Effect of Spinner Rotation Speed and Post-annealing on the Optical Constants of ZnO Thin Film

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ABSTRACT

Since five decades ZnO has been a workhorse material that finds applications in diverse fields including piezoelectric devices, spintronics, gas sensing, transparent electronics, biosensors etc. A simple band-gap tailoring in ZnO leads to it being used in various ways and the same is achieved by tweaking the deposition parameters and post-deposition treatments. In the present work sol-gel derived nanocrystalline thin films of ZnO are realized in the 20 – 60 nm nanoscale range. Band-gap energy variations in the ZnO thin films are investigated in the light of the thickness of the films deposited and which in turn are seen to be influenced by the spinner rotation speed. The band-gap energy values are noted to progressively move towards bulk value as the thickness of the ZnO films is seen to increase from 20 to 60 nm.

1. INTRODUCTION

The last two decades has seen an enormous rise in the research for development of nanocrystalline materials. Since the beginning of new interest in Zinc oxide (ZnO) in 1962 with its identification to be a piezoelectric material, it has gradually metamorphosed into a technologically important material and is currently considered to be a workhorse amongst semiconducting metal oxides. Known to be highly transparent in the visible region, ZnO is well-studied II – VI semiconducting material [1, 2]. It has a stable wurtzite structure with lattice constants, a = 3.2498 Å and c = 5.20661 Å. Exhibiting a direct and wide band-gap of 3.37 eV at room temperature, ZnO thin films have garnered intense attention while finding applications in latest fields related to spintronics, piezoelectric devices, gas sensing, transparent electronics, ultraviolet lasers and photodetectors and biosensors [3, 4]. With a background concentration of electrons as high as 1021 cm-3 and high exciton binding energy of around 60 MeV, thin films of undoped ZnO are widely known to exhibit n-type conductivity. In most of the investigations unique properties leading to ZnO's versatile applications are attributed to the presence of stress in the deposited films [5, 6]. Acting as a critical parameter the stress incorporated during the deposition/ processing of the thin films is reportedly seen to significantly affect its electrical and optical properties thus influencing performance of the devices.

Available literature indicates that processing conditions and thin film deposition technique adopted strongly influences the structural and optical properties of ZnO thin films. Specifically, deposition parameters are understood to affect the origin of stress and defining the microstructure of the ZnO thin films. Nanocrystalline films are reported to exhibit enhanced properties vis-à-vis their mechanical, optical and electrical properties. Worldwide researchers are actively engaged in tailoring the band-gap of ZnO thin films in the nanoscale domain for realization of optimized and desirable optical properties.

Sol-gel is one of the comparatively simple and preferred thin film deposition techniques for coating of large area substrates with uniform film thickness. Other advantages of sol-gel technique include reproducible stoichiometry besides control over doping in film composition.

In the present work ZnO thin films were fabricated through the chemical route technique of sol-gel method using zinc acetate as the precursor. The present study investigates the interesting influence of variation in band-gap of the ZnO films as a function of spinner rotation speed and post-annealing.

2. EXPERIMENTAL

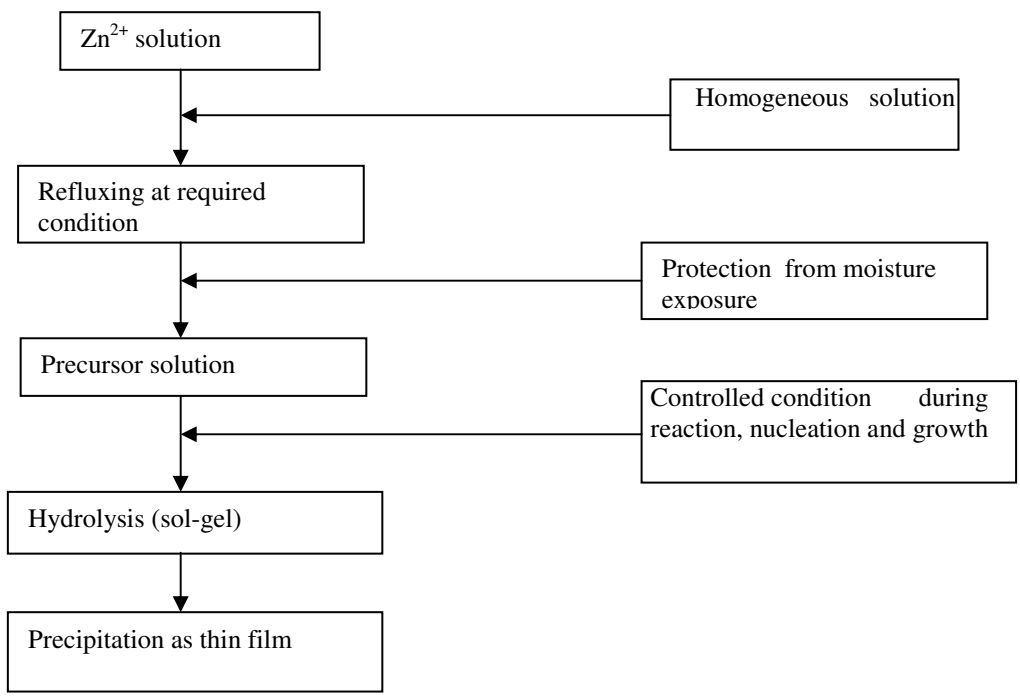

Figure 1: Flowchart of ZnO thin film deposition protocol

In the present study analytical grade reagents were used for the chemical synthesis of ZnO films using sol-gel method. Starting by dissolving zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) in 2-methoxyethanol ($((CH_3)_2CHOH$) and using [MEA] monoethanolamine ($H_2NCH_2CH_2OH$) as the stabilizing agent. Details of the molar ratios concerning measurements of MEA usage to zinc acetate are reported elsewhere [7]. The clear and homogenous solution for coating was realized by continuously stirring the mixture at 60°C for 1 hour and all coatings were done using freshly prepared solution. The flowchart in figure 1 summarizes the steps followed in the realization of the nanocrystalline ZnO thin film.

The as-deposited sol-gel derived thin films of ZnO were further subjected to a post-deposition annealing treatment in air at 300 ^oC in air for 3 hours. Variation in thickness (20 - 60 nm) of the ZnO films was achieved by changing the spinner rotation speed from 3000 to 5000 rpm. X-ray diffraction studies of the nanocrystalline ZnO thin films were measured using Panalytical Diffractometer with Cu Kα radiation (λ = 0.154 nm). Optical transmittance studies were carried out using UV-Visible double beam spectrophotometer model (Perkin-Elmer Lambda 35), and optical band-gap energy constant studies were calculated from the obtained data on transmittance and wavelength.

3. RESULTS AND DISCUSSION

X-ray diffraction study patterns of nanocrystalline ZnO thin films fabricated by sol-gel method are enumerated in figure 2. The XRD pattern clearly indicates the nanocrystalline nature of the deposited ZnO thin films.

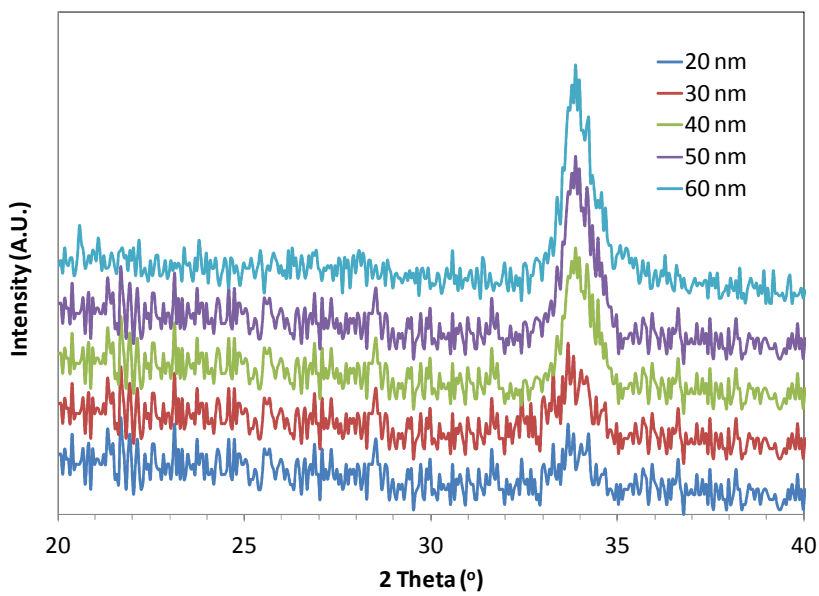

Figure 2: XRD pattern of the ZnO thin films of varying thickness

Corresponding to the peaks in the compiled standard for ZnO (JCPDS S6-314) the nanocrystalline ZnO thin films majorly exhibited the (002) diffraction peak. A preferential growth along (002) plane indicates that the nanocrystalline films are oriented along c-axis. Looking at the broad peak spectrum it is easily discernible that the crystallite sizes are in the nanoscale range.

Optical transmission spectrum for the nanocrystalline thin films of ZnO are plotted in figure 3 and the plot indicates that the average transmittance value in the visible range typically varies between 88% - 94%. Band-gap energy calculations are estimated from the fundamental absorption edge of the films.

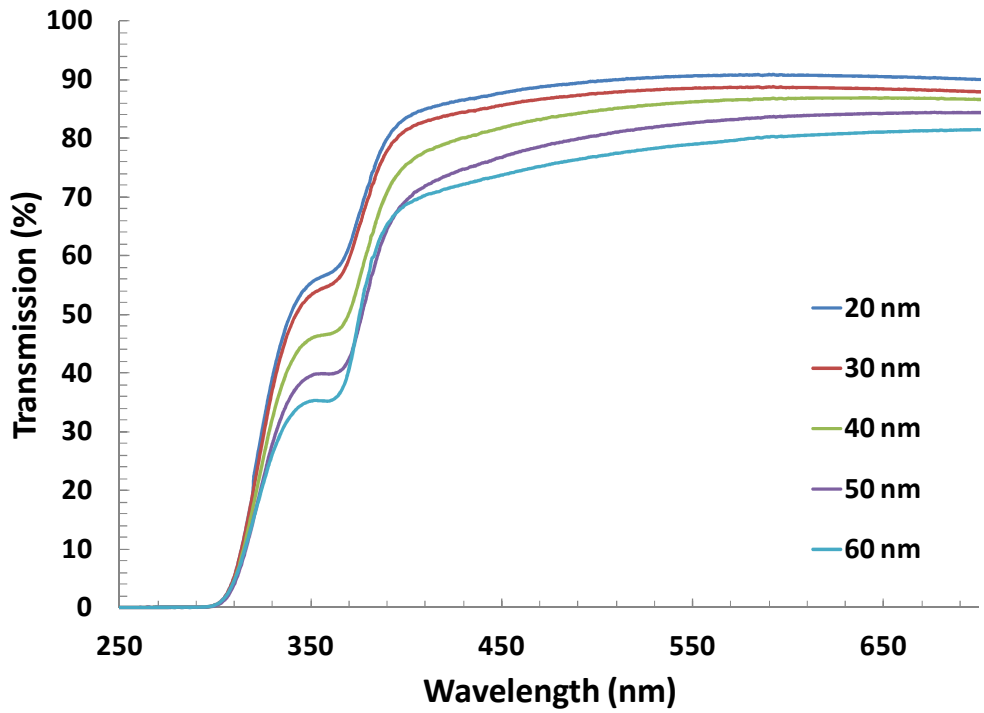

Figure 3: UV-Visible transmission spectra of the deposited nanocrystalline ZnO thin films of varying thickness

Figure 4 shows the $(\alpha hv)^2$ versus hv plots which are used to estimate the E_g values of nanocrystalline ZnO thin films. Figures 4 (a) and 4 (b) show the $(\alpha hv)^2$ versus hv plots for the 20 nm and 60 nm thick ZnO films and the conventional presence of a single slope in the plot indicates beyond doubt that the ZnO films have direct and allowed transitions. The standard extrapolation of the straight line portion of the plot onto zero absorption coefficient axis leads to band-gap energy calculation. Figure 5 exhibits the band-gap energy variation as a function of ZnO thin film thickness. It is interesting to note that as the film thickness of the ZnO increases from 20 nm to 60 nm the band-gap energy value is seen to progressively start shifting from the thin film values towards bulk (3.20 to 3.23 eV).

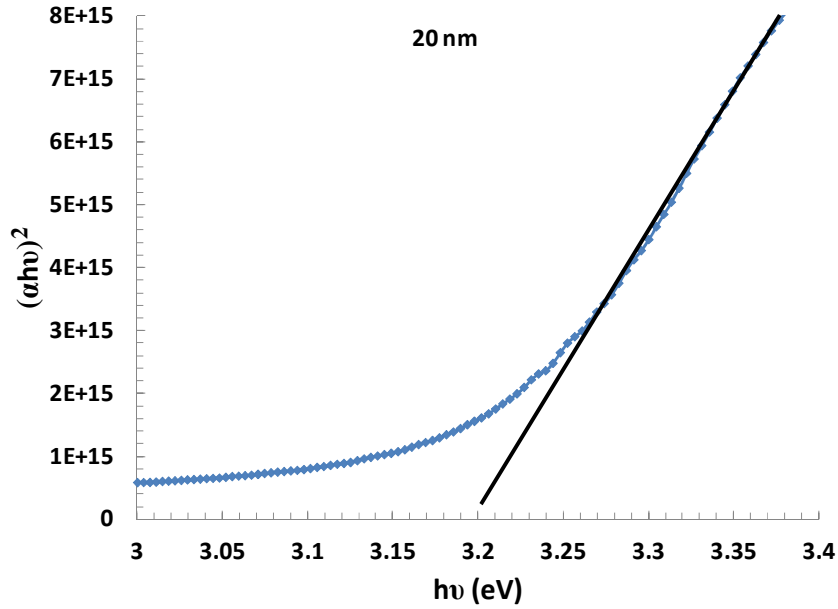

Figure 4 (a): Tauc plot of 20 nm thick ZnO thin film

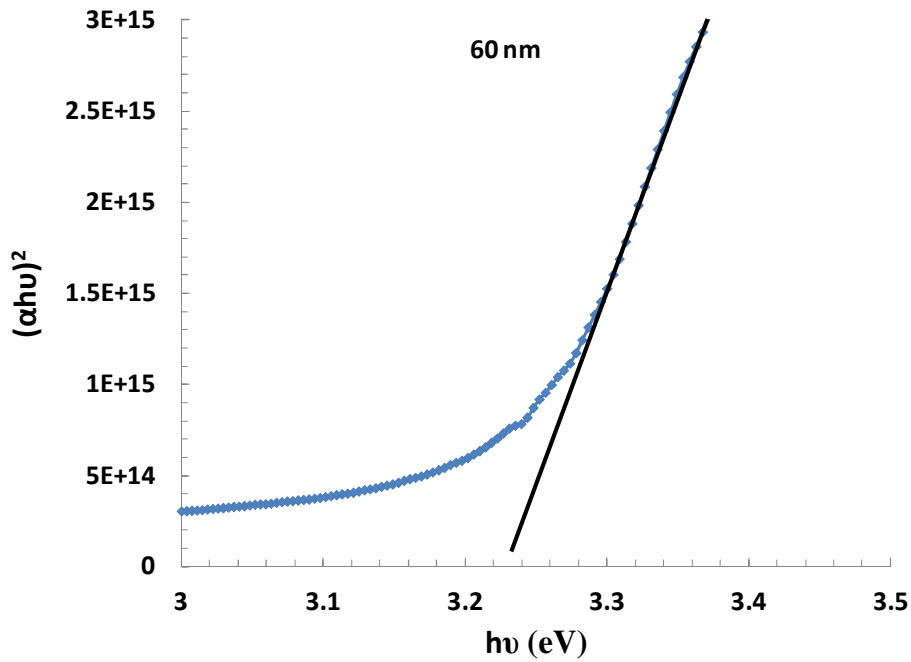

Figure 4 (b): Tauc plot of 60 nm thick ZnO thin film

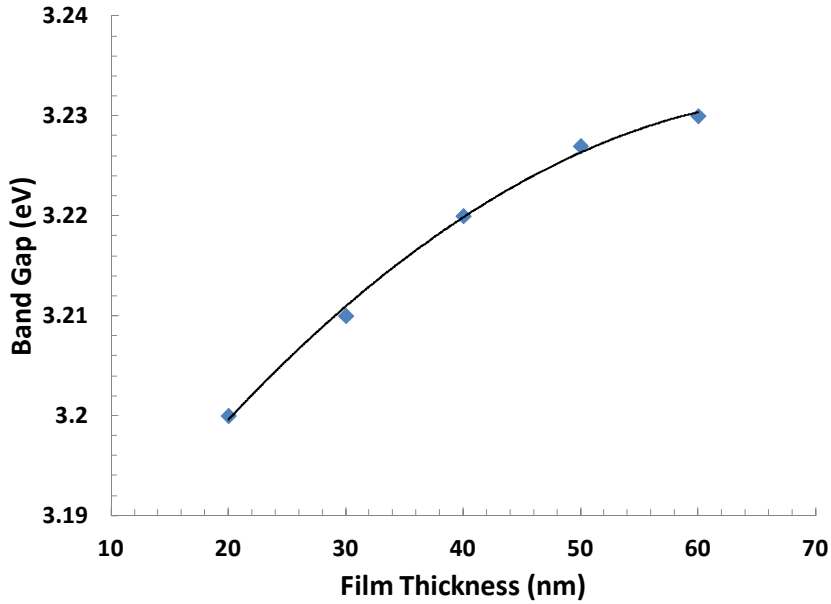

Figure 5: Variation of band-gap of deposited ZnO thin films as a function of thickness

4. CONCLUSION

The investigation indicates that nanocrystalline thin films of ZnO having stable stoichiometry could be easily and reproducibly fabricated using sol-gel technique. As the ZnO thin film thickness increased from 20 nm to 60 nm there is a perceptible shift in the band-gap energy value from thin film towards bulk value (3.20 to 3.23 eV).

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