Effect of Sol Concentration on Structural and Optical Behavior of ZnO Thin Films Prepared by Sol-Gel Spin Coating

Ans Farooq and Muhammad Kamran

Abstract—**Our present study on Zinc Oxide is for window layer of thin film based solar cells. ZnO thin films are of great importance and yields very promising results. ZnO thin films prepared by Sol-Gel process using spin coating at a speed of 2000 RPM for 30 seconds. The precursor sol was prepared by mixing of 2-proponal and zinc acetate dehydrate (ZAD) and using mono-ethanolamine (MEA) as stabilizer. ZnO sol was prepared varying sol concentration by 0.1M, 0.3M and 0.5M respectively. A comparison of optical and structural properties of ZnO annealed and un-annealed thin films are done by the help of XRD, SEM and UV-VIS-IR spectroscopy.**

Index Terms—**Zinc oxide, sol-gel, spin coating, optical characterization.**

I. Introduction

Transparent conductive oxides are of great importance now a day. ZnO is also a member of transparent conductive oxides. Zinc Oxide has a large band gap (Eg=3.37 ev), large excitation energy of 60 meV and categorized as a semi-conductor material primarily used for manufacturing of LEDs, OLEDs, Liquid crystal displays, flat panel displays, front contact of thin film solar cells and many other photonic devices [1], [2]. In particular, ZnO forms a technologically important class of material, exhibiting exceptional UV attenuation characteristics: blocking95% of all UV radiation, excellent transmittance in the long wavelength region, and outstanding antimicrobial properties [3], [4]. One area of great interest is the application of ZnO as a transparent conducting oxide (TCO).Many deposition techniques have been used to synthesize ZnO thin films, such as, sputtering, pulsed laser deposition. Physical vapor deposition (PVD) [5], spray pyrolysis, evaporation and sol-gel technique [6]. Sol-Gel Spin Coating synthesis is used in our work. It is used for several reasons, low cost, easy to understand procedure, uniform film thickness and large area deposition .ZnO is non-toxic and abundantly available [7]. In this paper we observed that by varying the ZnO sol concentration and annealing the samples at constant temperature of 450^{o}C yields a bigger grain size and abrupt optical behavior for 0.1, 0.3 and 0.5 Molar thin films.

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II. Experimental Procedure

Biological glass slides were used as substrate for deposition of Zinc Oxide thin films. The size of the glass slides used as substrate is of 1 inch x 1 inch. The substrate was cleaned with detergent and then dipped in chromic acid for about 5-10 minutes and then neutralized by sodium hydroxide. After cleaning the substrate was put into the box furnace for heating at 200^{o}C for 10 minutes to remove containments (water or solvent) on the substrate.

In the present work sol-gel method was used to prepare zinc oxide thin films using zinc acetate dihydrate [Zn $(CH_3COO)_2$. $2H_2O$]. Zinc acetate dihydrate was dissolved in iso-proponol [$(CH_3)_2CHOH$] to prepare ZnO sol and mono-ethanol-amine [($HOCH_2CH_2$) NH_2] was added drop wise in MEA: Zn ratio of 0.75 as a stabilizer. Magnetic stiring was done for 2hr at 60c than the solution was allowed to aged for 24 hr in room temperature. Three different solution are made varying the sol concentration of 0.1, 0.3, 0.5 Molar respectively. After that the aged solution was spin coated on the glass substrate at 2000RPM for 30 seconds and put it into the laboratory furnace with is pre-heated at 200^{o}C for evaporation of the residual solvent and any other containments. This cycle was done for 5 times to yield a smooth and uniform surface of thin films. After the spin coating procedure the deposited thin films are put into a high temperature furnace for annealing at 450C for 1 hour. After annealing the ZnO thin films, furnace is then left to cool down to ambient temperature. Below is the amount of Zinc acetate di hydrate and mono-ethanol amine which is used for preparing ZnO sol of different concentrations.

TABLE I: Amount of Zinc acetate Hydrate Used to Prepare Solutions of Different Molar Concentrations

IPA	0.1 M	0.3 M	0.5 M
50 ml	1.10gms	3.31 gms	5.52 gms
100 ml	2.21 gms	6.63 gms	11.05 gms
200 ml	4.42 gms	13.26 gms	22.10 gms

TABLE II: Amount of Mono Ethanol Amine Usedto Stabalize the Solutions of Ipa:ZAD

IPA	0.1 M	0.3 M	0.5 M
50 ml	1.10gms	3.31 gms	5.52 gms
100 ml	2.21 gms	6.63 gms	11.05 gms
200 ml	4.42 gms	13.26 gms	22.10 gms

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III. Results and Discussion

A. Structural and Morphological Studies and Optical Characteristics.

Spin coating process is easy and low cost but it has several problem which we have to handle with care like pin holes on the surface of film and uncoated areas. Pinholes occur due to air trap in on the surface of the film and uncoated areas can occur due very high speed of spin coater. If the spin speed is too high the solution will not stay on the film and will spread out of the film during the spin off process whereas if the speed is too low the solution will not reach to the boundaries of the thin film leaving behind the uncoated areas on the film. Similarly if the spin time is very short the film will be very thick and solution will also not reach to the boundaries of the substrate whereas if the spin time is very high it will also have a negative impact on film morphology. There must be a balance between spin speed and coating cycle time .To cover these issues we have to coat the same film several times. Scanning electron microscopy was done to observe the surface morphology. The SEM images shows the smooth surface which help us to say that thin films deposited have uniform surface and uniform grain size. SEM data shows that the grain size of 0.5M thin films is bigger than all other deposited thin films (0.1M and 0.3M). Grain size seems to increase with increase in molar concentration of the deposited thin films from smallest to largest of 0.1M, 0.3M and 0.5M thin films respectively. X-Ray diffraction and Scanning electron microscopy is used for structural and morphological studies of deposited thin films.XRD scan was done over a 2-theta of 0^o-60^o.XRD analysis shows the preferred peak is 101 which exactly matches with standard XRD card JCPDS 36-1451.A prominent difference is observed in annealed and un-annealed thin films of same molar concentration. The 0.5 M thin films show the most prominent peak whereas 0.1 M thin films show the least prominent peaks. XRD data also shows that peaks become sharper after annealing. Crystallite size is measured using Sheers formula, the crystallite size was also observed to be increasing with increase in molar concentration of deposited ZnO thin films. The crystallite sizes calculated using scherrer's formula [7] is as below:

TABLE III: Crystallite Size of Prepared Samples

Samples	Crystallite Size (nm)
0.1 M (un-ann)	Nil
0.1 M (ann)	11.4
0.3 M (un-ann)	12.3
0.3 M (ann)	14.1
0.5 M (un-ann)	17.2
0.5 M (ann)	22.1

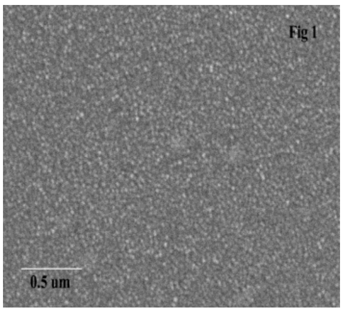

Fig. 1. SEM micrograph of 0.5 M thin film.

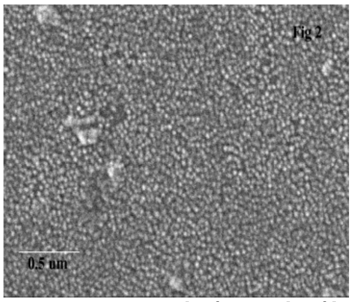

Fig. 2. SEM micrograph of 0.3 M thin film.

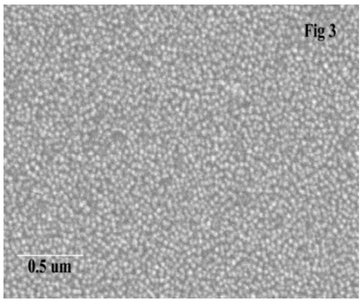

Fig. 3. SEM micrograph of 0.5 M thin film.

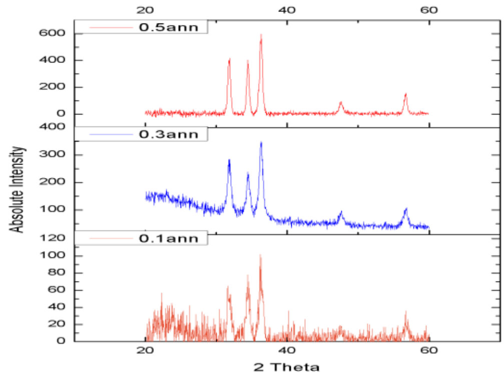

Fig. 4. Comparison of XRD patterns of annealed samples.

Optical properties [8], [9] were also studies using UV-VIS-IR Spectroscopy. The optical transmittance was observed in the range of 75%-92% in the wavelength range of 300nm to 800nm. Optical analysis was done on all deposited thin films and shows some surprising results, 0.5 molar film has maximum optical transmittance and 0.1 molar has the lowest optical transmittance (Fig. 5). Transmittance data also shows that thin films are highly transparent and allow maximum wavelengths to pass through the thin films.

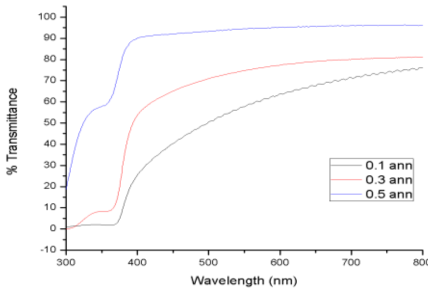

Fig. 5. Transmittance data comparison of annealed ZnO thin fims.

IV. Conclusions

The grain size is observed to be directly proportional to the molar concentration of the deposited thin films. Both XRD and SEM results shows that grain size is increasing with increase in molar concentrations of the deposited ZnO thin films. Annealing the deposited thin films also is a factor of increase in grain size. SEM data shows very smooth surface from which we can also estimate that surface morphology and grain are very much uniform .The thin films are transparent and yields very good optical properties. The transparency of these thin films can be used in developing Organic light emitting diodes (OLEDs), transparent displays for mobiles and other portable devices. The optical transmittance is in the range of 75%-92% which is very good for using it as window layer in solar cells [3] along with the CIGS or CZTS solar cells. Deposited ZnO thin films also can be used as gas sensors and water filters which is now a popular application of transparent conductive oxides.

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