^- substitutes in oxygen (O) sites in the ZnO lattice reduces the F^- ion (1.31 Å) and is a promising anion doping candidate belonging to its ionic radius being similar to the O^{2-} ion (1.38 Å) [17].

There are many methods available for preparing ZnO films such as the sol–gel [7], chemical vapor deposition (CVD), pulsed laser deposition [9,17], sputtering [8,18], spray pyrolysis [13] and ultrasonic spray pyrolysis [14]. The ultrasonic spray pyrolysis is

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an interesting technique, which was chosen for depositing films in this work. This technique can deposit films in a large scale. The micro-size droplets spray generated from the chemical solution by using an ultrasonic frequency nozzle that was depleted on heated substrates. These micron sized droplets can be accumulated to from nanostructured films [14,19].

In this work, F and Mg codoped ZnO films with a fixed amount of 20 at% Mg and 0–8 at% F were prepared by using the ultrasonic spray pyrolysis technique, and the properties of these films were investigated. The fixed level of 20 at% Mg was chosen for application to F and Mg codoped ZnO films. This film has showed a wide band gap 3.87 eV, which was suitable for being applied to photoelectronic devices. Furthermore, it does not have an impurity segregation phase from Mg doping and low resistivity [9].

2. Experimental

The codoped ZnO films were prepared from a solution of 0.02 M Zinc acetate dehydrate ($Zn(CH_3OO)_2 \cdot 02H_2O$) ($\geq 98\%$, Sigma-Aldrich), 20 at% Magnesium acetate tetrahydrate ($(CH_3COO)_2Mg \cdot 4H_2O$) ($\geq 98\%$, Sigma-Aldrich), and Ammonium Fluoride (NH_4F) ($\geq 99.99\%$, Sigma-Aldrich) with various F concentrations of 0–8 at%. These precursors were dissolved in a mixture of ethanol and deionized water with a volume ratio of 1:3. 0.01 M HCl was added for increasing solubility. After that, the solutions were sprayed on a glass substrate and heated to 400 °C by an ultrasonic spray pyrolysis system at 34 kHz. The flow rate of the solution was 2.5 mi/min for 5 min. Microstructure and phase formation of films were investigated by a scanning electon microscope (SEM, JSM-6335F, JEOL), atomic froce microscope (AFM, Nanoscope III, Digital Instruments) and X-ray diffraction (XRD, X'Pert Pro MPD, PANalytical). Optical properties were analysised by UV–visible spectrometry (UV–vis, Lambda 35, PerkinElmer), and electical properties were mesuared by a digital multimeter (3458A multimeter, Hewlett Packard) with a four point probe.

3. Results and discussion

The film thicknesses were estimated from the SEM cross-sections as shown in Fig. 1. It was found that the thicknesses of films were similar, in the range of 200–300 nm. The thickness of films depended on the time of spraying and flow rate of solution. The concentration of F^- ions were not significant for thickness.

The surface morphologies of the films with different F concentrations were investigated by SEM and AFM techniques and shown in Fig. 2. The surface morphologies of all films from SEM images showed spherical grain shapes. The average grain size and surface morphology of films were obtained from these SEM and AFM images, respectively and results are shown in Fig. 3(b and c). The average grain size of F and Mg codoped ZnO films with the addition of 0–4 at% F concentration was ~50 nm and this decreased to ~30 nm with higher than 4 at%. This result was similar to those of the In-F codoped ZnO films, which were studied by Vimalkumar et al. [20]. The surface roughness values were found to decrease then increase with F concentration. The concentration of F^- ions had effect on the smoothness of the surface of the films.

The crystal structure of F and Mg codoped ZnO films with different F^- concentrations of 0–8 at% are shown in Fig. 4. The XRD patterns were identified as polycrystalline hexagonal wurtzite structure of ZnO with (002) as a preferred orientation. In addition, it was found that the intensity of these patterns increased with increasing F concentration up to 4 at% and then decreased with further F concentration. These results were similar to the research studied by Bu [21], who discussed the improvement and reduction of the crystalline phase of F doped ZnO films. The improvement of the crystalline phase with F concentration was caused by the attachment of F into the oxygen vacancy sites in ZnO film. Then after doping F over limit of F^-, the crystalline phase will be reduced due to excessive interstitial F, which formed into secondary phases such as ZnF_2 and MgF_2. These second phases may be adsorbed into the ZnO surface, and this leads to the reduction of the crystalline phase.

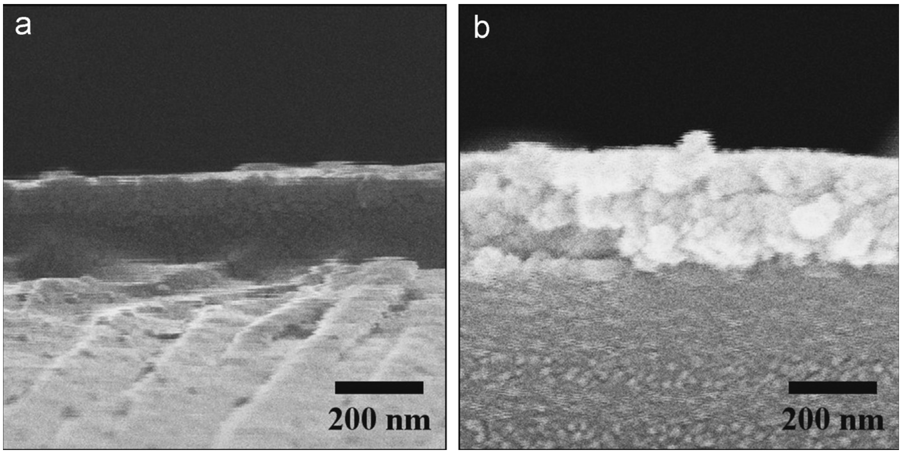

Fig. 1. Cross-section of microstructure of F and Mg codoped ZnO films on the glass substrate with different F concentrations of (a) 0 and (b) 4 at%.