Preparation and proposed mechanism of ZnO Nanostructure Thin Film on Glass with Highest c-axis Orientation

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Abstract
In this paper, ZnO thin film is deposited on slide glass substrate using the sol-gel process. Presenting well-defined orientation of ZnO thin films Nanostructure were obtained by dip coating of zinc acetate dihydrate, monoethanolamine (MEA), de-ionized water and isopropanol alcohol. The annealed ZnO thin films were transparent ca 85-90% in visible range with an absorption edges at about 375 nm. The morphologies and phase structure show that the ZnO/glass film is formed by a layer of ZnO nano-sized particles with average diameter of 40 nm. X-ray diffraction results showed polycrystalline wurtzite with a highest c-axis preferential (002) orientation with the only sharp X-ray diffraction peak at 34.40 corresponding to the hexagonal ZnO. The high c-axis orientation improved and the grain size increased by the annealing temperature. These results showed that the sol-gel deposited ZnO films have potential applications such as catalyst and transparent electrodes in optic and electronic devices.

Keywords: Thin Film; ZnO; Nanostructure; Sol-Gel; Dip coating;

1. INTRODUCTION
The sol-gel process has the unique advantage of allowing the preparation of the same composition, such as silica, in markedly different physical forms, fibers, coatings, monoliths, just by varying a few experimental conditions. Sol-gel chemistry has recently evolved into a general and powerful approach for preparing inorganic materials [1]. ZnO thin films are one of the most important materials due to technological applications. These wide variety of applications are including photoluminescence and transparent semiconductor [2], photocatalyst, piezoelectricity [3], gas sensors [4], UV light emitting devices [5, 6], varistors and Optical devices [7]. ZnO thin films have been prepared by various techniques, such as physical vapor deposition [8], chemical vapor deposition (CVD) [9], spray pyrolysis, sputtering [10], pulsed laser deposition (PLD) [11] and sol-gel method [12]. Some of the most important advantages of sol-gel processing, including conventional thin film deposition techniques, are the ease of chemical composition control, low temperature annealing and homogeneous of sol solution. These advantages make sol-gel process as a very attractive methods especially for preparation of ZnO thin films. In continuation of our efforts for preparation and characterization of thin films [13], in this study, ZnO thin film is deposited on glass substrate using sol-gel process.

2. EXPERIMENTAL
2.1 Film deposition
All the chemicals were analytic grade reagents without further purification, and purchased from Merck Company. To prepare sol solution, 6.20 g Zinc acetate dihydrate (Zn(CH$_3$COO)$_2$.2H$_2$O: ZnAc.2H$_2$O), 1.72 g monoethanolamine (MEA)
and adequate de-ionized water were added to 30 ml isopropanol alcohol, then heated to 60 °C with continuous stirring for 60 min. The sol-gel coating was made usually a day after the sol solution was prepared and the molar ratio of MEA to Zinc acetate was maintained at 1:1. Film deposition was carried out in air at room temperature by dip coating method on to substrate with a controlled withdrawal speed of 2 cm/min. After each coating, the films were pre-heated at 275 °C for 5 min, and post-heated at 350 °C, 450 °C, and 550 °C for 1 hour. The deposition was repeated for 5 times to obtain a film with different thicknesses.

2.2 Characterization techniques for thin films
The structure and crystalline size were determined by XRD diffraction (Bruker D8 advanced X-ray diffractometer: Cukα radiation, Scan rate 0.03 2. s-1) diffractometer. X-ray diffraction shows wurtzite structure with c-axis orientation (002). Transparent of films are measured by spectrophotometer(CECELL-CE7500) ultraviolet-visible spectrophotometer. The surface of the films was observed by scanning electron microscopy (SEM) with a Philips XL30 microscope.

3. RESULTS AND DISCUSSION
The morphology and texture of ZnO thin films made by sol-gel process were affected by solvent, preheating and post heating temperature, concentration of sol, substrate and procedure of coating. The results have shown that highest c-axis orientation nanostructure ZnO thin film was formed which influenced the optical and electrical properties of coating. Crystalline growth of predominately c-axis orientation in ZnO thin film depends on surface, energy of the film and the glass substrate and interfacial energy between them [14].

In proposed sol-gel mechanism, zinc acetate dehydrate Zn(CH₃COO)₂·2H₂O would transform to mono-acetate when it was added in isopropanol. So when [CH₃COOZn]⁺ is formed, it makes a complex with MEA during the process. The complex reactions are presumed as follows.

\[
\text{CH}_3\cdot\text{O}\cdot\text{Zn}\cdot\text{O}\cdot\text{CH}_3
\]

\[
[\text{CH}_3\cdot\text{O}\cdot\text{Zn}^+] + [\text{O}\cdot\text{C}\cdot\text{CH}_3]^-
\]

\[
\text{HO-CH}_2\text{CH}_2\text{NH}_2 + \text{[CH}_3\cdot\text{O}\cdot\text{Zn}^+] 
\]

\[
\text{HO-CH}_2\text{CH}_2\text{NH}_2\cdot\text{Zn-O-C-CH}_3
\]

The above reactions can offer an element of hydrolysis and dehydration polycondensation; the next process can be written as below:

\[
\text{HO-CH}_2\text{CH}_2\text{NH}_2\cdot\text{Zn-O-C-CH}_3 + \text{H}_2\text{O} 
\]

\[
\text{HO-CH}_2\text{CH}_2\text{NH}_2\cdot\text{Zn-O-C-CH}_3 + \text{CH}_3\cdot\text{C-OH} 
\]

\[
\text{HO-CH}_2\text{CH}_2\text{NH}_2\cdot\text{Zn-O-C-CH}_3 
\]

So when reactions continue other oligomer of \(\text{Zn}_2\text{(OH)(CH}_2\text{CH}_2\text{OH})_2\) may be formed. The resultant of the reaction when heated above 350 °C were transformed to ZnO [15, 16].

Fig. 1 shows the scanning electron microscopy (SEM) image of the nanostructure ZnO thin film. The average grain size of nanostructure ZnO thin films was near 40 nm. Fig. 2 shows the XRD pattern of the ZnO thin film on microscope glass slid by five spin-coating (5-layer) pre-heated at 275 °C for 5 min and post-heated for 1 hour at different temperatures, 350 °C, 450 °C, and 550 °C for 1 hour. Comparing the XRD patterns of the thin films with ZnO powder showed that thin films have lower intensity and higher FWHM (Fully Width at Half Maximum) than the powder and the films are predominantly (002) oriented, and finally films are crystallized at higher temperature (highest at 550 °C). The growth of ZnO thin films with a (002) orientation is kinetically preferred, which in turn reflects the fact that highest density of Zn atoms is found along the (002) plane.

Optical transmittance of ZnO thin films that preheated at 275 °C for 5 min and postheated at various temperatures, 350 °C, 450 °C, and 550 °C for 1 hour confirms the absorption at wavelengths about 375 nm corresponds to an electronic transition.
beyond the band-gap, 3.2 eV of the crystalline ZnO (Fig. 3). An increase in the transmittance of ZnO thin film is observed after the annealing treatment due to the release of hydroxide species remaining in the film. These results show that the sol-gel deposited ZnO films have potential application as transparent electrodes in opto-electronic devices.

4. CONCLUSION

The goal of sol-gel processing is to control the structure of a material on a nanometer scale from the earliest stages of processing. This goal has been achieved for pure material such as powders, thin films, fibers, and even monoliths. Transparent nanostructure ZnO thin films on glass substrates were prepared by sol–gel method using dip-coating technique for film deposition. The films were found to be high c-axis oriented. The transmittance of the films was higher than 85% in the visible range. The present work represents an alternative approach to previous studies and describes the synthesis of
ZnO nanocrystalline size starting from solutions not containing many additives to yield stable sols and to obtain homogeneous layers. Zinc acetate and MEA were used as starting compounds to obtain high quality pure coatings. These results show that the sol-gel deposited ZnO films have potential applications such as catalyst and transparent electrodes in optic-electronic devices.

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References