Effects of ageing time of ZnO sol on properties of ZnO films by sol gel spin coating

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Abstract

In recent years, there are many techniques developed to synthesize zinc oxide (ZnO) films. However, among the synthesis methods available, sol-gel technique has the most advantageous which offers cost effective features. In the present work, ZnO films were prepared by sol–gel spin coating technique. The effects of solution ageing times which varies at 2h 15 min, 3h 30 min and 24h were investigated. The structural, morphological and optical properties were studied using an x-ray diffractometer (XRD, Bruker D8 Advance), atomic force microscope (AFM, Tenko XE-100) and ultra violet-visible spectrophotometer (UV-Vis, Shimadzu UV 1800), respectively. Based on the XRD measurement, it was revealed that ZnO films were polycrystalline with hexagonal wurtzite structure. The crystallite size is in the range of 34.4 ~ 28 nm which decreased with ageing time increment. On the other hand, the AFM analysis revealed that the surface roughness of the films increased due to the increment of ageing times. Optical transmittance spectra indicate that all films were transparent (>75%) in the visible range which slightly improved with increasing of ageing times. The optical band gap was estimated to be around 3.24 ~3.26 eV using Tauc's plot. We revealed that the ageing time of ZnO sol influenced the material properties of ZnO films. Based on our finding we proposed that 24h ageing time is optimum for the fabrication of high quality ZnO films.

Keywords: Zinc oxide; Sol–gel; Spin coating; Ageing time; Transmittance.

1. Introduction

Zinc oxide (ZnO) is a n-type II-VI semiconductor with hexagonal wurtzite structure. It has direct bandgap (3.37 eV) and high exciton binding energy (60 mV) at room temperature [1]. In addition, ZnO also have excellent chemical stability, nontoxicity, good electrical and optical properties [2]. Due to its unique properties, ZnO has potential applications in electronic, optoelectronic, electrochemical, and electromechanical devices,

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such as ultraviolet (UV) lasers, light-emitting diodes, field emission devices, high performance nanosensors, solar cells, piezoelectric nanogenerators and nanopiezotronics [3].

Various deposition techniques have been used to fabricate ZnO films such as chemical vapour deposition (CVD) [4], molecular beam epitaxy (MBE) [5], pulsed laser deposition (PLD) [6], and the sol-gel method [7].

Among them, sol-gel method is one of the attractive techniques for fabricating ZnO film. It offers many advantageous such as simple process, low cost and also offers the possibility of preparing large area coating [8]. In addition, ZnO films fabricated by sol-gel method show good homogeneity, excellent compositional control with good properties of films [7-8]. In order to produce high quality of ZnO films, it is necessary to study the parameters that can affect the properties of ZnO films. The parameters include precursor, solvents, sol concentration, sol ageing time, sol pH value, annealing temperature, preheating temperature and so on. Sol–gel method is a wet chemical technique which usually depends on solution conditions. Therefore, the effect of sol ageing time is important to be studied because in the ageing process, some properties of the sol will change and have significant impacts on the properties of ZnO films.

In the present work, ZnO films have been prepared by sol–gel spin coating technique. The influence of ZnO sol ageing time on the structural, morphological and optical properties of ZnO films was systematically studied and reported.

2. Experimental Procedures

2.1 Films Preparation

ZnO sol was prepared using zinc acetate dehydrate [$Zn(COOCH_3)_2.2H_2O$], isopropanol [C_3H_8O] and monoethanolamine [MEA, C_2H_7NO] as a precursor, solvent and stabilizer, respectively. Zinc acetate dehydrate was first dissolved in a mixture of isopropanol and MEA solution. The molar ratio of MEA to zinc acetate was maintained at 1:1 and the concentration of zinc acetate was 0.4 mol/L. Three different solutions were prepared and aged at room temperature by varying the ageing time. Sample a, sample b and sample c was aged for 2h 15 min, 3h 30 min and 24h, respectively. Before the fabrication process, three substrates were cleaned with acetone and deionized water using ultrasonic cleaner to remove dust or organic contaminants. Then, each of the solution was spin-coated onto ITO substrate using 3 step programs (1000 r.p.m at 5s, 3000 r.p.m. for 30s and 1000 r.p.m. for 5s). Subsequently, all samples were preheated at 280°C for 3 minutes to remove the organic residuals. The same coating process was repeated for ten times. Lastly, all samples were annealed at 500ºC for 1 hour to obtain the crystalline ZnO films.

2.2 Characterization Techniques

The crystallinity of ZnO films were characterized using an x-ray diffractometer (XRD, Bruker D8 Advance) with CuK$_\alpha$ radiation, λ = 1.54 Å. The surface topology of ZnO films were investigated using an atomic force microscope (AFM, XE-100 Tenko). The thicknesses of ZnO films were measured using a KL-Tenko surface profiler and ZnO films were optically characterized using an ultra violet-visible spectrophotometer (UV-Vis, Shimadzu UV 1800).

3. Results and Analysis

3.1 Structural Analysis

The XRD spectra of ZnO films are shown in Fig. 1. It was observed that all films have sharp and narrow diffraction peaks, indicating that the materials exhibit high crystallinity. As we can see from the figure, the peaks identified correspond to (1 0 0), (0 0 2), (1 0 1), (1 0 2) and (1 1 0) plane reflections for Wurzite-type ZnO. It was found that, by increasing the sol ageing time, an enhancement of the intensity for all diffraction peaks occurs in general. In addition, the prominent peak (0 0 2) indicates preferential c-axis orientation of the crystals. Lie *et al.* also reported that the degrees of preferred crystal orientation along c-axis are improved by the increment of ageing time. However, compared to their result, the degree of sample crystallization in this study is much better due to the several peaks which can be observed from the XRD results.

The crystallite size (*D*) was estimated using the (0 0 2) diffraction peak from the XRD data in accordance to the Debye-Scherer's formula [9]

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

Where β is the full width hall maximum (FWHM) of the diffraction peak measured in radians, λ (1.5406 Å) is the wavelength of the x-ray, and θ is the angle of diffraction. An average crystallite size value corresponding to ZnO films deposited at different ageing time is listed in Table 1. According to these results, the crystallite size of the ZnO films decreases from 34.4 nm to 28 nm due to decreasing of sol ageing time. The dislocation density (δ), defined as the length of dislocation lines per unit volume of crystal structural using the following formula by Khan *et al.* [10]

$$\delta = \frac{1}{D^2} \qquad (2)$$

From the dislocation density data, one can clearly observe that the crystallization of the films is good because of their small dislocation density (δ) values which represent the amount of defects in the film.

3.2 Surface Topology Analysis

Fig. 2 (a-c) shows the three-dimensional surface topology images of ZnO films with different sols ageing time. As for Fig. 2 (a), its surface is relatively rough with some hillocks appeared and grain sizes are non-uniform. However, with the increase of sol ageing time, the surface roughness gradually decreases and the ZnO grains become more uniform. As we can see on Fig. 2 (b) and (c), both of them have smooth surface and uniform grains. Root-mean-square (RMS) roughness for a surface area of 5 μm × 5 μm of all ZnO films was calculated by AFM. All films showed RMS roughness in the range of 15.73 − 18.65 nm which reflect homogenous films surface resulting from uniform grains distribution and the increment in the roughness with the ageing time is due to the fact that the crystal growth rate is relatively faster at the liquid–solid interface at higher aging time. The sol–gel process is based on colloidal particles (sol), by increasing the solution ageing time, the colloidal particles are increased and therefore the reaction will be faster, similar explanation reported by X. Zhao *et al.* for their ZnO film [11]. Optimal sol ageing time was found at 24h which exhibits comparatively smoother surface with minimum values of RMS surface roughness.

Y. Li *et al.* [12] had also suggested 24 h sol aging time as ideal to obtain good quality and smoother ZnO films.
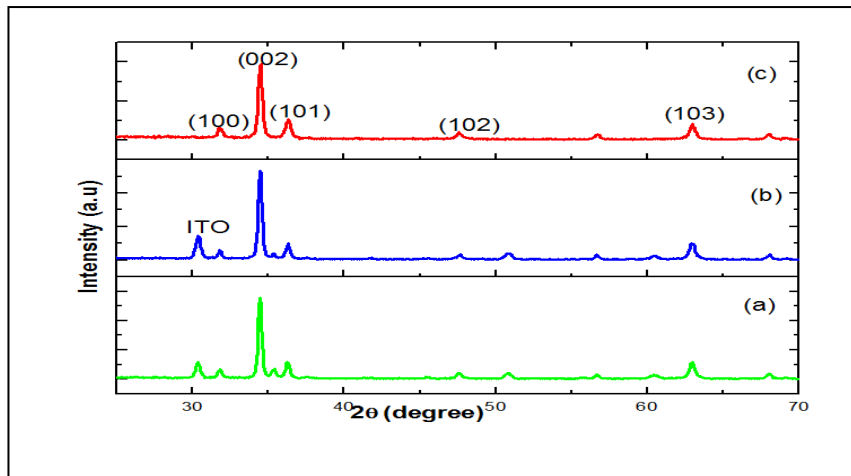

Fig. 1: XRD spectra of the ZnO film with different sols ageing time: (a) 2h 15 min, (b) 3h 30 min and (c) 24h.

Table 1: Evaluated structural parameters of ZnO films

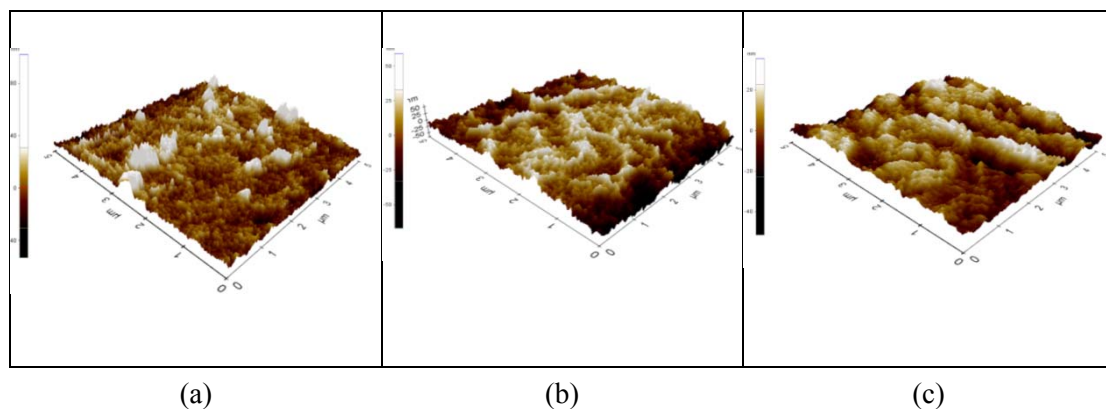| Time of aging of the solution	plane	FWHM (β)	2θ	D (nm)	$\delta \times 10^{-3}$ $(nm)^{-2}$
2 h 15 min	002	0.0043	34.44	34.4	0.845
3 h 30 min	002	0.0048	34.46	31	1.041
24 h	002	0.309	34.48	28	1.276

(a)   (b)   (c)

Fig. 2: AFM topography of ZnO films with different sol ageing time (a) 2h 15 min, (b) 3h 30 min and (c) 24h.

3.3 Optical Properties Analysis

Fig. 3 depicts the transmittance spectra of the ZnO films in the UV-visible region from 350 to 900 nm. All films have transmittance approximately around 75% and above in the visible range. Especially for sample B and C, both their average transmittance in the visible range is above 85%. It was found that the transmittance is gradually improved with

the increment of ageing time. Highest transmittance obtained in sample C may be due to the structural homogeneity and crystallinity as evidenced from Fig. 2. The transmittance of the films increases with the increase of ageing time as proved by study of Y. Li *et al.* [12].

The corresponding optical band gap of ZnO films is estimated by extrapolation of the linear relationship between $(\alpha h v)^2$ and hv according to the equation given by caglar *et al.* [13].

$$(\alpha h v)^2 = A(h v - Eg) \tag{3}$$

Where α is the absorption coefficient, *h* is the Planck constant, ν is the frequency of the incident photon, *A* is an energy-independent constant between 10^7 and 10^8 m^{-1} and *Eg* is the optical band gap. The absorption coefficient can be calculated based on the thickness of the films, *t* and the transmittance, *T* using the Lambert's formula [14]:

$$\alpha = \frac{1}{t} \ln \frac{1}{T} \tag{4}$$

The optical band gap values, *Eg*, of the ZnO films were obtained from the transmission measurements by plotting $(\alpha h v)^2$ versus (hv) and extrapolating the linear portion of the absorption edge to find the intercept with the energy axis. As can be seen in the Fig. 4, the band gap values of ZnO films are found to be 3.24 eV to 3.26 eV which is slightly smaller than that of bulk ZnO (3.37 eV). This difference is due to the fact that the values of *Eg* depend on many factors e.g. the granular structure, the nature and concentration of precursors, the structural defects and the crystal structure of the films. Based from the experimental study by D. L. Zhang *et al.* [15], the difference between the film and bulk ZnO is due to the grain boundary, the stress and the interaction potentials between defects and host materials in the films. Bao *et al.* [7] also reported that the band gap difference between the thin film and crystal is due to the grain boundaries and imperfections of the polycrystalline thin films.
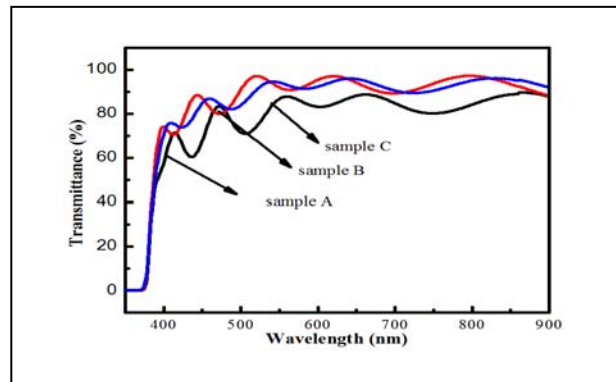

Fig. 3: Transmittance spectra of ZnO film with different sol aging time (a) 2h 15 min, (b) 3h 30 min. and (c) 24h.
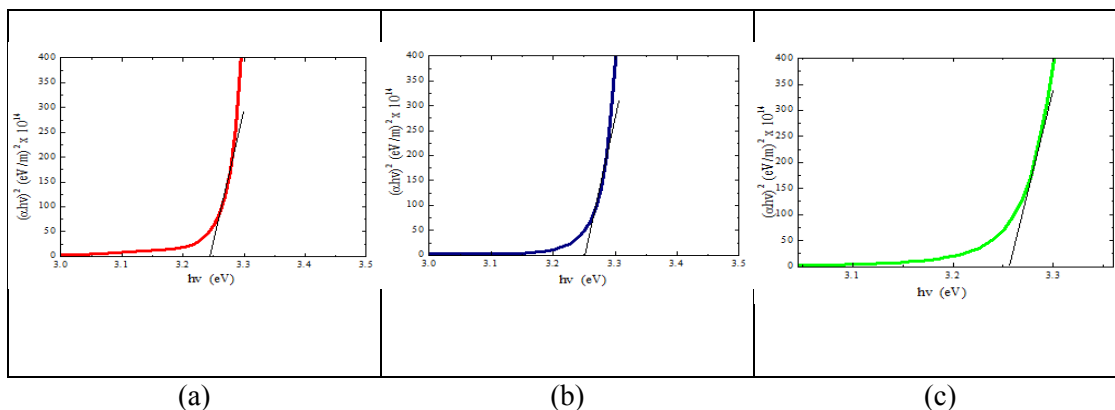
(a)   (b)   (c)

Fig. 4: Plot of $(\alpha h\upsilon)^2$ vs. $(h\upsilon)$ of ZnO film with different ageing time (a) 2h 15 min, (b) 3h 30 min.

4. Conclusion

ZnO films were successfully grown onto ITO substrate by sol-gel spin coating technique. The effects of sol ageing time on the structural and optical properties were investigated. Based on the XRD measurement, it was revealed that ZnO films were polycrystalline with hexagonal wurtzite structure along with c-axis oriented (002) plane. The crystallite size is in the range of 34.4 ~ 28 nm which decreased with ageing time increment. On the other hand, the AFM analysis revealed that the surface roughness of the films increased due to the increment of ageing times. Optical transmittance spectra indicate that all films were transparent (>75%) in the visible range which slightly improved with increasing of ageing times. This is because the sol had been very stable and homogenous with increasing ageing time. The optical band gap was estimated to be around 3.24 ~3.26 eV using Tauc's plot. We revealed that the ageing time of ZnO sol influenced the properties of ZnO films. Based on our finding we proposed that 24h ageing time is optimum for the fabrication of high quality ZnO films

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