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ZnO thin films prepared by a single step sol–gel process

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Abstract

ZnO thin films were prepared on fused silica from a single spin-coating deposition of a sol–gel prepared with anhydrous zinc acetate [Zn $(C_2H_3O_2)_2$], monoethanolamine [$H_2NC_2H_4OH$] and isopropanol. Crystallization annealing was performed over the range 500 to 650 °C. X-ray analysis showed that thin films were preferentially orientated along the [002] c-axis direction of the crystal. The films had a transparency of greater than 85% in the visible region for sol–gels with a zinc content of up to 0.7 M and exhibited absorption edges at ~378 nm. The optical band-gap energy was evaluated to be 3.298–3.306 eV. Photoluminescence showed a strong emission centered at ca. 380 nm along with a broad yellow-orange emission centered at ca. 610 nm. Single step sol–gel thin film deposition in the film thickness range from 80 nm to 350 nm was demonstrated. The effect of sol–gel zinc concentration, film thickness and crystallization temperature on film microstructure, morphology and optical transparency is detailed. A process window for single spin coating deposition of c-axis oriented ZnO discussed.

Keywords: Zinc oxide; Sol–gel

1. Introduction

ZnO thin films now attract significant attention due to their wide range of electrical and optical properties. They have potential application in electronics, optoelectronics and information technology devices including displays, solar cells and sensors [1,2].

Several thin-film deposition techniques have been used to produce pure ZnO films, including sputtering [3], molecular beam epitaxy [4], metal-organic chemical vapour deposition [5], pulsed laser deposition [6], spray pyrolysis [7] and the sol–gel process [8,9]. The sol–gel method has distinct potential advantages over these other techniques due to its lower crystallization temperature, ability to tune microstructure via sol–gel chemistry, conformal deposition ability, compositional control and large surface area coating capability [10,11].

The deposition of pure and doped ZnO thin films by the sol–gel process has already been reported [12–15]. However, to-date, multiple deposition steps have been generally necessary to produce thin films of the required film thickness for specific technological applications. Typical multi-step deposition processes that have been demonstrated include the use of five sequential depositions to achieve 100 nm [16] and seven sequential depositions to achieve 300 nm [17].

A single-step sol–gel process to deposit ZnO thin films in the hundreds of nanometer range is of considerable interest from both process cost-of-ownership and film quality aspects. A decrease in the number of coating applications would reduce both application and drying steps required and the number of interfaces within the resultant thin film which can contribute to reduced optical transparency.

In this study, a novel sol–gel process is investigated for deposition of c-axis orientated ZnO thin films with thicknesses up to 350 nm in a single spin-coating step. The use of anhydrous zinc acetate, which avoids the introduction of large amounts of water to the sol–gel, enabling control over reactions taking place within the sol–gel is described. In addition, the use of isopropyl alcohol (IPA), as a low boiling point solvent in place of 2-methoxyethanol (B.P.=125 °C) to facilitate efficient solvent removal and drying from thick films in order to avoid the occurrence of cracking during the crystallization annealing stage of processing is detailed. The effect of process deposition

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parameters, such as the zinc concentration of the sol–gel and furnace annealing temperature, on ZnO film microstructure, morphology and optical transparency was also examined.

2. Experimental

The ZnO sol–gel was prepared was as follows: zinc acetate (M=183.46, $Zn(C_2H_3O_2)_2$, 99.99% chemical purity) was first dissolved in isopropanol ($(CH_3)_2CHOH$) at room temperature. Then monoethanolammine (M=61.08, $H_2NCH_2CH_2OH$, MEA, AR) was added as a sol stabilizer [17]. The molar ratio of MEA to zinc acetate was maintained at 1.0 and the final concentration of the zinc acetate was varied between 0.3 to 1.3 mol/L. The resulting mixture was then stirred at 50 °C for 1 h to form a clear and transparent homogeneous mixture and upon cooling was syringe filtered using a 0.45 μm, Acrodisc Versapor® filter to remove any foreign particulates and aged for 24 h at room temperature. ZnO thin films were prepared by spin coating the aged solution onto UV fused silica (Spectrosil 2000) glass at rotation speeds of 2000 rpm for a duration of 30 s. To facilitate film thickness measurements, a section of the substrate was covered by adhesive tape which was subsequently peeled off after the spin-coating process [12]. The substrates were then dried on a hotplate at 60 °C for 1 h. On cooling, the samples were placed in a furnace for crystallization annealing at a heating rate of 5 °C/min to a final temperature of 650 °C. Samples was maintained at this temperature for 1 h before being air-cooled to room temperature. Fig. 1 shows a schematic of the sol preparation process.

The degree of crystallinity and crystalline orientation of the ZnO thin films was measured using a Phillips (PW3719) X'pert materials research X-ray diffractometer (XRD) with a Cu Kα radiation, and a scanning range of 2θ set between 25° and 50°. The average ZnO thin film particle size was calculated from the measured XRD peak height at FWHM data using the Lotgering formula and Scherrer's equation respectively [20]. Optical transmittance spectra were recorded using a Shimadzu (UV-2401 PC) UV–VIS recording spectrophotometer over the wavelength range between 200 and 800 nm. The surface morphology of the films was evaluated using a Philips (XL30TMP) scanning electron microscope (SEM). Thin film thickness was measured using a TENCOR (Alpha-Step 500) surface profilometer. The optical band-gap energy was estimated from optical transmittance and wavelength data, using an extrapolation of the linear portion of α^2 versus hν where α is the absorption coefficient and hν, the photon energy. The optical absorption edge was determined using a first derivative method was used to acquire the wavelength value required for calculation of the optical bandgap [18].

Photoluminescence (PL) spectra of the ZnO films on fused silica substrates were recorded using an in house optical system. Samples were optically pumped with an Innova Enterprise II argon (Coherent) ion laser and the emitted light collected using a Triax 190 0.19 m monochromator (Jobin-Yvon). PL spectra were acquired by directing the 350 nm excitation light onto the ZnO films at an angle of 27° to the plane of the sample, and collecting the resulting luminescence at an angle of 63 degrees.

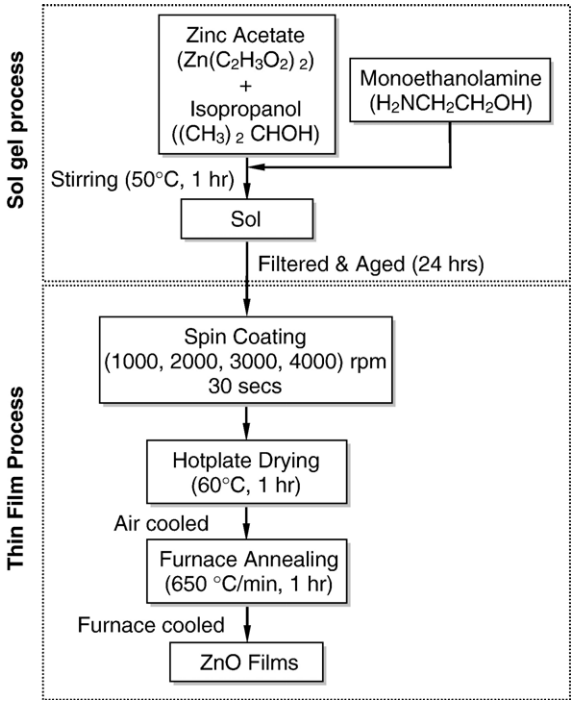

Fig. 1. Process flow chart showing the procedure for preparing the sol–gel and thin films.

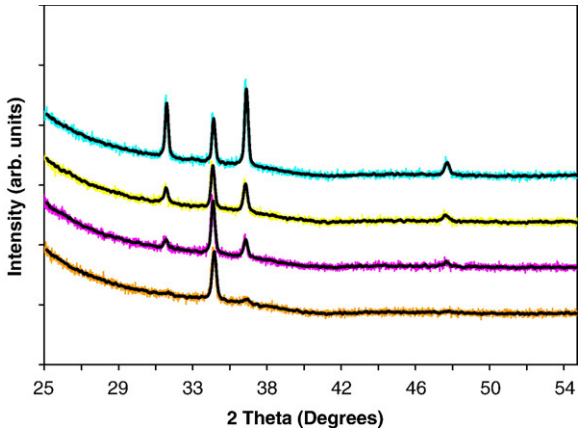

Fig. 2. The X-ray diffraction patterns of ZnO films prepared by a single coating process at different zinc concentrations. All films were spin-coated at 2000 rpm, dried at 60 °C and post annealed at 650 °C.

Table 1
Degree of preferred orientation, crystallite size and film thickness with respect to the zinc concentration of the sol–gel

Zn concentration (M)	Preferred orientation	Degree of (002) orientation	Crystallite size (nm)	Film thickness (nm)
0.3	(002)	0.96	288	84
0.6	(002)	0.62	385	185
0.7	(002)	0.50	315	188
1.3	(101)	0.22	348	437