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Influences of lead and magnesium co-doping on the nanostructural, optical properties and wettability of spin coated zinc oxide films

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ABSTRACT

The quality and optical homogeneity of thin films are necessary for optoelectronic devices and semiconductor technology. The influence of Pb doping, $Zn_{1-x}Pb_xO$ ($0 \le x \le 0.05$), and Mg co-doping, $Zn_{0.95-y}Pb_{0.05}Mg_yO$ ($0 \le y \le 0.05$), on the microstructural properties, optical parameters and wettability of ZnO films were investigated. X-ray diffraction (XRD) and field emission-scanning electron microscopy (FE-SEM) results show that the films have polycrystalline and hexagonal structure with a preferred (002) orientation combined with wrinkle network structure for the Pb doped films. The crystalline quality is slightly enhanced with the Pb doping and then deteriorated after Mg co-doping. The influences of the crystallinity and chemical composition on the film wettability are studied. All films show transparency between 85–93%. The reflectance and optical band gap of ZnO films decrease for Pb doping and then increase with Mg co-doping. Well-known Swanepoel's method is employed to determine the refractive index (n) and film thickness (d). The influences of Pb and Mg co-doping on the Urbach energy and optical dispersion parameters are also discussed.

1. Introduction

Film technology based on transparent conducting oxides (TCOs) has received considerable interest due to the application in various engineering and industrial fields. Zinc oxide (ZnO) is one of these TCOs and the second most widely studied semiconductor after Si [1]. It has a wide and direct band gap (3.25 eV) and large exciton binding energy of 60 meV. Hence, ZnO is considered as a next-generation light-emitting diode (LED) [2–4]. It is an excellent potential candidate for the fabrication of room temperature (*RT*) polariton lasers [3,5]. Its ability to block the UV light improved the uses of its nanoparticles (NPs) in cosmetics and paints [6,7]. Also, ZnO exhibit relatively high conductivity and high optical transmittance in the visible region. Therefore, it can be used as front contact material for dye-sensitized solar cells [5,8]. Because of its wurtzite structure, which can be defined by a hexagonal lattice in which the Zn^{2+} ions occupy the tetrahedral sites formed by the O^{2-} ions, ZnO shows strong spontaneous piezoelectric polarization [1]. Also, ZnO shows better performance in the degradation of dye molecules in both acidic and basic medium [9]. A ZnO surface is generally known to be hydrophilic; i.e. a flat ZnO surface had a water contact angle $\Theta < 90^\circ$ [10]. UV illumination and long-term

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dark storage (or heating) are simple methods for hydrophilic and hydrophobic transition. The potential application of this wetting transition, from a hydrophobic to a hydrophilic state are multiple, such as the production of antifogging materials, microfluidic devices, and the construction of self-cleaning surfaces [11,12].

Doping with specific elements is a facial method that could be used to improve the physical and chemical properties of ZnO material for some particular needs or applications. Lin et al. [8] reported increases in the chemical resistance and the heat stability of the ZnO thin films co-doped with (Al, Cr, and V). Anita and Luthra [13] and Valenzuela et al. [14] suggested the use of Ni–Al co-doped ZnO NPs, prepared by a co-precipitation method, and Ni-doped ZnO thin film, prepared by a diffusion–oxidation process, respectively, for spintronic applications. The influence of Al and Ga co-doping on the physical properties of the dip coated ZnO films [15] as well as the ZnO NPs [16] were also reported. Co-doping with 3 at% Al and 0.3 at% Ga was enough to obtain the finer grain size, lowest resistivity of $2.52\times10^{-3}\ \Omega$ cm and a highest relative density of 99.2% for ZnO [16]. Fang et al. [17] studied the influence of annealing temperature (500-800 K) on some of the physical properties of spin-coated $Zn_{0.92}Mg_{0.03}Al_{0.05}O$ thin films. Mary et al. [18] reported that, in the prepared $Zn_{1-2x}Ce_xMn_xO$ NPs, Ce doping governs the ZnO stability. Whereas, Mn doping plays an important role in the observed room temperature ferromagnetism. Wu et al. [19] have predicted that K–N co-doping is hopeful to get ZnO materials with more stable *p*-type conductivity. This is a result of the interaction of K 3*d* and N 2*p* states. Honglin et al. [20] also reported similar results for Al–N co-doped ZnO, in Zn-rich condition. In addition, mixing of multiwall carbon nanotubes with Al–N co-doped ZnO film enhances the photocatalytic degradation of methylene blue (MB) via creating conduction path for electron transfer and reactive oxygen groups [21].

Lead (Pb) is an important element in various applications in the semiconductor industry. Mg is expected to make a good solid solution with ZnO because the wider band gap of MgO [1]. Pb^{2+} doped ZnO nanorods [3] and nanodisks [22] synthesized by a hydrothermal method as well as Pb-doped ZnO nanowires fabricated using a thermal evaporation method [23,24] were reported. Pb nanoparticle tipped ZnO nanowires by long-pulse-width laser ablation (LPLD) was also reported [25]. On the other hand, Mg-doped ZnO NPs [26,28] and thin films prepared by sputtering technique [5,29,30], sol–gel [6,17] and spray pyrolysis [31,32] have been reported. Among the used techniques, the sol–gel process has a distinct advantage as it involves low temperature and provides excellent compositional control and homogeneity on the molecular level. This is beside it is cheap and enable the large area processing. In addition, solubility in sol–gel technique is determined by many factors that are controllable and can be optimized [2,26]. Based on the literature survey, there are few reports of Pb- doped ZnO thin films prepared by sol–gel spin coating technique. In this work, the effects of Pb and (Mg, Pb) co-doping on the structural, hydrophilic properties as well as the optical properties of the sol–gel spin coated ZnO thin films are reported.

2. Experimental procedures

2.1. Materials preparation

Un-doped, Pb-doped ZnO, and (Pb, Mg) co-doped ZnO films were deposited on glass substrates by the sol–gel spin coating technique. The source material was zinc acetate [$Zn(CH_3COO)_2\cdot2H_2O$, $M_W=219.49$, Panreac], and the dopants sources; lead acetate [$Pb(CH_3COO)_2\cdot3H_2O$, $M_W=379.33$, Interchem, UK] and magnesium acetate [$Mg(CH_3COO)_2\cdot4H_2O$, $M_W=214.45$, LOBA Chemie]. Ethylene glycol monomethyl ether [$C_3H_8O_2$, $M_W=76.1$] and monoethanolamine (MEA) [C_2H_7NO, $M_W=61.08$, Scharlab S.L., Spain] were used as a solvent and stabilizing agent, respectively. Seven solutions were prepared by dissolving 0.768 g zinc acetate in 7 mL $C_3H_8O_2$ (the concentration of the solutions = 0.5 mol/L) and the molar ratio of MEA to zinc acetate was maintained at 1:1. The additives were controlled to obtain the following film's compositions; ZnO, $Zn_{0.99}Pb_{0.01}O$, $Zn_{0.97}Pb_{0.03}O$, $Zn_{0.95}Pb_{0.05}O$, $Zn_{0.94}Pb_{0.05}Mg_{0.01}O$, $Zn_{0.92}Pb_{0.05}Mg_{0.03}O$, and $Zn_{0.90}Pb_{0.05}Mg_{0.05}O$. These were made by using: 0.0, 0.0132, 0.0398, 0.0663 g lead acetate (for the first four samples). To prepare the Mg co-doping films, 0.0075, 0.0225, 0.0376 g magnesium acetate were added beside 0.0663 g lead acetate. For simplicity, these compositions are named: un-doped ZnO, ZnO:1% Pb, ZnO:3% Pb, ZnO:5% Pb, 5% Pb +1% Mg, 5% Pb+3% Mg, and 5% Pb+5% Mg, respectively. The prepared mixtures were magnetically stirred at 60 °C for 2 h to obtain a clear and homogeneous solution. The solutions were then aged for 20 h prior to film deposition. Before the spin coating process, the glass substrates, of thickness of about 1.3 mm, were cleaned by sonication in acetone, ethanol, and deionized water for 10 min each. Finally, the substrates were dried using an air gun and baked at 100 °C for 20 min to remove any residual moisture. The deposited films were then heated at 200 °C for 10 min to evaporate the solvent and remove any organic residuals. This coating/drying procedure was repeated seven times. In the end, the films were annealed at 500 °C for 2 h in an air furnace and then cooled to *RT*.

2.2. Measurements

For identification of phases and crystallographic properties of the as-prepared oxide films, X-ray diffraction (XRD, Philips X'PertPro MRD) using Cu Kα radiation ($\lambda=1.5418$ Å) with a step 0.021, was used. Morphological studies of the fabricated nanostructure films were carried out using field emission-scanning electron microscopy, FE-SEM (model: ZEISS SUPRA 55 VP and ZEISS LEO, Gemini Column). The chemical compositional analysis was studied using energy dispersive X-ray (EDX; Oxford Link ISIS 300 EDX). The surface wettability of ZnO thin films was characterized via measuring water contact angle, WCA (Θ) using a CAM 200 Optical Contact Angle Meter (KSV Instruments), using the sessile drop method. A 5 μl droplet of distilled deionized water was positioned on the surface via a microsyringe and images were captured to measure