Synthesis, Structural and Optical Properties of Nanostructured ZnO Thin Films Prepared by Sol Gel Process

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Abstract

Nanostructured ZnO thin films have been synthesized by Sol Gel process. The ZnO precursors were prepared by using zinc acetate dehydrate and a mixed solution of monoethanolamine and ethanol, and were prepared with Zn^{2+} concentration 0.5mole. The films were deposited on glass substrates by spin coating at 3000 rpm for 30s at room temperature. These films were postheated at 400^{o}C for 1h at air. ZnO thin films have a polycrystalline and wurtzite structure. The crystallite size was determined by X-ray diffraction using Scherrer method. The crystallite size of ZnO thin film was 23.4nm. The transmittance spectra of ZnO films were 85% in the visible region from 600 to 800nm. The energy band gap is found to be 3.24 eV for ZnO film.

Keywords: ZnO, Sol Gel, structural properties, optical properties, thin film, crystallite size.

1.Introduction

Nanotechnology is the science and technology which deal with scales less than 100 nm[1]. ZnO is a wide range semiconductor with direct bandgap of (3.37ev) and large exciton binding energy (60meV) at room temperature[2]. Nanostructured ZnO thin films have a very important in various applications based on the interesting properties of nanostructured ZnO with bulk ZnO structure depending on crystallite size[3]. In recent years, semiconducting II-VI metal oxides especially tin dioxide (SnO_2) and zinc oxide (ZnO) have attracted attention of numerous researchers and scientists interested in gas sensing under atmospheric conditions. ZnO is an extremely useful as a solid state gas sensor material[4], acoustic wave devices[5], transparent conductive electrodes used for many devices such as electrochromic and electroluminescent displays and solar cell[6], UV photodetection and light emitting diode (LED) [7].

ZnO films have been prepared by several techniques: RF magnetron sputtering[8], pulsed laser deposition[9], chemical bath deposition, spray pyrolysis[10], electrochemical deposition[11], sol-gel method[12].

In this paper, nanostructured ZnO films were prepared by sol gel method. it advances result on structural (crystalline structure and particle size) by XRD. The optical properties of nanostructured ZnO thin films were measured by UV-VIS spectrophotometer at range (300-900nm).

2. Sol-Gel Process

The sol–gel technique is well known for preparing different forms of nanomaterials. In general, the principle of sol–gel synthesis is based on colloid chemistry in which the solid raw materials (usually inorganic materials) are dissolved in selected solvents and are then transmitted into homogeneous solution under controlled conditions (temperature, pressure, etc.). Then the dispersed phase is transferred into gel under similarly controlled conditions[13].

Sol-gel process is a wet chemical technique (chemical solution deposition) for the synthesis of colloidal dispersions of oxides starting either from a chemical solution or colloidal particles (sol for nanoscale particle) to produce an integrated network (gel). Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form a colloid, a system composed of solid particles (size ranging from 1 nm to 1 μm) dispersed in a solvent.

Hydrolysis reaction is a chemical reaction for which water reacts with a precursor to produce other compound, for example,

$$M(OEt)_4 + xH_2O \Leftrightarrow M(OEt)_{4-x}(OH)_x + xEtOH$$

Condensation reactions include formation of a metal oxide by connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo in solution.

$$M(OEt)_{4-x}(OH)_x + M(OEt)_{4-x}(OH)_x \Leftrightarrow (OEt)_{4-x}(OH)_{x-1}(MOM(OEt)_{x-1} + H_2O$$

After hydrolysis a condensation reactions, The sol evolves then towards the formation of an inorganic continuous network containing a liquid phase (gel), this process is called a Gelation. A gel is formed when one molecule reaches macroscopic dimensions so that it extends throughout the solution. Then, ageing of the gel network, the process of change in gel structure and properties after gelation is termed ageing process.

The drying process serves to remove the liquid phase from the gel thus forming a porous material, then a thermal treatment may be performed in order to favor further polycondensation and enhance mechanical properties. The precursor sol can be either deposited on a substrate to form a film by dip-coating or spin-coating, cast into a suitable container with the desired shape (e.g. to obtain a monolithic ceramics, glasses, fibers, membranes, aerogels), or used to synthesize powders (e.g. microspheres, nanospheres) as shown in figure 1.

Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio)sensors, medicine (e.g. controlled drug release) and separation (e.g. chromatography) technology[14- 18].

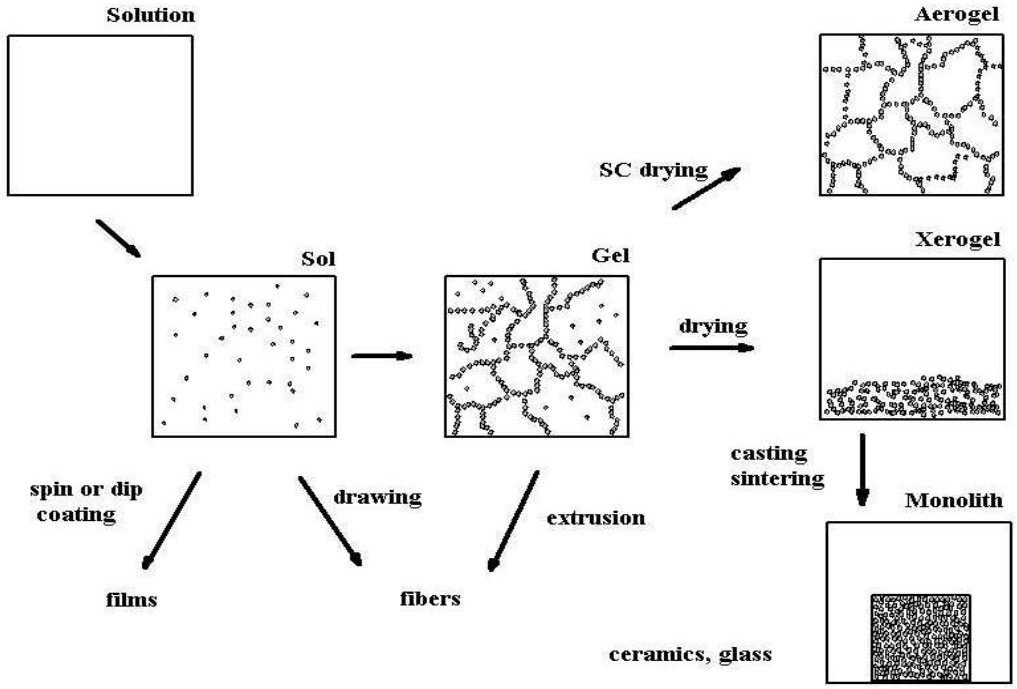

Figure 1: Sol-Gel process [14].

3. Experimental

3.1 Preparation of Nanostructured ZnO thin films

Nanostructured ZnO thin films were synthesized by addition of monoethanolamine (MEA) in ethanol with stirring to 10min by using magnetic stirrer at room temperature 25°C. then, zinc acetate dehydrate was dissolved in mixture of MEA and ethanol with stirring to 1h at 70°C to form ZnO colloidal. the molar ratio of MEA to zinc acetate dehydrate was 1.0 and the concentrations of zinc acetate dehydrate were prepared with 0.5mole/L. Nanostructured ZnO thin films were deposited by using spin coating technique onto glass substrates. Before the deposition that glass substrates were washed with distillation water and detergent, and then cleaned in HCl (15% concentration) for 1h by using ultrasonic cleaner and then cleaned in ethanol and acetone for 10min by ultrasonic and after that washed with distillation water and dried by air. The ZnO colloidal dispersions were stored to 1 day to complete growth of ZnO nanoparticles and form ZnO colloidal. The ZnO colloidal was dropped onto glass substrate with rotating by using spin coater at speed 3000 rpm for 30s. After the deposition, the film was preheated at 300°C for 10min in furnace to remove the solvent and organic residual. The procedure was repeated four times from deposition to preheating. Then, the film was crystallized by postheating at 400°C for 1h in air. Figure 2 shows the chart of preparation of nanostructured ZnO thin films.

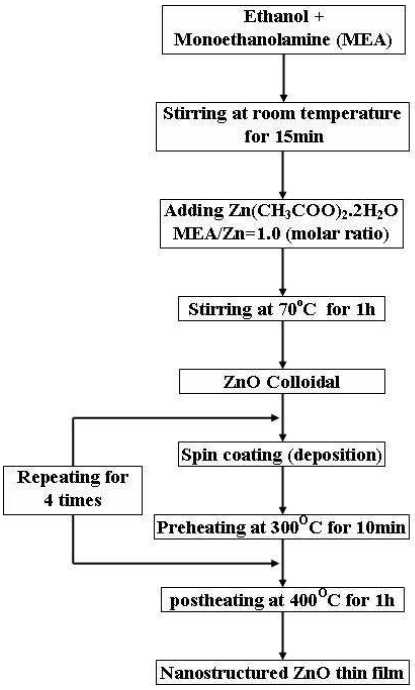

Figure 2: Chart of preparation of nanostructured ZnO thin film by sol-gel method.

3.2 Films Characterization

The X-ray diffraction (XRD) patterns of the thin films were recorded at room temperature using a system type: X'Pert Pro MPD by PANalytical company, with CuKα radiation. The optical transmittance was measured using a UV-VIS Spectrophotometer (Model Thermospectronic) in the wavelength range 300-900nm.

4. Results and discussion

4.1 Structural Properties

The structural properties of the thin films were investigated by X-ray diffraction. XRD patterns of ZnO thin films annealed at 400°C in air are shown in figure 3. The diffraction peaks which belong to (100), (002), (101), (102), (110), (103) and (200) diffractions are consistent with the JCPDS data of ZnO, these peaks which are indicated on a wurtzite structure, polycrystalline and random orientation of ZnO thin films. The XRD patterns of thin films indicated enhanced intensities for the peaks corresponding to (002) plane.

The crystallite size (D) could be calculated from XRD data by using Scherre's formula.

$$D = \frac{k\lambda}{\beta \cos\theta} \quad \text{.....1}$$

Where k is constant (k=0.9), λ is wavelength (λ=1.54 $\overset{o}{A}$), β is the full width at half maximum of (002) plane.

The crystallite size of nanostructured ZnO thin films were shown in table 1. These results indicated that the crystallite size of sol gel produced films is 23.4nm.

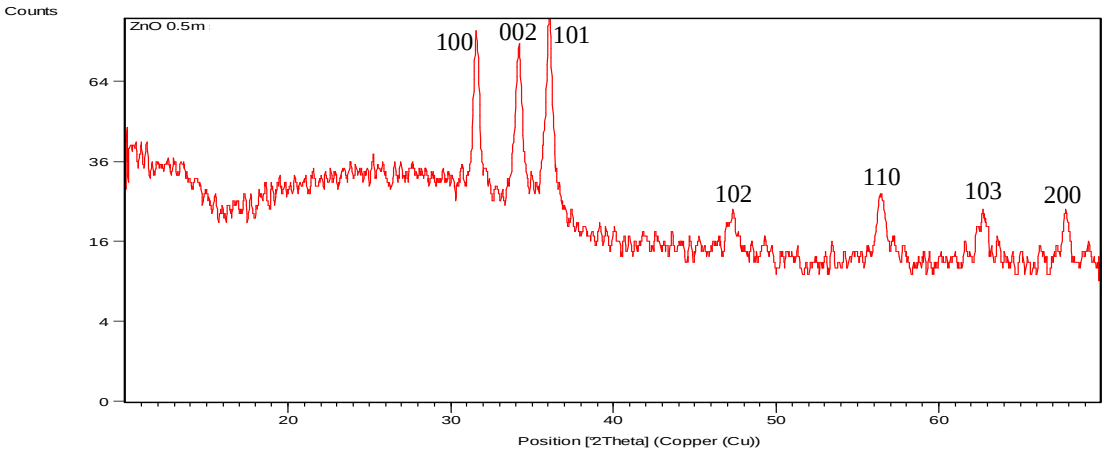

Figure 3: XRD patterns of nanostructured ZnO thin films

Table 1: Crystallite size of nanostructured ZnO thin film.

hkl	Pos. [°2Th.]	FWHM [°2Th.]	Crystallite Size (XRD) (nm)
002	34.2460	0.3555	23.4

The particle size of ZnO thin films as determined by the Scherrer method depends on some parameters. The Scherrer method delivers only estimates for the actual particle size, since in real systems, the surface and the measurement apparatus also contribute to the broadening of the peaks resulting in an estimation of the actual diameter. Thus, the finding of larger particles in the XRD measurements were preferred on crystallite size of ZnO thin films.

On the other hand, the broadening of the XRD peaks takes into account the sizes of all crystallites. Despite its lack in applicability to small (irregular) particles, the Scherrer method might be more suitable for the determination of the average particle sizes of large ZnO particles [19].

4.2 Optical properties

The transmittance spectra of ZnO films deposited on glass substrates is shown in figure 4. The ZnO films show transmittance above 85% in the visible region from 600 to 800nm. The optical absorption edge

shifts towards the wavelength 382nm for ZnO film as shown in figure 5. This result can be attributed to the increase in structural homogeneity and crystallinity.

From the absorption spectra of ZnO thin films the E_g energy band edge was calculated as below.

$$E_g = \frac{hc}{\lambda_{cut}} \text{.....2}$$

Where h is the Planck constant, c is speed of light and λ_{cut} is the cut-off wavelength which estimated from the intersection of the tangent line of the peak with the wavelength axis.

The Energy band gap for nanostructured ZnO thin film is found to be 3.24eV. ZnO thin film has sharp absorption edge is observed in the ultraviolet region

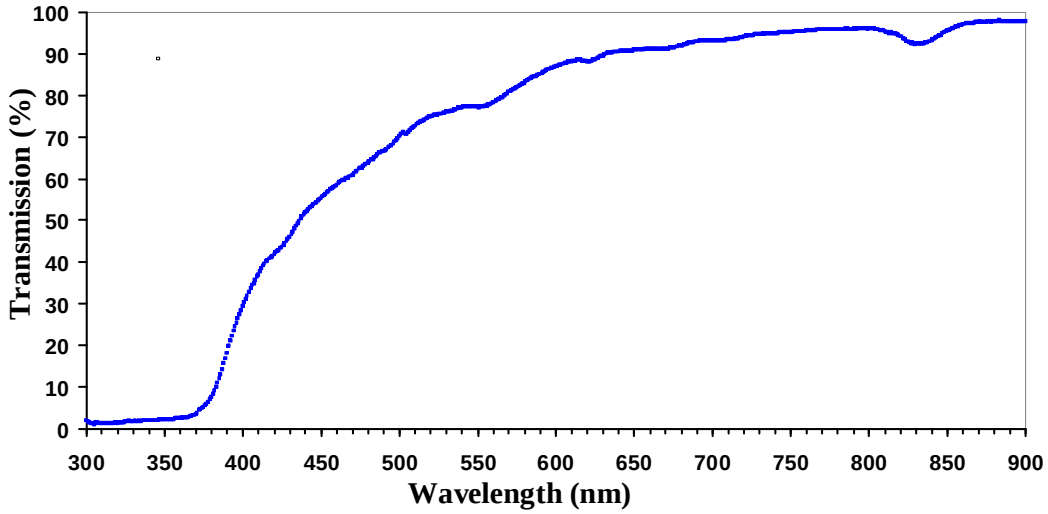

Figure 4: Transmission spectra of nanostructured ZnO thin film

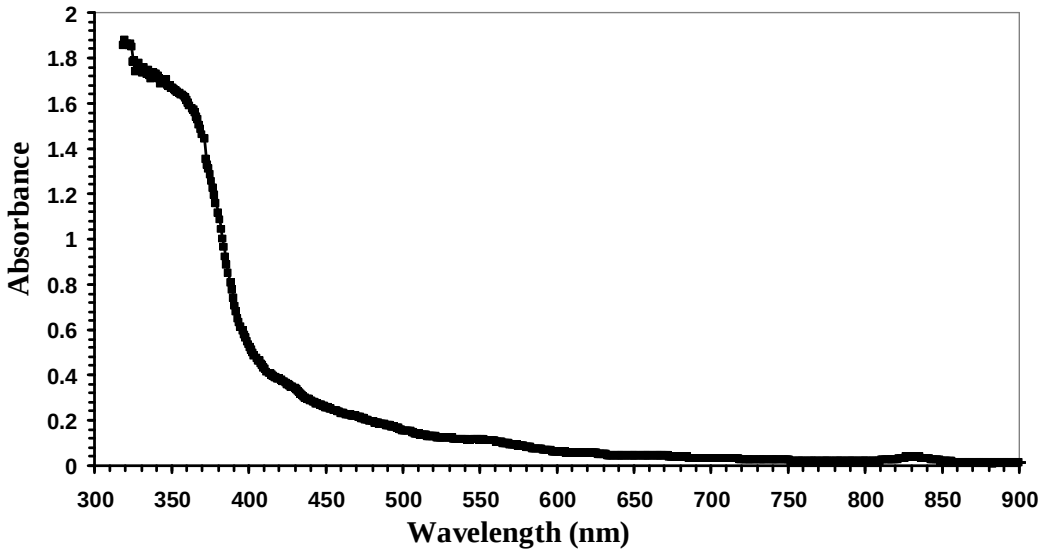

Figure 5: Absorbance spectra of nanostructured ZnO thin film

4. CONCLUSIONS

Nanostructured ZnO thin films have been prepared by the sol-gel process. We have investigated the structural and optical properties of ZnO thin films which fabricated by sol–gel process. XRD pattern reveals that the compound is polycrystalline with a randomly orientation with the wurtzite c-axis perpendicular to the film plane. The crystallite size of nanostructured ZnO films is 23.4nm. The films have an optical transparency up to 85% at 600 nm and above .

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المستخلص:

حضرت اغشية أوكسيد الزنك النانوتركيبية بواسطة عملية Sol Gel. وتم تحضيرها باستخدام خلات الزنك المائية ومحلول ممتزج من احادي اثانول امين ومذيب الايثانول وقد كان تركيز Zn (0.5 مول). وتم ترسيب المادة المحضرة على الزجاج بواسطة جهاز الطلاء عن طريق التدوير Spin Coating بسرعة قدرها 3000 دورة لمدة 30 ثانية وفي درجة حرارة الغرفة وتم الاحماء النهائي للاغشية بدرجة حرارة 400^{o}C ولمدة ساعة واحدة. تم دراسة الشكل التركيبي للاغشية باستخدام الـ XRD، اذ امتلكت الاغشية الرقيقة لاوكسيد الزنك تركيباً متعدد التبلور وتركيب wurtzite. وتم حساب حجم التبلور باستخدم حيود الاشعة السينية بواسطة معادلة شرر، اذ وجد ان حجم تبلور غشاء أوكسيد الزنك هو 23.4nm . اثبتت دراسة الخصائص البصرية لاغشية اوكسيد الزنك من ملاحظة طيف النفاذية زيادة النفاذية من 85% فما فوق عند الطول الموجي 600nm لاغشية اوكسيد الزنك بتركيز 0.5 مول. كذلك أثبتت دراسة الخصائص البصرية لأغشية اوكسيد الزنك ان فجوة الطاقة كانت (3.24eV).