Morphological, Structural and Optical Properties of ZnO Thin Films Deposited by Dip Coating Method

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Zinc oxide (ZnO) thin films were deposited on glass substrat by dip coating technique. The effects of sol aging time on the deposition of ZnO films was studied by using the field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), and optical transmission techniques. The morphology of the films strongly depends on preparation route and deposition technique. It is noteworthy that films deposited from the freshly prepared solution feature indistinct characteristics; had relatively poor crystalline quality and low optical transmittance in the visible region. The increase in sol aging time resulted in a gradual improvement in crystallinity (in terms of peak sharpness and peak intensity) of the hexagonal phase for all diffraction peaks. Effect of sol aging on optical transparency is quite obvious through increased transmission with prolonged sol aging time. Interestingly, 72-168 h sol aging time was found to be optimal to achieve smooth surface morphology, good crystallinity and high optical transmittance which were attributed to an ideal stability of solution. These findings present a better-defined and more versatile procedure for production of clean ZnO sols of readily adjustable nanocrystalline size.

Keywords: *ZnO, characterization, thin films, sol aging time, optical properties.*

1. Introduction

For a decade, there has been a great growing interest in nanomaterials because of its distinguishable difference in properties from macroscopic and bulk materials. Research in this area has focused on the synthesis, characterizations and applications of nanometer-sized metals, semiconductors and ceramics[1]. Indeed, designing nanomaterials is a critical issue for industrial applications, because the properties of nanomaterials play a significant role on the performance of devices[2]. Particularly, ZnO nanostructures have been studied intensively and extensively over the last decade not only for their remarkable chemical and physical properties, but also for their diverse current and future technological applications. They possess several interesting properties such as optical transparency, electrical conductivity, piezoelectricity, non-toxicity, wide availability, low cost and chemical stability[3-5]. ZnO is used as transparent electrodes, photocatalysts, energy saving coating materials for window glasses, acousto-optic devices, ferroelectric memories, reduction gas detection sensors[6] and solar cells[7]. So far, ZnO-based thin films have been prepared by many different techniques based on vacuum deposition and solution-based processes[8]. While physical methods are capable of producing high-quality, single-crystalline nanostructures, these processes run into some deterrents notably, high-temperature-synthesis, ultra-high vacuum in some cases, and other restrictions in terms of sample uniformity, substrate choice, and low product yield. On the contrary, the chemical processes do not undergo these drawbacks and are capable of producing unconventional shapes and structures[9]. A wide variety of chemical methods have been reported in the literature such as chemical bath deposition (CBD)[10], electrodeposition[11-15], hydrothermal[16], spray pyrolysis[17], ultrasonic spray pyrolysis[18] and co-precipitation method[19]. Compared with the above methods, sol–gel method is the most widely used due to its high versatility, simplicity, low equipment cost, the ability of accurate control of stoichiometry over the molecular level mixing, large area coating, high homogeneity and relatively low process temperature[20-22]. Although the sol–gel method is a relatively simple technique for depositing ZnO thin films, there are still some factors affecting the properties of the prepared films. The factors including sol aging time, sol concentration[23], heat-treatment conditions, substrate[24], film thickness[25], dopants[26], pH of solution[27], solvents[28] and chelating agents[9] have been under continuous investigation. Among the deposition parameters mentioned; sol aging time is an important parameter which can have remarkable impact on thin films properties. Heretofore, the promising effects of ZnO sol aging time in terms of crystallinity and reaction-assisting are somehow described in previous reports[29]. However, to

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the best of our knowledge, no study has ever been done before concerning effects of sol aging time on the sol–gel behavior and the properties of sol–gel derived undoped ZnO thin films deposited by dip coating route. In this context, an attempt was made to investigate the influence of sol aging time on the properties of ZnO thin film during synthesis process in order to accomplish a better control over growth process. We believe that an appropriate sol aging may be a better choice which will ultimately provide high quality zinc oxide thin film using a simple method.

2. Experimental Procedure

2.1. Materials

For the preparation of ZnO sol, the following materials were used zinc acetate dihydrate and methanol. Distilled water was used to rinse substrates. All chemicals were of analytical grade, obtained from commercial sources, used as received without further purification.

2.2. Films preparation and processing

Transparent ZnO thin films were prepared by sol-gel method through dip coating on glass substrates. Specifically, zinc acetate dihydrate was dissolved in methanol under magnetic stirring at 70°C for an hour to yield a clear and homogeneous solution of 0.1 M. The product was then divided into four equal amounts and stored in four different beakers and aged for different time before deposition (Table 1). The final solutions were kept in the dark at room temperature, in order to avoid some light-assisted reaction that may affect the solution. After underwent an appropriate aging, the precursor was ready to be applied on a glass substrates. Before dipping the substrate into the precursor sol, the glass substrates were properly cleaned ultrasonically initially by acetone then nitric acid and finally with distilled water to remove all contamination which could affect thin film properties.

Film deposition was carried out in air at room temperature by the dip-coating method onto the substrate with a controlled withdrawal speed of 5 cm/min. They have been deposited from as-prepared as well as the sols aged for long time.

After each coating, the samples were left to dry, to evaporate the solvent and remove organic residuals, on a hot plate at 170°C for 15 min and were held in the horizontal position to avoid draining of the transferred sol, which could lead to different thicknesses in the coatings. The procedures from coating to drying were repeated several times until the film reached the desired thickness. The as-prepared films were then inserted into a furnace and annealed at 500 °C for an hour in the air and cooled down at room temperature. The atomic force microscopy (AFM) and field emission scanning electron microscope (FE-SEM) are employed to observe the morphology of synthesized samples. The phase structure of ZnO thin films were analyzed by X-ray diffraction (XRD) technique. XRD measurements were performed on a BRUKER D8 FOCUS diffractometer operating at 35 kV and 40 mA using CoKα radiation ($K\alpha_1 = 1.78901$ Å). The diffraction patterns were collected over 25–100° with a step size of 0.02° and a step time of 33.50 s. The optical transmission spectra were obtained using a UNICAM UV 300 as UV–visible spectrophotometer.

3. Results and discussions

3.1. Chemical reactions

The growth of ZnO thin films from zinc acetate dihydrate precursor using sol–gel process generally undergoes four stages, such as solvation and formation of methoxyacetate complexes, hydrolysis (by water originating from Zn $(Ac)_2 \, 2H_2O$ itself), polymerization of the complexes and transformation into ZnO. The size and activity of solvent have obvious influence on the reacting progress and product. Methanol has smaller size and a more active –OH and $–OCH_3$ groups. It can react more easily to form a polymer precursor with a higher polymerization degree, which is required to convert sol in to gel.

The dissolution of zinc acetate dihydrate accompanies solvation of zinc and acetate ions by methanol (MeOH). Hydrated water molecules form hydrogen bonding with MeOH. The kinetics of hydrolysis and polymerization are greatly influenced by water concentrations in the solutions. The zinc ion has a solvation number of six and forms an octahedral inner coordination sphere, $[Zn \, (MeOH)_6]^{2+}$.

Table 1: Effects of sol aging time on the microstructural properties of ZnO thin films.

Aging time (hour)	2θ (deg.)	d (002) (Å)	FWMH (deg.)	D (nm)	Lattice parameters (Å)	
					c	a
as-prepared	40.33	2.594	0.705	13.93	5.189	2.995
72	40.34	2.594	0.424	23.17	5.188	2.995
168	40.39	2.590	0.300	32.76	5.181	2.991
312	40.35	2.593	0.284	34.60	5.186	2.994

Thus the reaction scheme is invoked as:

$$[Zn(MeOH)_6]^{+2} + mMeOH + Ac^- \longleftrightarrow$$
$$[Zn(MeOH)_{5-m}(MeO)_m Ac]^{1-m} +$$
$$mMeOH_2^+ + MeOH \qquad (1)$$
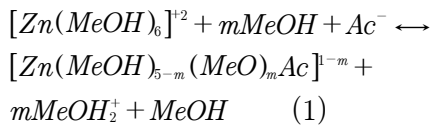
The formation of the methoxyl group is due to the enhanced acidity of the solvating MeOH causing the deprotonation by free MeOH. A reaction between the methoxyacetate complexes and water is considered. The water concentration in the solution does not exceed double of the zinc concentration because water was supplied only from the starting material, $Zn(Ac)_2 2H_2O$. Therefore the hydrolysis reaction is expected to proceed considerably slowly. At lower water concentrations, water acts as a nucleophilic reactant. The nucleophilic substitution with a leaving group of MeOH and/or CH_3COOH leads to hydrolysis of the complexes,

$$[Zn(MeOH)_{5-m}(MeO)_m Ac]^{1-m} + (m+1)H_2O \longleftrightarrow$$
$$[Zn(MeOH)_{5-m}(OH)_{m+1}]^{1-m} + mMeOH + AcH \quad (2)$$
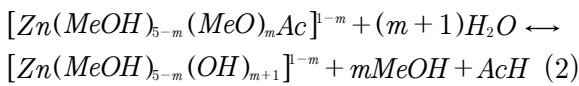
A polymerization reaction between mononuclear complexes generally occurs if at least one hydroxyl group is bounded to the metal ion. The first step of polymerization is the construction of an "ol" bridge in which a hydroxyl group is caught between the two metal ions. Writing the zinc hydroxide complex simply as Zn–OH, an olation reaction is expressed schematically by:

$$Zn-OH + OH-Zn \longleftrightarrow Zn-(OH)-Zn + OH \quad (3)$$
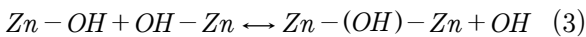
That is, "Zn (OH) Zn" bridges are formed by an olation reaction resulting in polynuclear zinc hydroxide clusters. When more than one hydroxyl group is brought to the complex, polymerization among the complexes proceeds, generating polynuclear zinc hydroxide clusters. Thus the "Zn O Zn" bonds are constructed and the complexes are finally transformed into solid ZnO[30-32] after annealing.

3.2. Aged sol and coatings

From visual inspections, the sol remains transparent, stable and indistinguishable from each other, regardless of the aging time. No gelation occurred over an aging period as long as several weeks. Also, films are transparent, homogenous, hard and are crack free. Such films were specularly reflecting and tightly adherent to substrate and could not be removed by abrasion with a tissue.

3.3. Morphological analysis

Figure 1 shows FE-SEM images of the ZnO thin films obtained after different aging time. It's clear from later images that surface morphology is considerably affected by sol aging time. Effectively, the as-prepared film produces
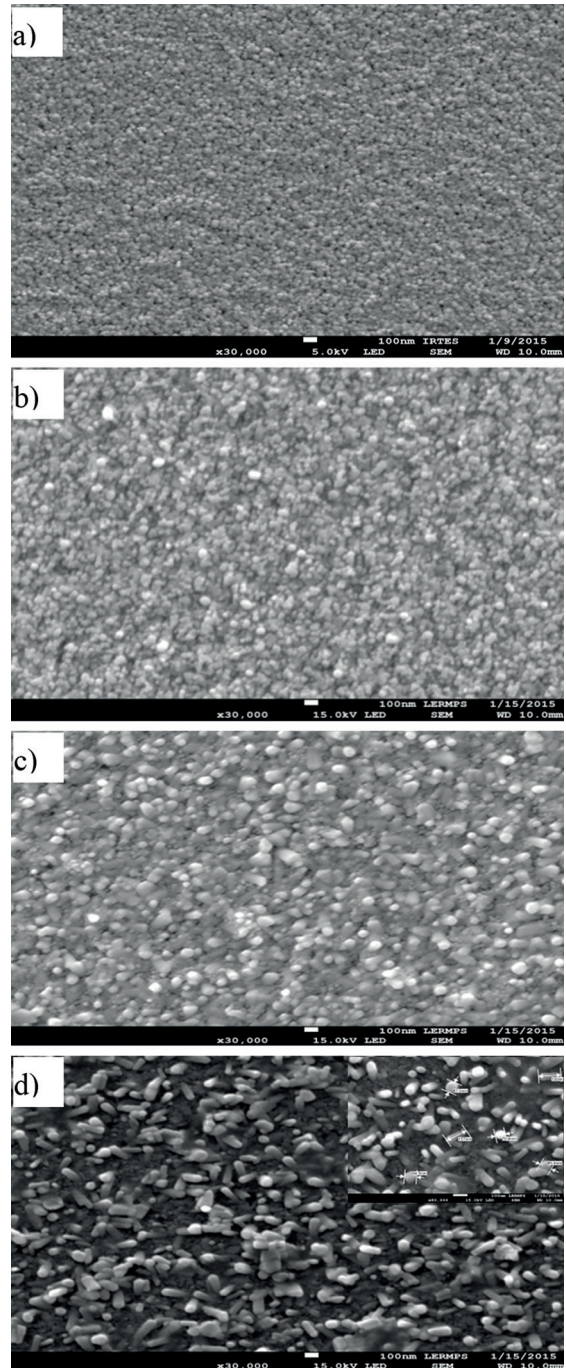
Figure 1: FE-SEM images of the ZnO thin films for different aging time: a) as-prepared, b) 72 h, c) 168 h, and d) 312 h. The inset shows the magnified surface morphology.

the appearance of a granular structures composed of small grains that appear somehow aggregated with porosity around. After, by increasing the sol aging time, films exhibit a finer texture in which bigger particles formed by nanocrystals agglomerate that are more effectively packed, giving denser structures characterized by lower porosity. For sols reached an aging time as long as 168 and 312 h,

the ZnO thin film is composed of vertically aligned densely packed randomly oriented nanorod with diameter in the range 43–87 nm having various lengths. The results from FE-SEM images are consistent with the observations from XRD. ZnO nanostructures have different orientations with particle size increasing as a function of aging period. Kanade et al.[33] explained that when a solvent with higher saturated vapor pressure such as methanol is utilized as a reaction media, the amalgamation of the nucleus is not intense due to the lower boiling point of the solvent, which results in mixed spherical and rod like particle morphology in case of methanol mediated ZnO. The aspect ratios (length divided by width) of the nanorods ranges from 1 and 2 nm. Especially, the length of the grain depends on the sol aging time. An average value of about 155 nm was observed for the samples deposed after sol being aged 312 h, i.e. longer aging time results in higher nanorod length. The differences in the film morphologies can be correlated with the particles shape.

In addition, the film surface morphology and surface roughness were also studied using an AFM technique. Figure 2 displays AFM images in tapping mode of ZnO thin films deposited from aged sol. It reveals that all films have a smooth surface morphology, and the cracks and pinholes were absent. For scanning area of $5 \times 5 \mu m^2$, the root-mean square (RMS) of average surface roughness for all samples was determined. The measured roughness parameters were 10.67, 5.07, 5.72 and 7.33 nm for ZnO films corresponding to the aging time t = 0, 72, 168, and 312 h, respectively. From this data, it could be also found that the surface roughness of the films decreased as sol aging time increased then slightly increased for sol aged 312 h. The increase of surface roughness along with sol aging time may be attributed to the larger grain formation and more porosity of the films. Generally, by increasing the sol aging time, more uniform, compact and smoother films were obtained. This is in good agreement with the FE-SEM results. Accordingly, the quality of ZnO thin films prepared by aged sols is improved.

3.4. Structural characterization

The XRD patterns of the deposited ZnO films as a function of sol aging time are shown in Figure 3. From XRD pattern the polycrystalline nature of the ZnO films clearly appears. All peaks have been indexed and were found to be in agreement with those of the hexagonal wurtzite phase of ZnO. Either peak position or peak intensity is in good agreement with the data from JCPDS card No. 00-036-1451. Moreover, no other peaks were detected, implying that the prepared nanostructured materials are pure ZnO.

Results indicate that thin film prepared from sol without aging represent bad crystallinity. Similar results were reported by Lie et al.[34], they attribute it to the stability of the sol, i.e. the as-synthesized sol is not stable enough in which the colloidal-particle sizes and colloidal-particle distribution

are non-uniform. As a result, the film deposited by the as-synthesized sol has relatively poor quality.

The crystallite size was calculated using the Scherrer formula[35]:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where D, θ, and λ are the mean crystallites size, the Bragg angle, and the wavelength of the incident X-ray (0.17889 nm), respectively. K is a shape factor and usually takes a value of 0.94 and β is the full-width at half maximum (FWHM) of the diffraction peak.

Table 1 shows the values of crystallites size and other microstructural parameters. From this data it's evident that crystallite size increased significantly with the increment of sol aging time. Also, the calculated lattice constants 'a' and 'c' of the prepared films were found to be close to those of pure bulk ZnO (a = 3.249 Å, c = 5.206 Å). It is clearly seen that film crystallinity of the as-synthesized is enhanced by increasing the sol aging time, meaning that more longer aging time promote more grain growth and hence narrower peaks with higher intensities which is evidenced by Figure 4. It is worthwhile to notify that different degrees of crystallinity could be reached regarding the aging time, i.e. the more the sol is aged; the greater is the crystallinity with random orientation. This is consistent with Dutta et al.[36]. Also, Fathollahi et al.[37] found a threefold increase in the intensity of (002) reflection of zinc oxide films using a 3-week-aged zinc acetate solution in comparison to the freshly prepared solution when all the other variables were kept fixed. Similarly, Singh et al.[38] synthesized ZnO nanoparticles via Sol-gel route; they found that the crystallite size as well as the crystallinity of the nanoparticles increased with aging. Ibrahim et al.[29] observed that by increasing the precursor aging time, an enhancement of the intensity for all diffraction peaks occurs in general. Despite the difference in precursor composition as well as the deposition route, both we and these previous reports found that sol aging time is of paramount importance in the improvement of the crystallinity. But our results are much better which is manifestly demonstrated from the peaks number and sharpness. According to Brinker et al.[39], chemical reactions that cause gelation continue long after the gel point, producing strengthening, stiffening, and shrinkage of the network. Wright et al.[40] recognized aging for improvement of material properties, and explained that Shrinkage occurs because new bonds are formed where there were formerly only weak interactions between surface hydroxy and alkoxy groups. This shrinkage leads to expulsion of liquid from the pores of the gel, so that gel samples in sealed containers gradually change in appearance from homogeneous gels to transparent shrunken solid monoliths immersed in liquid. This process is known as synersis. Another process associated with ageing is often referred to
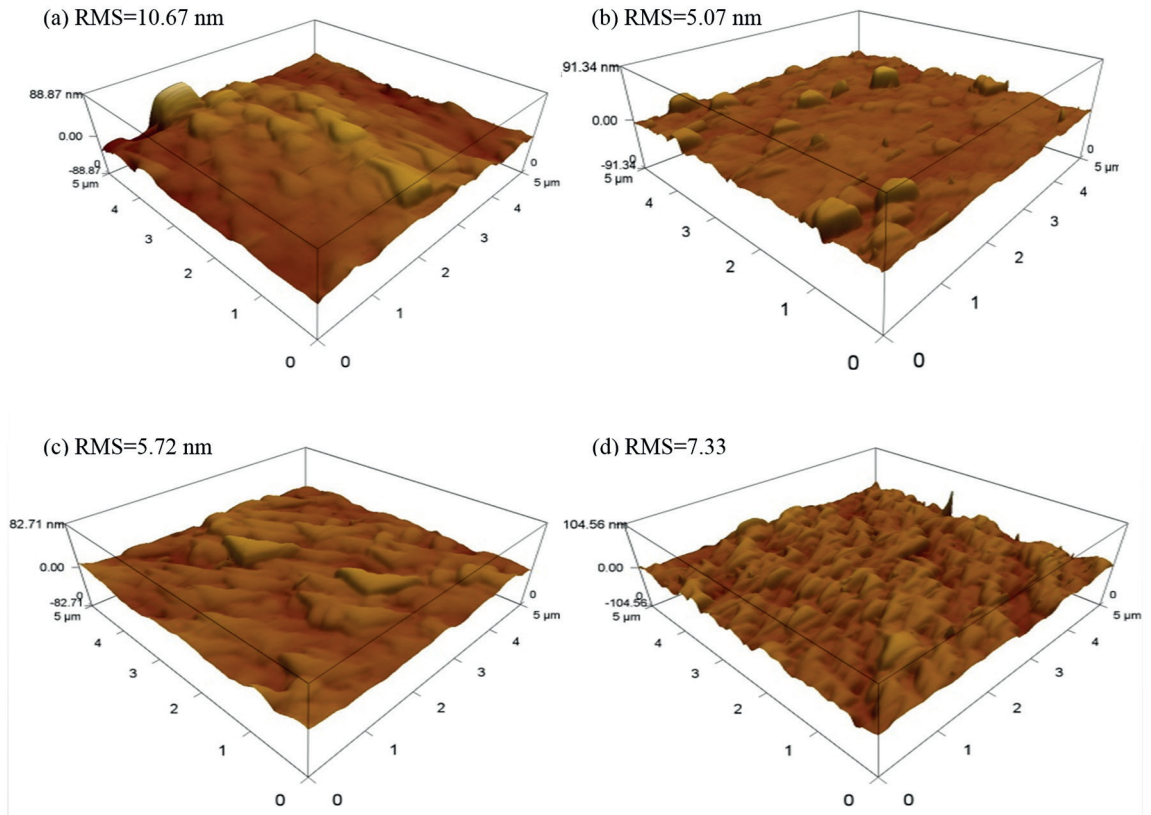
Figure 2: AFM surface morphology images of the ZnO thin films after different aging time: a) as-prepared, b) 72 h, c) 168 h, d) 312 h.
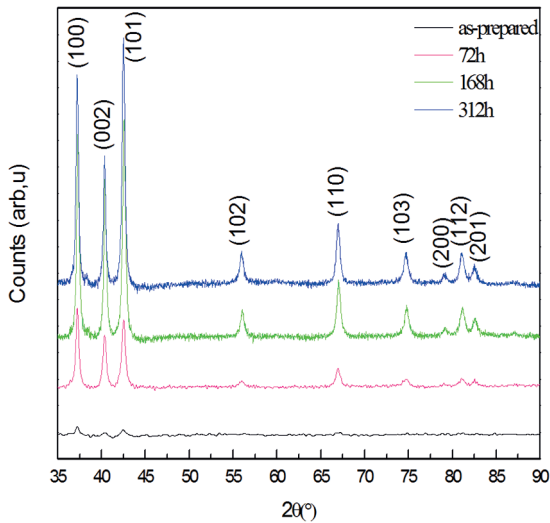
Figure 3: X-ray diffraction patterns of ZnO thin films prepared after different aging time.

as coarsening or ripening. In this process, material dissolves from the surface of large particles and deposits on the initially narrow "necks" which join particles to each other and hence the grain size increases.
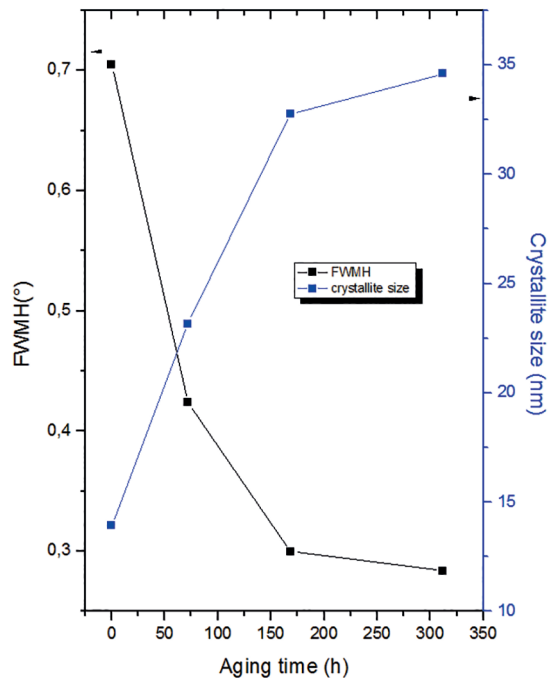
Figure 4: Variations of crystallite size and β of ZnO thin films as a function of sol aging time.

3.5. Optical properties

Figure 5 depicts the optical transmission spectra of ZnO films recorded in the wavelength region of 300–700 nm for different sol aging time. The deposited films are highly transparent with an average transmission exceeding 70–80 % in the visible range, which slightly improved with aging time. There has been an increase in optical transmittance. This increase is due to the decrease in surface roughness of films as confirmed by AFM images. Later these grains grow up in disordered manner resulting in scattering of light and a slight decrease in optical transmittance of the films. As shown in Figure 5, the aging time, from 0 to 168 h, does not affect the strong absorption property of ZnO thin films in the ultraviolet range and the fundamental absorption edges of the samples all locate at ~ 370 nm which corresponds to optical bandgap transition of ZnO. Later, it was found that further increase in aging time resulted in a small variation in absorption edges.

In the direct transition materials such as ZnO, the absorption coefficient (α) can be expressed by applying the Tauc model in the high absorption region[41]:

$$(\alpha h v)^2 = A(h v - Eg) \quad (4)$$

where α denotes the optical absorption coefficient, h is Planck's constant and v is the frequency of the incident photon, Eg is the optical band gap and A is a constant for a direct transition. Assuming the absorption coefficient $\alpha \sim -\mathrm{Ln}(T)$ corresponding to the direct band gap of the Wurtzite structure, a plot of $(\alpha h v)^2$ versus the photon energy hv yields in the sharp absorption edge for the high quality films by a linear fit[42].

Figure 6 shows the plots of $(\alpha h v)^2$ versus hv for the ZnO thin films deposited from sol being aged for different time. Optical band gap (Eg) can be determined by a linear extrapolation of the $(\alpha h v)^2$ plot against hv to the energy axis. The inset in Figure 6 indicates the variation of band gap energy with the sol aging time; its observed that an increase in optical energy gap from 3.19 to 3.25 eV occurred when the sol aging time varied between 0 and 312 h, respectively. We presumably attribute the variation of optical Eg with sol aging time to the improvement in the crystalline quality of the films, already proved by XRD results.

4. Conclusion

In summary, pure ZnO films have been successfully synthesized via sol–gel dip coating method on glass substrates. This process eliminates the addition of basic or acid solutions containing foreign elements, high temperature and complex systems. In the present contribution, the effects of aging time on the morphological, structural and optical properties of ZnO films were investigated systematically. Morphological analysis revealed that thin films prepared from aged sol were
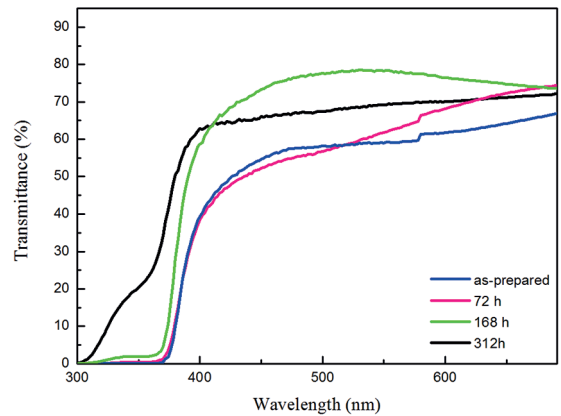
Figure 5: Optical transmission spectra of ZnO films for different aging time.
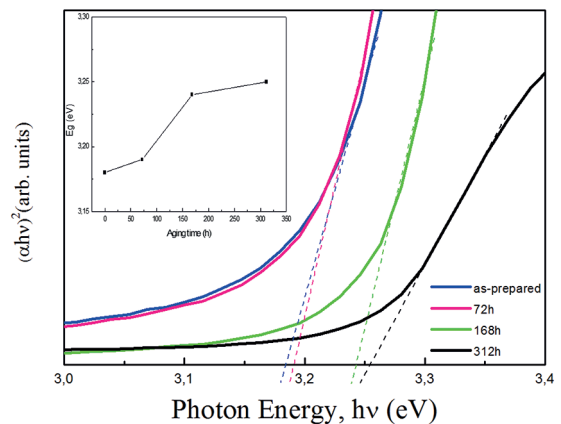
Figure 6: Plot of $(\alpha h v)^2$ vs. photon energy (hv) of ZnO film with different sol aging time. The inset represents band gap values obtained by extrapolating the linear part of the curves.

relatively smoother with minimum surface roughness and the heavily aged samples exhibits nanorods morphology. The obtained ZnO films exhibit wurtzite structure with random orientation and an apparent increase in crystallinity was observed with increasing sol aging time. Experimental results have shown that the prepared zinc oxide thin films by this method have higher crystallinity spectra as compared to other methods. Moreover, the optical transparency of films was significantly enhanced by aging the solution for longer times. An optimum sol aging time was determined for thin film formation providing a useful guideline for the process control purposes. These results meant that ZnO films prepared from the sol with longer aging time were still suitable for practical applications.

5. References

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