Structural, Compositional, Morphological, and Optical Properties of Electrodeposited Nanocrystalline ZnO Thin Film

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Abstract

ZnO is a wide band-gap (3.37 eV) II–VI compound semiconductor with hexagonal wurtzite structure. These films were deposited by electrodeposition technique, containing very low concentrations of sodium citrate and 30% hydrogen peroxide. Ammonium hydroxide is added to control the reaction. The structural, compositional, Surface morphology and optical analysis were studied by X-ray diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDS), Scanning Electron Microscope (SEM), and Atomic Force Microscopy (AFM).The hexagonal structure of ZnO (101) is observed with average grain size 48nm. The average RMS surface roughness of the film is observed to be 328.621nm. The bandgap of the ZnO film is observed to be 3.35 eV. The strong peak of ZnO at 381 nm is observed in photoluminescence spectroscopy.

Keywords: Zinc Oxide, Thin Film, Electrodeposition, Characterization etc

I. INTRODUCTION

ZnO is a n-type semiconductor with wide bandgap whose energy lies typically between 3.1 and 3.4 eV at room temperature[1]. ZnO is an important semiconductor material with a large bandgap (3.37 eV) [2], which continues to attract attention because of its low toxicity and its many applications[3]. According to its physical and chemical properties, ZnO can be used as a thin film or as a bulk material[4]. In recent years ZnO is attracting attention for its application in UV lightemitters[5], varistors [6], transparent high power electronics[7], surface acoustic wave devices [8], piezoelectric transducers [9] gas-sensing [10] and as a window material for display and solar cells [11]. ZnO thin films can be deposited by both physical and chemical methods. Physical method includes sputtering [12], pulsed laser deposition [13],

Molecular beam epitaxy [14], RF magnetron sputtering [15], and chemical method includes chemical bath deposition [16] Sol–gel [17] electrodeposition [18-21] Among these preparation methods, electrodeposition is widely used in order to obtain oxide materials with specific chemical and physical properties. Choosing an electrodeposition strategy for oxide film formation offers several advantages in comparison with other deposition techniques [22]. Electrodeposition produces denser films with lower resistivity, due to required material continuity for charge transfer [23]. In this paper, we report on the synthesis of nano-structural ZnO grown via electrodeposition method. The morphology and structure characterizations of the ZnO thin films were analysed in detail using X-ray diffraction (X'Pert PRO, PANalytical B.V., PW3040/60, Netherlands), scanning electron microscopy (JEOL JSM 6480 LV, Japan) equipped with Energy dispersive Xray spectroscopy EDS and Atomic Force Microscopy (Nano Surf EZ2, AFM Instrument,Switzerland). Photoluminescene (shimadzu RF-5301PC, Japan) and UV Visible Spectroscopy (Lambda-25Perkin Elmer; USA) measurements were performed on electrodeposited ZnO thin film for optical property examination.

II. EXPERIMENTAL

The ZnO thin films were deposited from a solution of analytical grade sodium citrate and 30% hydrogen peroxide in an alkaline solution of ammonia and distilled water. Commercial Zinc plates used as substrates, were cleaned in ethanol ultrasonically. The zinc plates were kept vertically in a closed beaker. We prepared different types of samples by varying the times and concentration of the dipping solution. The electrodeposition is carried out using zinc plate as anode and cathode.

40 ml of distilled water was taken in a beaker. In that 0.1M of AR grade sodium citrate and 30% hydrogen peroxide were introduced. The pH of the electrolyte was maintained at 9.5 to 10 by introducing AR grade of ammonia solution. The electrolyte was stirred moderately using magnetic stirrer. The bath was maintained at room temperature.

The two zinc plates were put in the electrolyte in a parallel configuration with an interelectrode srperation of 1 cm. The deposition was carried out catholically at -0.4 V at room temperature. The duration of the deposits was 15 minutes. The asdeposited films were whitish grey in colour. After the deposition is completed the substrate was removed from the electrolyte and washed with distilled water.

Compound formation were studied using x-ray diffractometer fitted with curved position sensitive detector. Compositional and Structural data for thin films were obtained using Energy Disspersive Spectroscopy, Scanning electron microscope and Atomic Force Microscopy. Optical measurements of ZnO thin films were carried out using UV-VIS spectroscopy and spectrofluorophotometer. Bandgap of ZnO is measured using absorbance curve.

III. RESULTS AND DISCUSSIONS

Fig. (1) shows the XRD spectra of asdeposited ZnO film on zinc substrate. The structural analysis clearly indicates the diffracted prominent peak of ZnO (101) plane. The film exhibits good crystallinity and all the peaks are indexed for a hexagonal ZnO lattice. The peaks of Zn (100), Zn(101), Zn(102), Zn (103) and Zn (110) are observed due to the substrate. From the table 1 it is clear that the observed 2θ and D values are in well agreement with the standerd values. The standard 2θ and d values are verifying using JCPDS data file number 361451. The average crystallite size has been calculated with Scherrer relation.

$$D = 0.94\lambda/ \beta\cos\theta, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where D is the mean crystallite size, β is the full width at half maxima of the diffraction line, θ is diffraction angle, and λ is the wavelength of the X - ray radiation. The particle size measured is 48nm.

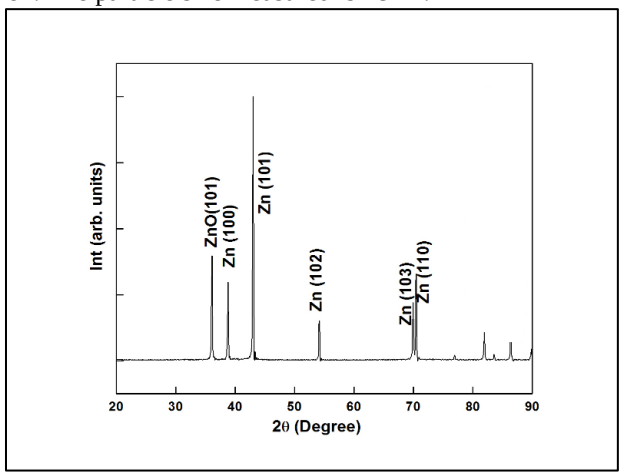

Fig. 1: XRD Analysis of Zno Film

Table -1

Sample	*Observed Value*		*Standard value*		*Miller indices*
	2θ	*dÅ*	*2θ*	*dÅ*	
ZnO	*36.12*	*2.48*	*36.21*	*2.47*	*101*
Zn	*38.8*	*2.31*	*38.91*	*2.09*	*100*

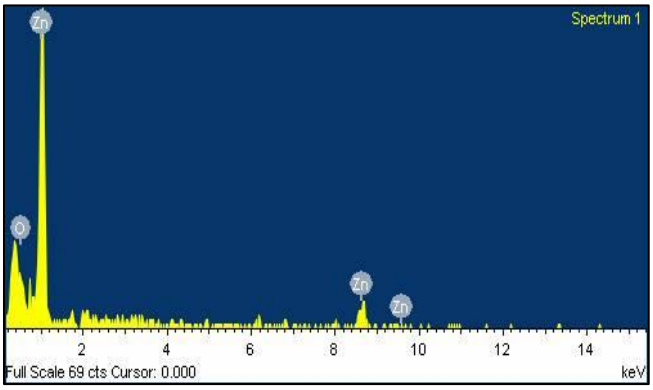

Fig. 2: EDS Analysis of ZnO film

Compositional analysis of the film were analysed by Energy dispersive X-ray spectroscopy. Zn and O are also clearly observed in the EDS spectrum of thin film. The atomic and weight percentage of the film were given in the table 2.

The scanning electron microscopy for prepared samples are shown in the figure 3. This is a single layer film whose deposition time is 15 minutes. The grains are well connected and uniformly distributed. The grains are densely packed, free from pin holes

pits and voids as is evidence from the contrast of the film. This SEM image shows a uniform film of ZnO at this concentration and deposition time.

Table -2
Atomic Weight Ratio Composition Of The Constituent Elements Measured By EDS

Element	*Weight %*	*Atomic %*
Zinc	*92.74*	*75.76*
Oxygen	*7.26*	*24.24*

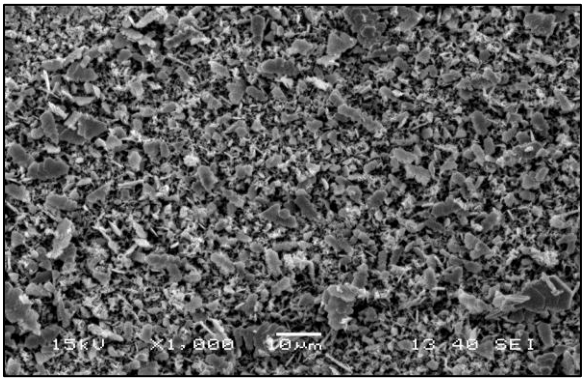

Fig. 3: SEM Image of ZnO film

Figure 4 shows the AFM images of ZnO films with deposition time of 15 minutes. At room temperature films are observed to have smaller grains, uniform grain size and random orientation with poor degree of crystallinity. . The variation of the surface roughness was observed at different temperatures. The RMS roughness is 328.62nm.

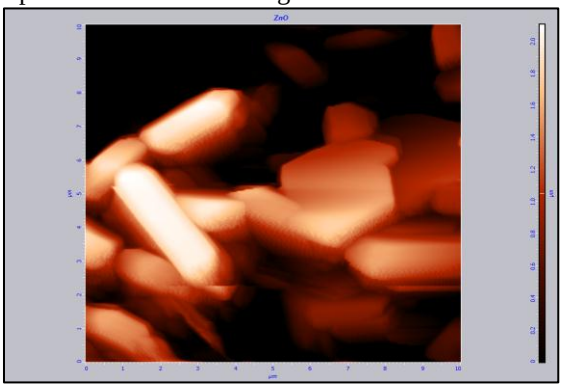
Fig. 4: AFM Analysis of Zno Film (2D)

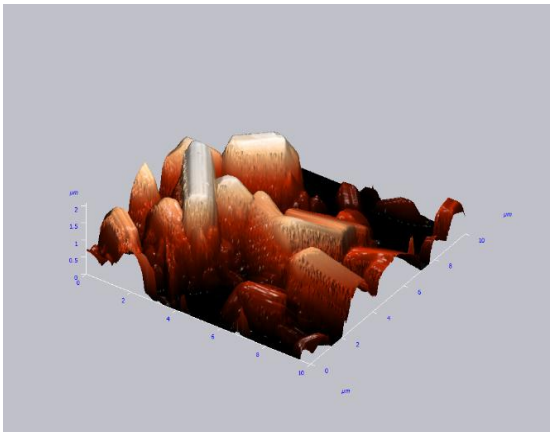
Fig. 5: AFM Analysis of Zno Film (3D)

UV-visible absorption spectroscopy is an efficient technique to monitor the optical properties of quantum-sized particles. Fig. 6 shows optical absorption spectra of ZnO thin film. Bandgap of the film is also determined by Tauc formula which is as follows:

$$(\alpha h\nu)^{1/n} = A(h\nu - Eg) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

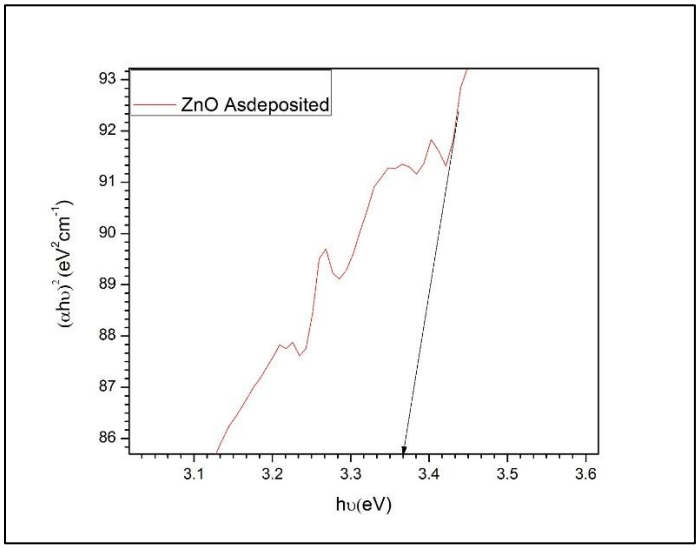

Fig. 6: Bandgap Determination of ZnO Film

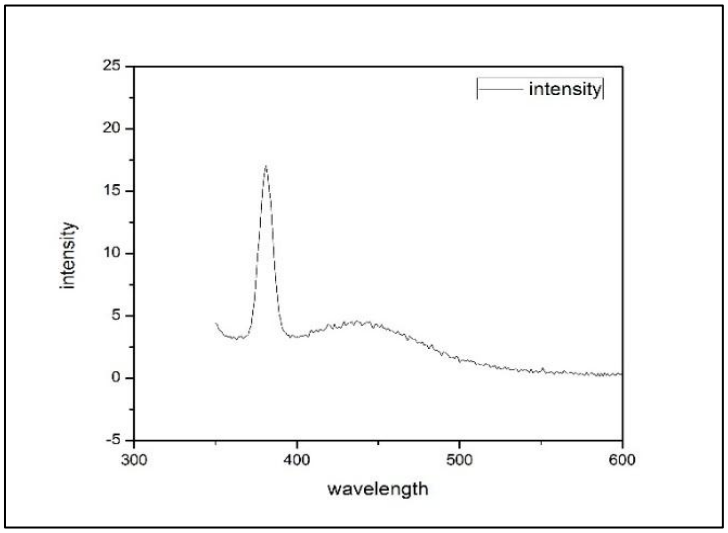

Fig. 7: PL Peak of ZnO film

Where, α, h, ν, A, Eg are absorption coefficient, plank constant, frequency of vibration, proportionality constant and band gap respectively. The energy band gap is found to be 3.35 eV.

Spectrofluorophotometer is also used to know the optical properties of quantam sized particle. The photoluminescence originates from the recombination of surface states. Figure7 shows the Photoluminescence spectrum of ZnO thin film. The PL peak is about 381 nm which is due to the presence of structural defects in the crystal of ZnO, called Urbach Tail [24].
This corresponds to luminescence from the surface states. Photoluminescence is observed at 381 nm which corresponds to emission of low energy near infrared light.

IV. CONCLUSIONS

The hexagonal shaped ZnO thin film is successfully deposited on zinc substrate using electrodeposition technique. The films are characterized for structural, compositional and optical properties. The hexagonal phase ZnO is observed by XRD analysis. The crystallite size of ZnO particle are observed to be 48 nm. The SEM images show uniform, compact, void-free surfaces, and varying orientation of film. The RMS roughness is 328.62nm. The energy band gap is measured to be 3.35eV. ZnO film presented have good characteristic to be used as a window layer for photovoltaic applications, optoelectronics, sensor applications

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