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Synthesis and characterization of nanocrystalline $Mg_xZn_{1-x}O$ films deposited by spin coating method

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Analysis of structural, optical, chemical and mechanical properties of sol-gel deposited nanocrystalline $Mg_xZn_{1-x}O$ thin films has been carried. Zinc acetate, Magnesium acetate as precursors and ethanol as solvent were used to prepare the gel solution. Films were deposited on silicon (100) substrate for different Mg concentrations (x = 0.05 to 0.3). The annealing was carried out at temperature 400°C to achieve dense crystalline nature of the films. EDAX spectrum clearly shows the incorporation of Mg into ZnO. The effect of Mg doping concentration on various properties of $Mg_xZn_{1-x}O$ films has been investigated. XRD spectra clearly reveal the peaks of ZnO. The refractive index of the films was observed to be decrease with an increasing Mg mole fraction. FTIR study depicts the stretching bond position of fundamental ZnO peak to be shifted from 407 to 415 cm^{-1}.

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1. Introduction

Zinc oxide is a wide bandgap II-VI group semiconductor with large exciton binding energy (60meV), which causes the stimulated emission at the room temperature. It has attracted considerable attention due to the possibility of fabricating reliable high efficiency photonic devices based on ZnO and its alloys, such as solar cells, transparent conductors for displays, light emitters, sensors, modulators and ultra-violet detectors [1]. It is having direct band gap of 3.37 eV [2-3]. Therefore, it has attracted the attention of fabrication and commercialization of efficient short wavelength light emitting devices [4-6]. Due to the excellent optical properties, the heterostructure devices based on ZnO has shown a promising applications in light emitting devices [7, 8]. To fabricate ZnO heterostructure waveguide, ternary $Mg_xZn_{1-x}O$ alloys have been synthesized due to its wider bandgap than ZnO, to serve as cladding layer for light emission in ultraviolet range. The early work has shown that an increase in Mg mole concentration in ZnO changes the crystalline structure from hexagonal to cubic phase and the bandgap from 3.37 to 7.7eV [9]. Ohtoma et al. [10] have grown hexagonal $Mg_xZn_{1-x}O$ films ($0 \leq x \leq 0.33$) and choopun et al.[11] have reported metastable cubic phase $Mg_xZn_{1-x}O$ films($0.5 \leq x \leq 1$) using pulsed laser deposition (PLD) method on sapphire substrate.

Various deposition techniques can be used to fabricate the MgZnO films such as, pulsed laser deposition (PLD)[12,13], molecular beam epitaxy (MBE)[14], electron beam evaporation [15], metal organic chemical vapor deposition [16] and sol-gel method [17-19]. The sol-gel deposition technique has several advantages over other methods. It does not require vacuum apparatus and has potential to produce films with large areas on various substrates. In order to prepare thin films of compound semiconductors, the sol-gel process is known to have the distinct advantages of process simplicity, lower costs and ease of composition control [20].

Zhao et al. [18] has studied $Mg_xZn_{1-x}O$ alloys for optical properties like transmittance and photoluminescence using the sol-gel deposition on silicon substrate. This group composed the sol of zinc acetate, magnesium acetate and polyvinyl butyral (PVB) in ethanol. Despite of this, Yow-Jon Lin et al. [19] studied Mg alloy deposited on both glass and silicon for the photoluminescence study. This group has used zinc acetate, magnesium acetate, methanol and KOH for the preparation of the gel solution. However, they have not reported the effect of Mg doping on the refractive indices and the stress of MgZnO films.

To the best of our knowledge, no body has reported the study of stress and refractive index of MgZnO films on silicon substrate using sol-gel deposition method. This paper reports the effect of Mg incorporation on the refractive index of nanocrystalline MgZnO films along with chemical and structural analysis. Moreover, we have measured the stress of the films to have clear insight of mechanical strength. We have taken zinc acetate, magnesium acetate, ethanol and lactic acid for the gel preparation. Here, the spin coating method was used to deposit $Mg_xZn_{1-x}O$ alloy films on the Si substrate for the investigation of structural, optical, chemical and mechanical properties.

The paper is organized in four sections. Following section of the paper describes the experimental procedure used to deposit the MgZnO ternary alloy films. The results are discussed in detail exploring effect of Mg mole concentration on structural, optical, chemical and mechanical properties of the nanocrystalline MgZnO films in section III. Finally, conclusions are highlighted.

2. Experimental procedure

Zinc acetate dihydrate $[Zn(CH_3COO)_2.2H_2O]$ and Magnesium acetate $[Mg(CH_3COO)_2]$ were used as starting precursors. Ethanol $[C_2H_5OH]$ and lactic acid $[CH_3CHOHCOOH]$ were used as solvent and reagent respectively. The Mg and Zn precursors were dissolved in ethanol and stirred vigorously at ~80°C for an hour on magnetic hot plate. The MgZnO films were deposited for 0.05, 0.1, 0.15 and 0.3 mole concentrations of Mg. The solution was heated and stirred with the reflux apparatus to avoid evaporation of ethanol and to keep the same quantity of the solution for an hour. Initially, the solution became milky-white and then converted into the transparent after stirring for one hour. Prepared transparent solution was used for the deposition of the nanocrystalline films. The deposition of films was carried out on Silicon (100) substrates at room temperature using homemade spin coater. The silicon substrates were thoroughly cleaned by trichloroethylene, acetone and methanol sequentially before the deposition of the films. This ensures the proper cleaning process of the substrate and removal of the native oxide from the surface of the substrate. The speed of the coater was kept at ~2000 rpm for all the films. The coating procedure was repeated for six times to achieve the desire film thickness. After each coating, the films were pre-annealed at 250°C for 10 minutes to evaporate the solvent. Finally, the deposited samples were annealed at 400°C for one hour to burn the organic compounds and crystallize the MgZnO material.

The structural properties of films were studied using Bruker AXS-D8 X-ray diffractometer (XRD) having source of Cu-K_α and wavelength of 1.54056Å. The surface morphology and elemental composition of deposited films were studied by using JEOL Scanning Electron Microscopy (SEM). The index of refraction, thickness and stress of the films were measured using PHILIPS (SD-1000) Ellipsometer, which is having He-Ne laser source of 632.8nm wavelength as a source. The absorption spectra were recorded using FTIR (Nicollet –380) within 400-4000 cm^{-1} wave number range with $4cm^{-1}$ resolution at the room temperature. The detailed chemical analysis of various bonds in the FTIR spectra was carried out. Energy dispersive analysis by X-ray (EDAX) has been used to have clear insight of Mg incorporation in MgZnO films.

3. Results and discussion

We have studied the effect of Magnesium concentration on the refractive index and stress of the nanocrystalline MgZnO films. Effect of Mg incorporation in MgZnO films on the refractive index has been shown in Fig. 1. It was observed that the refractive index of the films decreases with corresponding increase of the mole concentration of the Mg in ZnO. Decrease in the refractive index is due to increasing incorporation of Mg^{2+} ions in the MgZnO films. We were successful to modulate the refractive index value of nanocrystalline MgZnO films from 1.50 to 1.15 corresponding to increase in Mg mole fraction from 0.05 to 0.3 respectively. The annealing temperature of all films was kept constant at 400^0C. Therefore, it is evident that decrease in refractive index was definitely due to more incorporation of Mg in the MgZnO films.

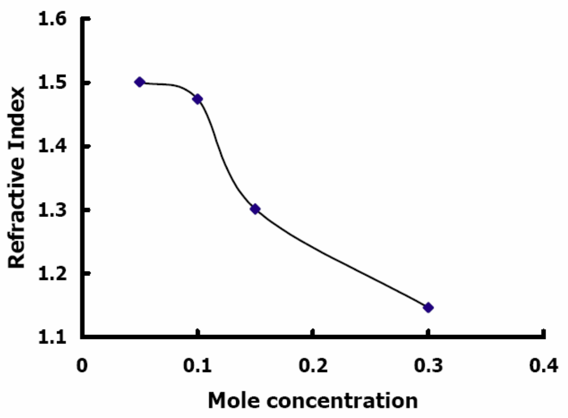

Fig. 1. Effect of Magnesium mole concentration. on the Refractive index of MgZnO films.

The stress is one of the important mechanical properties, which can significantly affect the performance of the deposited MgZnO films. It was observed that all the films showed compressive nature of stress. The measured stresses were 2.77, 1.35, 3.41 and 1.7 Mpa (x10^5) for 0.05, 0.1, 0.15 and 0.3 mole concentrations respectively. The compressive stress occurring in the films was due to chemical reactions occurred during the deposition and annealing process. It has been attributed to the densification and shrinkage occurring in the films. The thickness of the films measured by the ellipsometer setup were 623, 549, 1029, 1198Å for the 0.05, 0.1, 0.15 and 0.3 mole concentrations respectively. Table 1 lists the values of refractive index, stretching bond positions, thickness and stress for samples BS13, BS18, BS23 and BS38 corresponding to 0.05, 0.1, 0.15 and 0.3 mole concentrations.

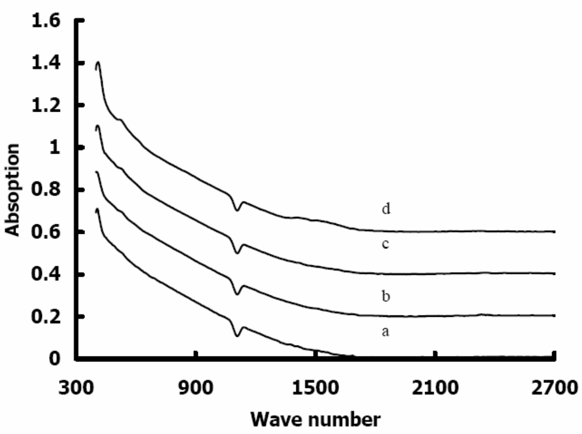

Fig. 2. FTIR spectra for $Mg_xZn_{1-x}O$ films at a) 0.05, b) 0.1, c) 0.15 and 0.3 mole concentrations.

Table 1. Physical Parameters measured for different Mg mole concentrations

Sample No	Mole Concentration	Refractive Index	Peak wave No.(cm^{-1})	Thickness (Å)	Stress (MPa)
BS13	0.05	1.50	407	623	$2.77x10^5$
BS18	0.10	1.47	409	549	$1.35x10^5$
BS23	0.15	1.30	413	1029	$3.41x10^5$
BS38	0.30	1.15	415	1098	$1.70x10^5$

In order to investigate the chemical composition of the films deposited on Si (100) substrate at different mole concentrations annealed at 400°C temperature, FTIR analysis was carried out in absorption mode. Figure 2 shows the recorded infrared absorption spectra of the MgZnO films. The intense absorption peaks has been observed at 407, 409, 413, 415 cm^{-1} wave numbers for the 0.05, 0.1, 0.15, and 0.3 mole concentrations respectively. It clearly indicates the presence of stretching bonds as we have already reported [23] for the ZnO material (400 cm^{-1}). It shows that the complete crystallization process of MgZnO took place at 400^0C temperature.

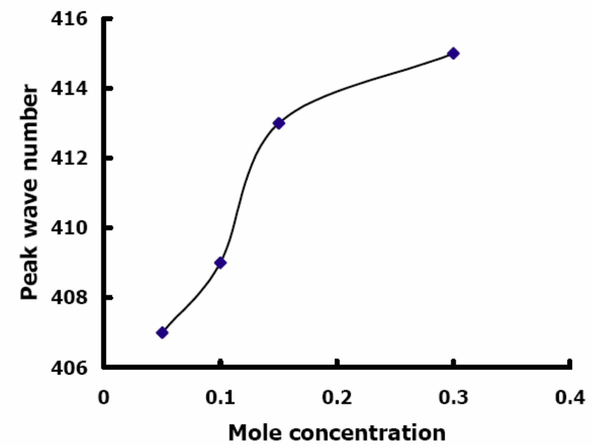

Fig. 3. Variation of stretching bond positions with Mg mole concentration

It was confirmed that the films were transformed in to nanocrystalline form through dehydration and removal of organic compounds by annealing process. Figure 3 illustrates the variation of absorption stretching bond position (wave numbers) of Zn-O with mole concentration of Mg in the MgZnO films. We observed that stretching bond position shifts to higher wave number with an increase of Mg mole concentration. It has been attributed to substitution of Mg^{2+} ions in place of Zn^{2+} ions at the lattice sites of ZnO material.

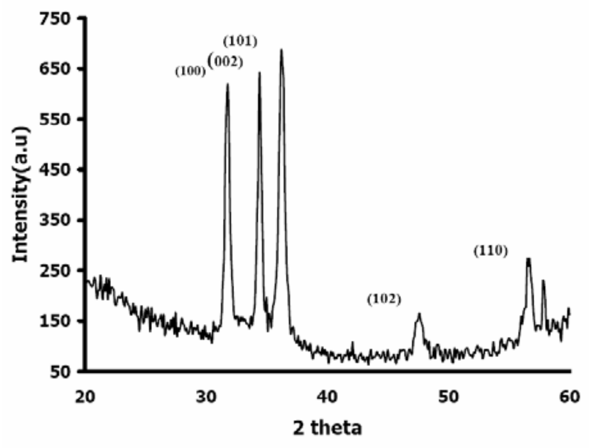

Fig. 4. XRD spectra of $Mg_xZn_{1-x}O$ film.

Nanocrystalline film of $Mg_xZn_{1-x}O$ deposited for Mg mole concentration of x = 0.05 was characterized using X-ray diffraction to observe structure of the films in θ-2θ mode with 0.1° step size. The XRD spectra recorded for the sample BS13 was depicted in figure 4. In this spectrum, three main peaks were appeared belonging to (100), (002), (101) planes at 31.8, 34.4 and 36.2° diffracting angles respectively. The peak intensities were 618, 639, 685 a.u. respectively. These XRD peaks are associated with the JCPDS card no. 36-1451 of the hexagonal ZnO structure. The XRD peak positions of our results for $Mg_xZn_{1-x}O$ films are similar to those reported by Zhao et al. [18]. There were two more diffracting peaks belonging to (102) and (110) planes corresponding to wurtzite structure [17, 20]. It was observed from the XRD spectra that all three diffraction peaks were strong and dominant which attributes the polycrystalline and wurtzite nature of MgZnO films. We have optimized the process to grow the nano-crystals of MgZnO at annealing temperature of 400°C to get good crystal quality of the films [17]. The full width at half maximum (FWHM) of the peak (101) at 36.2 ° was estimated to be 0.3°.

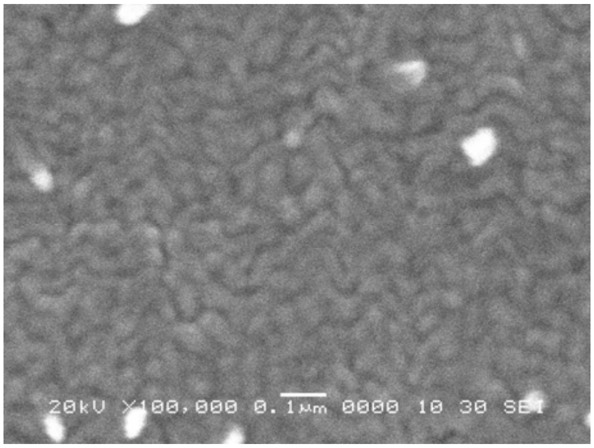

Fig. 5. SEM image of the nanocrystalline $Mg_xZn_{1-x}O$ film

The size of the grains of the MgZnO film was obtained by substituting value of FWHM in the Scherrer's formula [22],

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

Where D is grain size of crystal, λ (= 1.54059 Å) is the wavelength of the used X-ray source, β is the broadening of diffraction line measured at half of its maximum intensity in radians (FWHM) and θ is the angle of diffraction peak. The grain size value of the crystalline MgZnO film was deduced to be 28 nm.

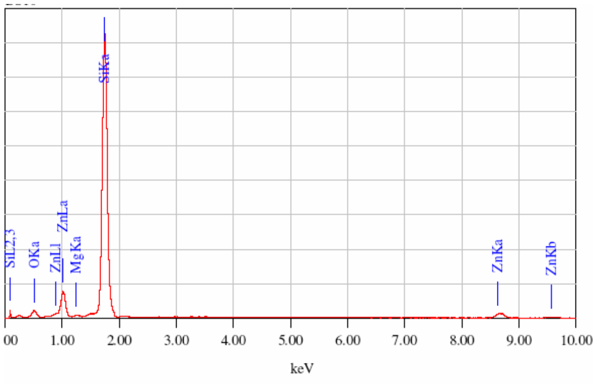

Fig. 6. EDAX spectra of the deposited $Mg_xZn_{1-x}O$ film for 0.05 mole concentration.

The surface morphology of the MgZnO films was studied using Electron Scanning Microscope (SEM) operating at voltage of 20kV. The SEM image of the deposited MgZnO film annealed at temperature 400°C with the magnification of 270,000 times the operating voltage is as explored in figure 5. It shows nanocrystalline nature of deposited MgZnO film in the scale of 0.1µm with average crystal size of ~ 50 nm. SEM image clearly indicates the MgZnO grains in nanocrystalline scale. It confirms that we were successful to deposit the nanocrystalline MgZnO films.

Fig. 6 explicates the elemental composition of the MgZnO film achieved using EDAX. The position of Mg peak incorporated in the MgZnO film having Mg concentration of x=0.05 was observed at 1.253 keV. It clearly shows the incorporation of Mg element in the MgZnO films. In spite of this, it shows other peaks for the Zn, O, and Si. The strong peak appeared at 1.8 keV represents the signal coming from silicon substrate because of the large thickness of Si substrate than MgZnO film. The position of other peaks for ZnK_a, ZnK_b and OK_a were present at 8.63keV, 9.6keV and 0.53keV respectively.

4. Conclusions

Thin films of MgZnO have been successfully deposited on Si substrates using spin coating method and effect of Mg incorporation on the various properties has been investigated. The deposited thin films were nanocrystalline in nature and average size of the grains was about 50 nm. The refractive index of the films was found to be decreased with the increase of Mg composition in the MgZnO films. FTIR spectra clearly reveals shift of stretching bond position due to substitution of Mg^{2+} ions in place of Zn^{2+} ions at the lattice sites of ZnO material. EDAX spectra explore the successful incorporation of Mg in the ZnO films. In conclusion, we have successfully deposited nanocrystalline films of MgZnO to investigate effect of Mg incorporation on the various properties.

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