Effect of Mg Doped ZnO Thin Film Develpoed by Electrodeposition Method

Shashikant Rajpal, S.R. Kumar

Abstract— Zinc magnesium oxide (ZnMgO) is a ternary II-VI direct band gap semiconducting material whose band gap varies from 3 to 4 eV. The semiconducting material is used as the window material in photovoltaic solar cell. In this study, pure Mg-doped ZnO (ZnMgO) thin films were prepared by electrodeposition technique using AR grade MgCl2, sodium citrate and 30% hydrogen peroxide. The solid state properties and optical properties of the as deposited films were carried out by XRD, EDS, SEM, AFM, UV–visible spectrophotometer, and photoluminescence spectrophotometer. The diffraction peak observed at 2θ = 36.15° with (101) plane indicate the crystalline hexagonal phase of ZnMgO film. Compositional analysis reveals the presence of Zn, Mg and O. The average crystalline size is observed to be 46 nm. The band gap and luminescence peak of the ZnMgO films are observed to be 3.27 eV and 372 nm respectively.

Index Terms— Characterization,Electrodeposition,Optical Properties,SEM,Thin Film,XRD,ZnO etc

1 INTRODUCTION

In recent decades, the electronics industry has predominantly focused on semiconductor and display applications [1].

Zinc oxide is an ideal material for fabrication of short-wavelength optoelectronic devices since it has wide bandgap (Eg=3.37 eV n-type semiconductor) at room temperature with large exciton binding energy of 60 meV [2]. Higher exciton binding energy of zinc oxide enhances its luminescence property. It is direct bandgap n type semiconductor with hexagonal wurtzite structure [3]. Zinc oxide (ZnO) has received much attention since the last decade due to three key advantages: semiconducting with a direct wide band-gap and a large exciton binding energy, biocompatible, and piezoelectric [4]. For these reasons, wurtzite structured ZnO can be used towards versatile applications in electronics [5], optoelectronic [6], transistors [7], LEDs [8], photovoltaic [9] and bioimplantable sensors [10]. The bandgap of ZnO can be modified by alloying Cd and Mg [11]. A number of techniques have been employed in the synthesis of high quality thin film such as magnetron sputtering [12], spray pyrolysis [13], Chemical Vapour deposition [14], Pulsed laser deposition [15], molecular beam epitaxy [16], hydrothermal method [17], sol gel method [18]. In this paper, we developed ZnMgO ternary II-VI semiconductor by electrodeposition method. 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. Very thin layers with specific composition, morphology and good adhesion between the deposited film and the substrate can be easily prepared by electrochemical techniques. [19].

2 Experimental Procedure

2.1 Sample Preperation

The Magnesium doped Zinc Oxide thin films were developed by electrodeposition method. In 40 ml of distilled water 0.1M of AR grade sodium citrate, 20 mg MgCl2 and 30% hydrogen peroxide were introduced. By using ammonia solution pH of the electrolyte was maintained between 9.5 to 10 .The electrolyte was stirred moderately and maintained at room temperature. Zinc plates were used as substrates and first polished by 400 grit carborandum paper. Thereafter it was cleaned with soap solution, water and finally was dried in an oven. . The electrodeposition was carried out using zinc plate as anode and cathode. The working electrode were put vertically in reaction chamber. The electrodeposition was carried out catholically at -0.4 V at room temperature. The duration of the deposits was 15 minutes. After the deposition is completed the substrate was removed from the electrolyte, washed several times with distilled water and finally dried in air.

2.3 Characterization of Samples

The Compound formation were studied using X-ray diffractometer fitted with curved position sensitive detector (X'pert pro Pananalytical BV PW3040160). Compositional and structural data for thin films were obtained using Energy Dispersive Spectroscopy attached with Scanning Electron Microscope (Jeol JSM 6480LV) and Atomic Force Microscopy (Nanosurf EZ2). Optical measurements of ZnO thin films were carried out using UV-VIS spectroscopy (Lambda- 25 Perkin) and spectro-fluorophotometer (Shimadzu RF5301PC). Bandgap of ZnO is measured using absorbance curve.

3 RESULTS AND DISCUSSIONS

The ZnO films deposited on Zn substrate are physically stable and shows good adhesion.

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3.1 XRD results

Figure Fig. 1 show the XRD spectra of as deposited ZnO and ZnMgO thin film respectively. It is clear from the spectra of ZnO and ZnMgO that a polycrystalline deposits are there at 36.13° and 36.15° with preferred (101) and (101) plane orientation. The ZnMgO films exhibits a similar XRD pattern as the ZnO film. We observe that ZnMgO peak is more intense with respect to ZnO. Reflections due to (100), (101) planes of the substrate are also observed. The sharpness of the peaks show the crystallinity of both the films. The average crystallite size has been calculated with Scherrer relation by using the full width at half maximum (FWHM) values of the (101) peak.

$D = 0.9\lambda / \beta\cos\theta$,

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 average crystalline size decreases from 48nm to 46 nm.

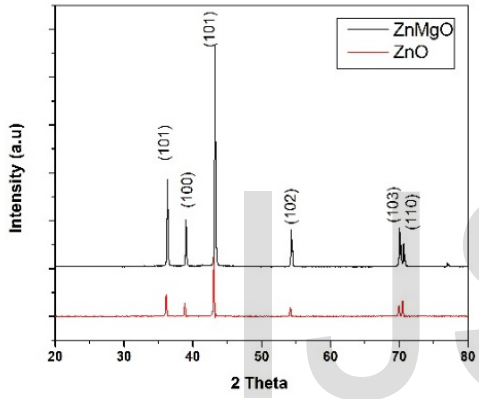

Fig.1 –XRD Spectra of as deposited ZnO and ZnMgO

Table 1- Observed and standard value of
2θ, d (Å) and Miller Indices of ZnO and ZnMgO films

Observed Value			Standard Value(JCPDS)		
	2θ Degree	d (Å)	2θ Degree	d (Å)	Miller Indices
ZnO	36.13	2.48	36.21	2.47	101
ZnMgO	36.15	2.48	36.68	2.44	101

3.2 SEM

Fig. 2 and 3 show the SEM photograph of as deposited ZnO and ZnMgO films. It is clear from the photograph that grains are uniform and densely distributed over the surface. The contrast of the photograph indicates that some charging effects are seen on the as deposited film. Charging effects are due to loosely bound semiconducting grains. The incorporation of Mg plays a vital role for influencing the surface morphology of the film. In Mg doped sample the grains are of bigger size and spherical. The larger crystalline size are achieved by high molar concentration of magnesium. The increased crystalline size after the Mg introduction is in agreement with XRD results, which shows in figure 1. The peaks of Zn, Mg and O are observed in the films as it is evident from EDS spectra in Fig. 4 and Fig 5. Table 2 and 3 shows the atomic percentage and weight percentage of ZnO and ZnMgO films respectively.

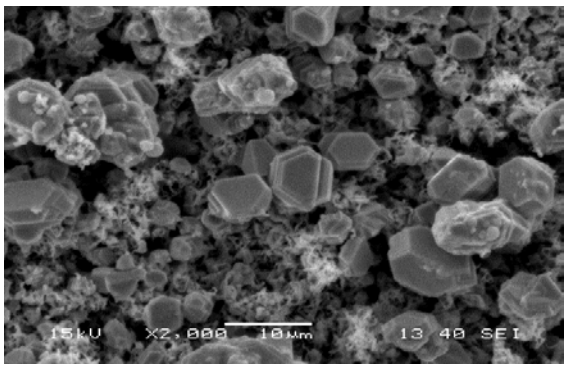

Fig 2- SEM photograph of ZnO film

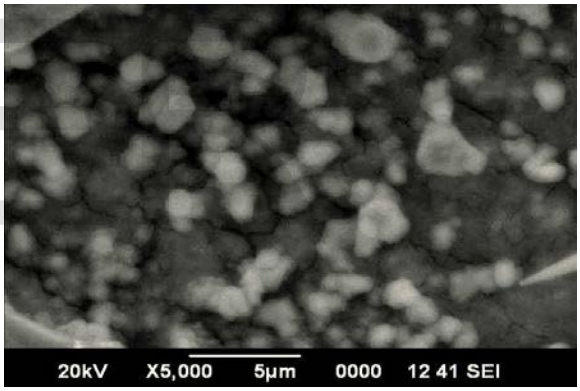

Fig 3- SEM photograph of ZnMgO film

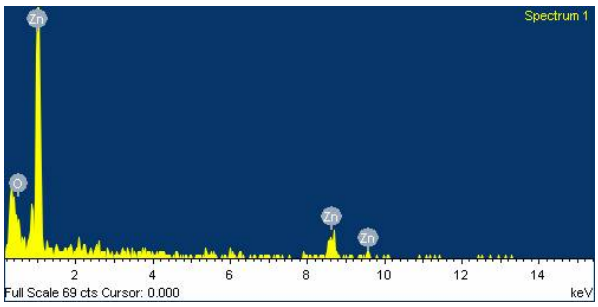

Fig.4 –EDS spectra of ZnO film

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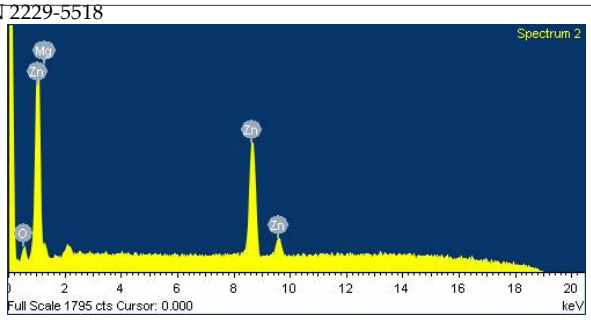

Fig 5- EDS spectra of ZnMgO film

Table 2- The weight and atomic percentage of ZnO film

Element	Weight %	Atomic %
Zinc	85.55	59.13
Oxygen	14.45	40.83

Table-3 The weight and atomic percentage of ZnMgO film.

Element	Weight %	Atomic %
Zinc	88.04	68.34
Oxygen	6.17	19.57
Magnesium	5.79	12.09

3.3 AFM

Atomic Force Microscopy technique are used to investigate the surface morphology and roughness of ZnMgO thin film. Figure 6(a) shows the AFM image of asdeposited ZnO in 3D. Figure 6 (b) and 6(c) shows the 2D and 3D AFM images of ZnMgO films in as deposited with deposition time of 15 minutes. From this technique root mean square (RMS) roughness, grain size, and surface morphology of the films are studied. In as deposited case of ZnO, RMS roughness is observed to be 328nm. At room temperature films are observed to have smaller grains, uniform and random orientation. The variation of the surface roughness was also observed at different temperatures. When Mg is used as dopent in ZnMgO, the average RMS roughness is slightly decreases and it is nearly equals to 301 nm in asdeposited case. Here grains boundaries slightly decreases since magnesium is incorporated with zinc oxidenat grain boundries. The RMS roughness represents the standard deviation between the height of topographic feature and the mean feature height.

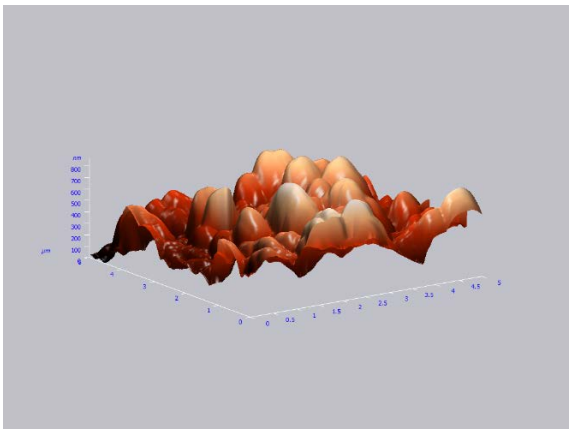

Fig. 6 (a)AFM image of ZnO film

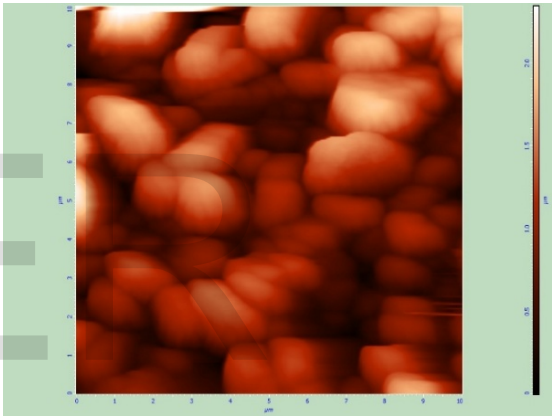

Fig 6 (b)- AFM image of ZnMgO film(2D)

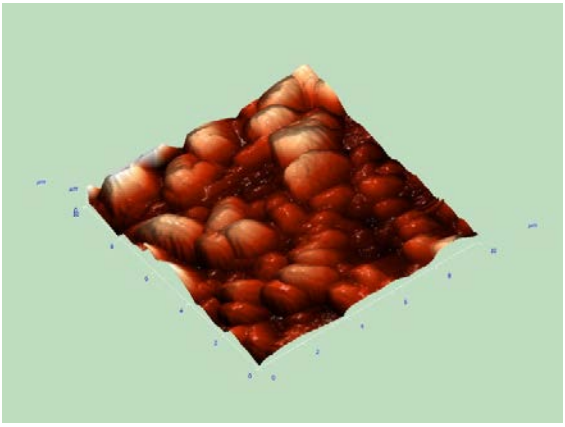

Fig 6(c)- AFM image of ZnMgO film(3D)

3.4 Optical Results

The semiconductor with direct bandgap follows the relatioship $(\alpha hv)^{1/n} = A(hv-Eg)$ for hv>Eg, where α, hv, Eg, A are absorption coefficient, photon energy, bandgap and proportionality constant respectively.Figure 7 shows optical absorption spectra of ZnMgO thin film which is plot of $(\alpha hv)2$ vs hv and the band gap, Eg of ZnMgO is obtained by extrapolation of the curve for $(\alpha hv)^2 = 0$. The energy band gap is found to be 3.35 eV in as deposited case. In this work the band gap of the film increases from 3.35 eV to 3.46 eV (13,20).

Spectrofluorophotometer is also used to know the optical properties of quantum sized particle. Photoluminescence measurement of the as deposited ZnMgO film is carried out at room temperature with 280 nm excitation. Figure 8 shows the Photoluminescence spectrum of ZnMgO thin film in as deposited case. In this figure the strong and broad emission spectra is shown which is mainly located at around 372 nm in asdeposited. Xia Zhang et.al also reported the PL spectra of ZnMgO at 349 nm to 369 nm with different concentration of magnesium. This shows ZnMgO is promising ultraviolet light emitting material. The photoluminescence originates from the recombination of surface states. This is attributed to near band edge emission of wide bandgap ZnMgO.

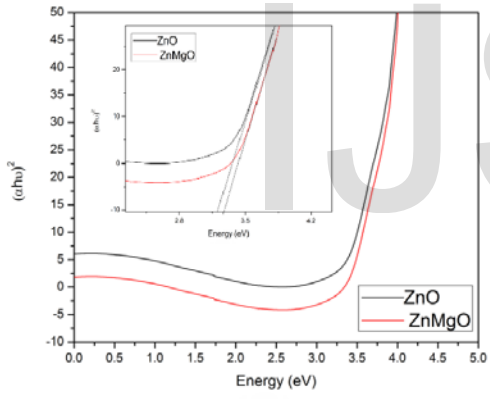

Fig 7- Bandgap determination of

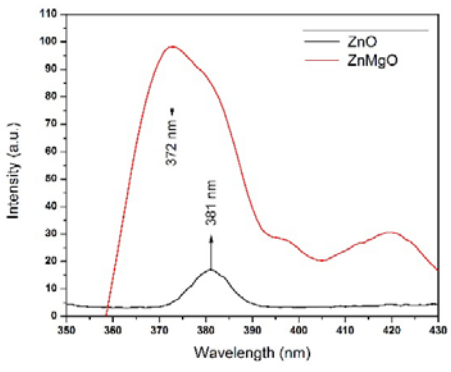

Fig 8- PL Spectra of as deposited ZnMgO and ZnO

4 Conclusions

The ZnMgO thin film can be electrodeposited on zinc substrate using a aqueous solution containing sodium citrate, Magnnesium chloride and hydrogen peroxide. The as deposited films are crystalline in nature. The roughness and bandgap of the film reduces due to doping. EDS confirms the deposition of semiconducting material. In this case doping slightly increases its optical bandgap also it will be helpful for the fabrication of optoelectronic devices and sensors.

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