Effect of Annealing Temperature on Structural and Optical properties of Dip and Spin coated ZnO Thin Films

B.W. Shivaraj a, H .N. Narasimha Murthy a*, M. Krishna a, B.S.Satyanarayana b

a Department of Mechanical Engineering, R V College of Engineering, Bangalore,560059, India
b Department of Electronics Communication Engineering, R V College of Engineering, Bangalore,560059, India

Abstract

This paper reports the influence of annealing temperature on crystalline size, film roughness, surface morphology and photoluminescence properties of ZnO thin films prepared by dip and spin coating techniques. Thin films were annealed at 400 °C and 500 °C for one hour each and their structural properties were studied using XRD, AFM and SEM. The coatings were characterized for photoluminescence using UV-visible Spectrometer. The films produced by both the methods conformed to hexagonal wurtzite structure. The grain size of dip coated films annealed at 400 °C and 500 °C were 291 and 312 nm and for spin coated films were 140 nm and 172 nm respectively. The surface roughness values of the dip coated films corresponding to the two temperatures were 17.31nm and 23.52 nm and those for spin coated films were 16.74 and 21.43 nm respectively. Annealing temperature significantly influenced crystallinity and surface roughness of the thin films in both methods of coating.

Keywords: ZnO thin films ; Annealing Temperature ; Spin coating ; Dip coating ; Structural properties.

1. Introduction

ZnO films has been studied due to their numerous applications such as gas sensors Biplob Mondal et.al (2014)

* Corresponding author. Tel.: +91 9901745089 fax: 91-80-28600337.
E-mail address: hnndatta@yahoo.com
display units [G.R.Gattorno et al. (2003)] transparent conductive electrodes [T.Minami et al. (1985) ] and solar cells [C.H. Liang et al. (2014)] due to is wide band gap energy of 3.37 eV with very large excitation binding energy of 60 meV at lab temperature. In the modern era, the researchers are trying to improve the production of ZnO nanocrystalline thin films using several methods such as reactive magnetron sputtering [Lee et al. (2007)] chemical vapor deposition [Guangyao Zhu, et al. (2012)] spray pyrolysis [Prasad Rao et al. (2014)], pulse laser deposition [Wei et al. (2009)] solvothermal technique [Doungporn Yiamsawas et al. (2010)] and sol gel technique [Lin Cui et al. (2013)]. Sol gel technique is one of the simplest and efficient method for fabrication of large area films and easily controlled composition, being able to carry out doping at molecular level [John Berlin et al. (2014)] Crystallographic orientation (grain orientation) of undoped / doped ZnO films directly varies on annealing temperature [Davood Raoufi and Taha Raoufi et al. (2009)]. Many researchers reported the influence of annealing temperature on improvement of grain size, surface roughness and photoluminescence and thermoluminescence of ZnO films [Chang et al. (2007)], [Hou et al. (2003)] TiO$_2$, In$_2$O$_3$ films [Mehmet Tumerkan Kesim and Caner Durucan (2013)] and SnO$_2$ [Kewe Sun et al. (2012)] films under different annealing temperatures. [Hsu et al. (2010)] studied the influence of annealing temperatures of AZO at 400 to 600 °C films on electrical, structural, morphological and optical properties by R.F sputtering as annealing temperature increases the X-ray peaks also increases with improve in crystallinity of films with lowest electrical resistivity of 2.31x10$^{-3}$ Ω cm, about 90% optical transmittance in visible region and surface roughness of 12.25 nm. [Zendehnam et al. (2013)] studied the effect of annealing temperature for range of 500 to 700 °C by DC magnetron sputtering to study the PL spectra with increase in interstitial zinc with increasing annealing temperature and morphology indicating that the annealing temperature produces larger grains and rough surfaces at higher temperatures. [Cui et al. (2007)] observed that PL intensity of ZnO films increasing with increase in annealing temperature from 500 to 900 °C. Violet peak shifted from 412 to 407 nm and 394 to 399 nm. This shift was due to the radiative defects in the interface traps existed at grain boundaries and also the stress in films changed from compressive to tensile so that the violet emission peak shifts from 412 to 409 nm. The 394 nm violet luminescence is attributed to free excitonic emission and increase in crystal size may also result in violet emission peak from 394 to 399 nm. [Habibi and Sardashti (2008)] reported that the crystallographic orientation of undoped ZnO films depends on coating technique and also observed that grain size of ZnO films increased with increase in annealing temperature from 350 to 550 °C was 16 to 25 nm for spin coating and for dip coating was 19 to 24 nm respectively. [Nanda Shakti and Gupta (2010)] studied the effect of annealing temperature 400 to 600 °C on ZnO film along three diffraction planes and stated that crystallite size increased from 34 to 54 nm and energy band gap 3.212-3.216 eV respectively. [Seung Wook Shin et al. (2010)] reported the gallium doping on ZnO films. The diffraction peak of GZO thin films were enhanced with increasing substrate temperature i.e. 250 to 450 °C. As a result larger grain size was obtained which improves the crystal quality because of thermal energy in the grains and also fewer defects in grain boundaries. [Harith Bahadur et al. (2006)] prepared ZnO films by sol gel spin coating and RF sputtering methods the films grown by RF sputtering have shown a lower refractive index and less compact than the films grown by sol gel spin method. Nano-structured ZnO grains of size ranging from 20 to 60 nm were obtained on the film grown by sol gel spin process using zinc nitrate as precursor material. [Ohyama et al. (1997)] prepared ZnO films using dip coating technique with three different withdrawal speeds i.e. 1.2, 2.5, 7 cm/min and observed that lower withdrawal speed results in denser films but also the thickness of film per single dipping is small so that the solvent can easily evaporate from the film. C-axis orientated was found for films with lower withdrawal speed of 1.2 cm/min. The authors also stated that increase in the dipping number also increases the thickness of the films from 50nm to 100 nm. [Keh Moh Lin and Paijay Tsai (2007)] studied AZO films thickness could be easily adjusted by controlling the Precursor concentration and number of dipping times i.e., with concentration of 0.3 and 0.5 M thicknesses was about 42 and 76 nm for each dipped layer. However, many researchers reported the influence of annealing temperature on improvement of grain size of ZnO films. The sol gel by spin coating and dip coating technique involves many process parameters such as molar concentration of precursor, pre and post heat treatment, aging time, drying time, doping concentration, annealing temperature, withdrawal speeds and dipping number which will directly or indirectly influence the quality of ZnO films. Hence, it requires a greater understanding of the annealing temperature and the process parameters of spin and dip coating in order to obtain good quality film. Review of literature revealed that the characterization of thin films for determination of crystalline size, surface roughness, surface morphology and photoluminescence for different annealing temperatures by spin and dip coating technique has not reported yet. The objective of the research was to synthesize ZnO film by spin and dip coating sol-
2. Experimental

2.1. Preparation of ZnO Solution

Solution preparation, coating and drying are the three stages of thin film coating process. ZnO sol was prepared by dissolving stichometric amounts of Zinc nitrate and sucrose in 20ml of distilled water in a cylindrical petridish. The solution was stirred using magnetic stirrer for 30 minutes and heated at 150 °C for 45 minutes to obtain gel and the gel was aged at room temperature for 24 hours. Before the deposition of ZnO sol, the glass substrates were cleaned with detergent, rinsed with acetone and ultrasonically cleaned with dilute HCL solution for 20 minutes. Substrates were also rinsed with DI water and dried at room temperature.

2.2. Film deposition

2.2.1 Spin coating

Spin coater with speed range 100-10,000 rpm and spinning duration up to 120 seconds was used for the research. The films were coated with a spinning speed of 3000 rpm for duration of 60 sec. After deposition the films were dried at 250 °C for 15 minutes.

2.2.2 Dip coating

Dip coating was carried out using dipping apparatus with a withdrawal speed of 1.2 cm/min for film deposition. After deposition the films were dried at 250 °C for 15 minutes.

2.3. Characterization of ZnO films

The structural property of the films was studied using a high resolution X-ray Diffractometer (XRD Maxima-7000, Shimazdu) at a scanning rate of 2° min-1 using Cu-Kα radiation (λ = 1.54 Å) from scanning range of 25° to 75° operating at 40 kV and 30 mA. The surface roughness was measured using Atomic Force Microscope, (AFM, Nanosurf Easy Scan 2). Scanning Electron Microscope (SU-1500, HITACHI) was used for studying the morphology of films with an accelerating potential of 15 kV and beam current of 20 mA. The PL measurement was carried out using habib Spectrometer with Xe lamp source with 323 nm excitation wavelength.

3 Results and Discussion

3.1 X-ray Diffraction (XRD) XRD pattern of the synthesized ZnO film obtained by spin coating is shown in Fig.1(a) and Fig.1 (b) with three strongest diffraction peaks indicating that the films are polycrystalline with a hexagonal wurtzite structure which is in agreement with ICDD card no.35-1451 and preferred orientation along (100), (002) and (101) planes. It can be observed that the films prepared by spin coating have a grain size of 21 and 25 nm for different annealing temperatures [Elilarass R and Chandrasekaran (2010)]. Dip coated films revealed that grain size was 20 and 23 nm. With increase in annealing temperature grain size also increased [Sharul Ashikin Kamaruddin et al. (2011)]and the effect of annealing temperature on grain size is summarized in Table 1.
Further, quality and crystallinity of the film were superior for the films prepared by dip coating and annealed at 500 °C. Grain size was calculated by Debye-Scherrer’s equation [Keh Moh Lin and Paijay Tsai (2007)]

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

where D is grain size, \( \beta \) is the full width at half maximum (FWHM), \( \lambda = 1.54 \) Å is X-ray wavelength and \( \theta \) is scanning angle.

Table 1 Effect of annealing temperature on grain size for coating technique.

<table>
<thead>
<tr>
<th>Coating technique</th>
<th>Annealing temperature (°C)</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin coating</td>
<td>400</td>
<td>140</td>
</tr>
<tr>
<td>Spin coating</td>
<td>500</td>
<td>172</td>
</tr>
<tr>
<td>Dip coating</td>
<td>400</td>
<td>291</td>
</tr>
<tr>
<td>Dip coating</td>
<td>500</td>
<td>312</td>
</tr>
</tbody>
</table>

3.2 Atomic Force Microscopy (AFM)

Fig. 2 (a) and 2(b) shows a two dimensional surface morphology image of the ZnO films prepared by spin coating. The images were obtained using Atomic Force Microscope by contact mode with scanning area of 40 μm x 40 μm, which reveals that the spin coated sample surface is relatively rough and grain sizes are not uniform. Film roughness was 17.31 and 23.52 nm for annealing temperature of 400 and 500 °C respectively.
Fig. 3(a) and 3(b) shows that the dip coated sample surface is smooth and grain sizes are uniform. The measured value of film roughness is 16.74 and 21.43 nm for annealing temperature of 400 and 500 °C respectively with increase in annealing temperature the surface roughness of film increases which was due the grain sizes becomes larger with the increase in annealing temperature, at high temperatures atoms had enough diffusion activation energy to occupy the site in crystal lattice and the grains with lower surface energy becomes larger [Joy dip Sengupta et al. (2011)].

Table 2. Effect of annealing temperature on roughness film

<table>
<thead>
<tr>
<th>Coating technique</th>
<th>Annealing temperature (°C)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin coating</td>
<td>400</td>
<td>17.31</td>
</tr>
<tr>
<td>Spin coating</td>
<td>500</td>
<td>23.52</td>
</tr>
<tr>
<td>Dip coating</td>
<td>400</td>
<td>16.74</td>
</tr>
<tr>
<td>Dip coating</td>
<td>500</td>
<td>21.43</td>
</tr>
</tbody>
</table>

Table 2. shows the effect of annealing temperature on roughness film of ZnO film which ranges from 16 to 24 nm for both spin and dip coating technique respectively which indicates that surface roughness of ZnO film increases with annealing temperature [Liu Y.C et al. (2006)].

3.3 Scanning Electron Microscopy (SEM)

SEM micrographs is shown in Fig 4(a) and 4(b) revealing the nanostructure of the synthesized ZnO thin film for spin coating with an average grain size of 19 to 25 nm, for annealing temperature of 400 and 500 °C respectively, thus agreement with XRD data and also removes the impurity [Sharul Ashikin Kamaruddin et al. (2011)]. Porous granular and irregular grains on the surface of film can be observed which is due to the shortage of hydroxyl group in ZnO solution which was evaporated due to the shorter time for drying of the solution.
Fig. 4 (a) ZnO films annealed at 400°C by spin coating  

Fig. 4 (b) ZnO films annealed at 500°C by spin coating

Fig. 5(a) and 5 (b) show the dip coated films are porous in nature with an average grain size of 20 and 23 nm for annealing temperature of 400 and 500 °C respectively increase in annealing temperature the grain size of film increases [Keh moh Lin and Paijay Tsai (2007)].

3.4 Photoluminescence (PL)

Fig 6 (a) and Fig 6 (b) shows the PL spectra for as formed ZnO thin film in room temperature by spin and dip coating technique upon 323 nm excitation, the emission spectrum of ZnO has visible region It is observed that as annealing temperature is increased the wavelength intensity increases because due to the oxygen and zinc atoms move from interstitial to lattice sites and surface area of grain increases [Linhua Xu et al.(2014)].The PL spectrum shows violet emission peak at 356 nm, blue emission at 442 nm and green emission at 533 nm. The violet emission was due to near band edge emission of wide band gap of ZnO due to annihilation of excitation. Blue band emission was due to the surface defects in ZnO such as oxygen vacancies and zinc interstitials and green emission was due to the intrinsic defects due to zinc vacancies and oxygen interstitials [Yaoming Li et al. (2010)].
From both the spectra it can be observed that UV emission depends on annealing temperature [Khojier et al.(2014)] and both spin and dip coating can be attributed to the polycrystalline nature of the films.

4. Conclusions
Spin and dip coated ZnO films have been deposited by a sol gel coating technique. Dip coating process gives a smooth film but in spin coating as the film formation and the evaporation occurs simultaneously so films do not have uniform surface. XRD pattern showed the polycrystalline wurtzite structure with increase in annealing temperature that grain size also increased. AFM results showed that uniform surface morphology for dip coating compared to that of spin coating technique with minimum roughness value was 16.74 nm SEM images also showed the polycrystalline nature of films and clear distinguish cannot between grains and grain boundaries for spin coated films but sharp and well defined grain boundaries can been seen on the surface of dip coated film at annealed at same temperatures using SEM micrographs. This study also reveals that dip coated is a simple and viable method of producing ZnO thin films and also dip coated film can provide film smoother surfaces. The PL spectra of both spin and dip coating techniques show the near band edge UV emission.

Acknowledgements

Financial support for the present research was provided by TEQIP-II Sub- Comp: 1.2.1 RVCE

References


Yong Jin Noh, Seok-In Na, Seok-Soon Kim., 2013. Inverted polymer solar cells including ZnO electron transport layer fabricated by facile spray pyrolysis. Solar Energy Materials and Solar Cells 117, 139-144.