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XRD Studies on Sol Gel Spin Coating $Zn_{1-x}Mg_xO$ Thin Films

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The ZnO and $Zn_{1-x}Mg_xO$ thin films were prepared on glass and silicon substrates by spin coating method using 2-methoxyethanol solution of Zinc acetate dihydtate and magnesium acetate dihydrate stabilized by monoethanolamine. The effects on drying and annealing condition of structural and optical properties of the films were studied. It was found that the samples annealed at 650°C improves significantly the crystallographic orientation of the ZnO films grown by the sol-gel process. Two types of substrates were used to examine the substrate effects on the growth of $Zn_{1-x}Mg_xO$ thin films. On Corning glass substrates, the lattice constant little bit decreased with increasing the concentration of Mg whereas in the case of silicon substrates, the lattice constant decreased rapidly with x when compared to the glass substrates. The optical band energy gaps of $Zn_{1-x}Mg_xO$ thin films were slightly increased with increasing concentration of Mg.
Key words: sol gel, Zinc Oxide, X-ray diffraction, lattice constant, $Zn_{1-x}Mg_xO$

1. INTRODUCTION

ZnO is one of the important candidates for semi conducting material because it possesses hexagonal wurtzite structure and wide band gap energy. It has highly preferred C-axis orientation and high electrical resistivity, which is important for longitudinal bulk wave transducer and surface acoustic wave (SAW) filters using Rayleigh wave and for the fabrication of amorphous silicon solar cell [1]. At room temperature ZnO thin films exhibit very strong emissions by exciton because it has binding energy of 60 meV. Recently it is one of the materials for the potential application as ultraviolet light emitting diodes and laser diodes. For high performance LD and LED device, hexagonal wurtzite structure of $Zn_{1-x}Mg_xO$ alloy thin films were suitable barrier layer for ZnO/ $Zn_{1-x}Mg_xO$ super lattice [2].The $Zn_{1-x}Mg_xO$ alloy films with Mg have hexagonal wurtzite type structure and it can be stabilized by Mg content. The $Zn_{1-x}Mg_xO$ films were synthesized by many researchers using different process like pulsed laser deposition (PLD), electrophoresis deposition (EDP), molecular beam epitaxy (MBE) metal organic vapor phase epitaxy (MOVPE) and sol gel etc.,[3]. Among these, sol gel method is very economical and very easy to carry out the experiment. This method is an attractive process due to the controllability of compositions, and simple facilities, but thin films prepared by sol gel do not have good quality.[4]. In this work we aimed to improve the quality and opto-electrical properties of thin films by doping magnesium oxide in to the zinc oxide and also study the structural properties of $Zn_{1-x}Mg_xO$ thin films by sol gel spin coating method.

2. EXPERIMENTAL METHODS

The sol of $Zn_{1-x}Mg_xO$ was synthesized by aqueous solution of zinc acetate dihydrate, magnesium acetate dihydrate, 2-methoxy ethanol and monoethanolamine (MEA). The molar ratio of MEA added into the solution to the total metal ions in the solution was 1.0. The concentration of Mg in the ZnOMg films are 0, 0.0175, 0.035, 0.0525, 0.07 and the concentration of total metal ions in the solution was 0.35mol/l. The mixed solution was served as a precursor solution, which kept in stirrer at 60°C for 2h. Before coating, the substrates were cleaned with acetone and methanol and dried in a oven for 30 minutes. The sol was coated on (100) silicon and corning glass (7059) substrates by spin coater at a speed of 1000rpm for 20 seconds and followed by second rotation at a speed of 3000rpm for another 20 seconds. After the coating procedure, the substrates were first dried at several temperatures such as 150°C, 250°C and 350°C in air for 5 min to evaporate the solvent. This procedure was repeated for ten times and thermal annealing was performed for 2h in air at different temperatures. The annealed temperature was maintained between 450 and 650°C to get the good crystalline of the $Zn_{1-x}Mg_xO$ thin films.

Crystallinities of the $Zn_{1-x}Mg_xO$ thin films were measured by X-ray diffractometer with Cu K_α radiation. Surface morphologies were observed by scanning electron microscope. The optical characterization was studied by UV-VIS Spectrometer at a wavelength 250 to 700nm.

3. RESULTS AND DISCUSSION

The ZnO and $Zn_{1-x}Mg_xO$ films were spin coated on Si (n-type) and corning glass substrates.

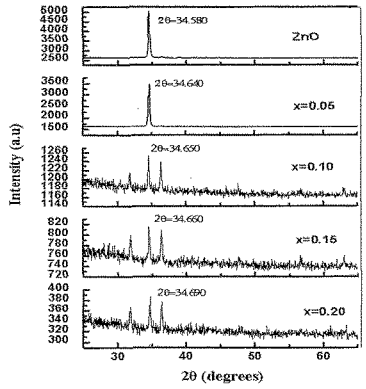


Fig.1 X-ray diffraction pattern of $Zn_{1-x}Mg_xO$ thin films dried at 350°C and annealed at 650°C coated on corning glass substrates.

Fig.1and Fig.2 show the X-ray diffraction pattern of $Zn_{1-x}Mg_xO$ thin films coated on corning glass and silicon substrates and these films were dried at 350°C and annealed at 650°C for five minutes and 2hours, respectively. The X-ray diffraction pattern of ZnO (002) reflection shifts slightly to the larger 2θ angle with increasing concentration of Mg on both corning glass and silicon substrate [5]. On corning glass substrates, when the value of x increased above 0.05, two more peaks were appeared which correspond to the (100) and (101) direction of the ZnO wurtizite structure. On silicon substrates, three peaks were appeared which correspond to (100), (200) and (101) direction for all the composition. It seems that, in coring glass substrates, the C-axis orientation is very stronger for ZnO and $Zn_{1-x}Mg_xO$ thin films but (002) reflection peak of ZnO and cubic MgO related peaks were not found at 43° for all the films, which indicate that the Mg^{2+} ion occupies the substitutional position in the ZnO films.[6].

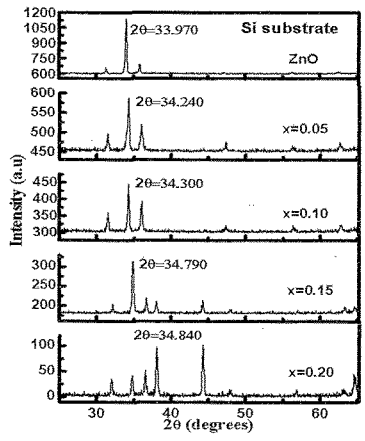
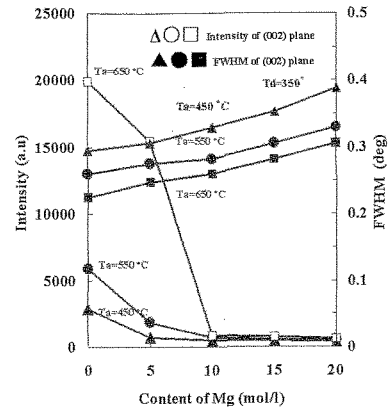
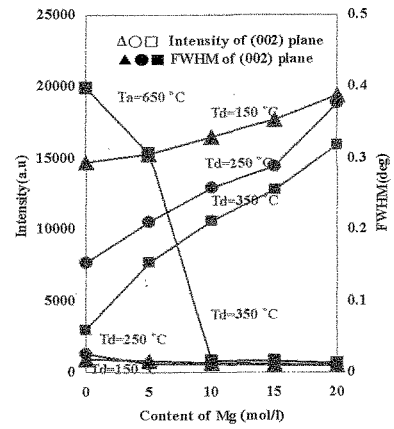


Fig. 2 XRD pattern of $Zn_{1-x}Mg_xO$ thin films dried at 350°C and annealed at 650°C coated on silicon substrates.

Further, on silicon substrates, the C-axis orientation (002) becomes weak when increasing the concentration of Mg^{2+}in the ZnO thin film. When the concentration of Mg^{2+} exceeds 0.15, a peak appears at 43°, which belongs to the (200) direction of the MgO cubic structure. This is due to the orientation of the substrate that has some influence on the orientation of the ZnO films. It seems that the crystalline substrate and the concentrations of dopant have little impact on the ZnO microstructure. It is good agreement with previous report that MgO thin films on si (100) substrates deposited at 350°C and annealed at 650°C showed 2θ at 36.8 and 42.8° [7].



(a)



(b)

Fig.3 The full width at half maximum and the peak intensity of (002) plane for $Zn_{1-x}Mg_xO$ thin films with different concentration of Mg and at different conditions as a function of annealing temperature (a) and drying temperature (b).

In fig.3 shows the full width at half maximum (FEHM) and peak intensity for $Zn_{1-x}Mg_xO$ films with different Mg composition as a function of annealing temperature (a) and drying temperature (b). The drying temperature is 350°C in Fig.3 (a) and the annealing temperature is 650° in Fig.3 (b). In this case, the films have more a preferred (002) reflection, since the structural relaxations of the gel before crystallization were easily accepted by monoethanolamine and resultant organics substance were evaporated at higher temperature [8]. The peak intensity of (002) reflection becomes

higher when increasing the annealing temperature. The other two reflections at (100) and (101) were decreased with increasing the annealing temperature. The peak intensity of (002) reflection was maximum when the coated gels were dried at 350°C and annealed at 650°C for 2hrs. The full width at half maximum of $Zn_{1-x}Mg_xO$ thin films depends on the concentration of Mg. The FWHM value increased with increasing concentration of Mg and decreased with increasing annealing temperature. The peak intensities of the $Zn_{1-x}Mg_xO$ thin films annealed at 650°C are higher than those of the films annealed at 450°C and 550°C. The similar results were observed for different drying temperatures.

Fig.4 shows the lattice constant perpendicular to the surface grown on Si substrate and glass substrate for different Mg concentration. In this figure, the variation in the lattice constant with increasing concentration of Mg is deserved. On both silicon and corning glass substrate the lattice constant increases with increasing concentration of Mg^{2+}. On corning glass substrates, the lattice constant little bit decreased with increasing the concentration of Mg but in the case of silicon, the lattice constant rapidly decreased with Mg when compared to the glass substrates. On corning glass substrates, Mg occupies the substitutional position of ZnO and it leads to the small decrease in the lattice constant when increasing the concentration of Mg. Whereas in the case of the silicon, the value of x above 0.10, the lattice constant suddenly decreased due to the excess amount of MgO coated on silicon substrates and it grows along the (100) direction.

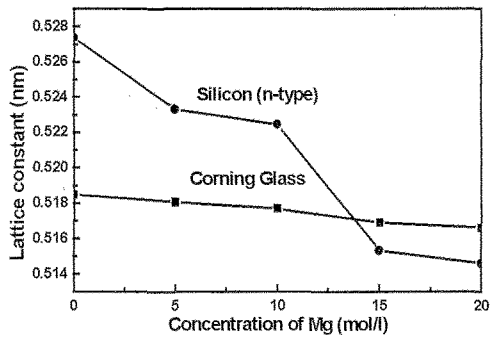
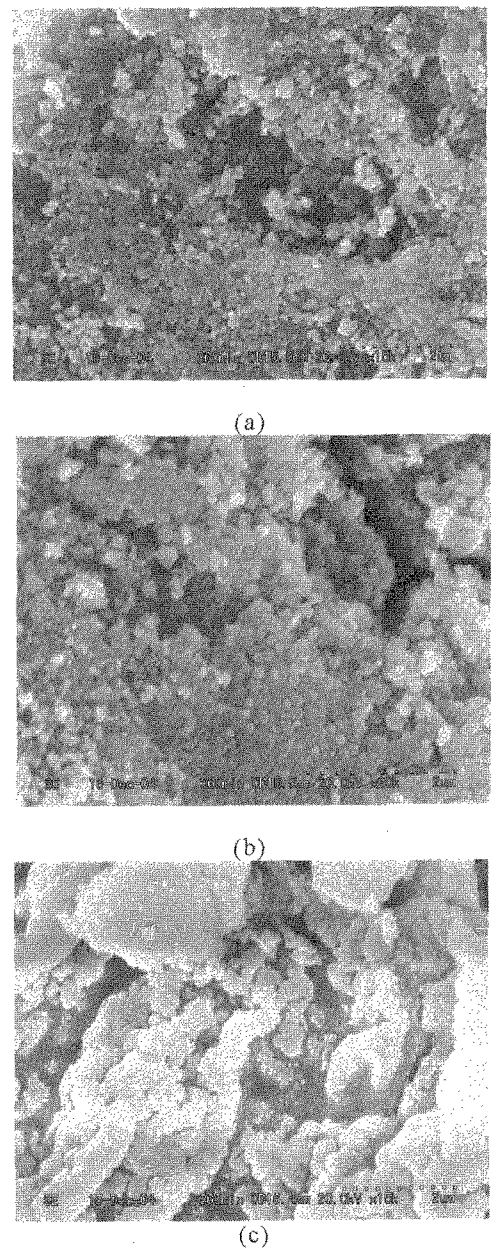


Fig.4 Lattice constant of $Zn_{1-x}Mg_xO$ on silicon and corning glass substrate of different x at T_d=350°C and T_a=650°C.

Figures 6 and 7 show the SEM images of pure ZnO and $Zn_{1-x}Mg_xO$ thin films coated on silicon and glass substrates. The dense growth was observed for $Zn_{1-x}Mg_xO$ thin films, which were coated on corning and silicon substrates. On both the corning and silicon substrates, the grain sizes were increased with increasing the concentration of Mg when compare to the grain sizes of pure ZnO. The SEM images showed that the $Zn_{1-x}Mg_xO$ nano particals closely connected with the wall of both silicon and corning glass substrates. The silicon substrates have more dense particals than the corning glass substrates as shown in fig 6 (c) and Fig7 (c). It may be due to fact that the MgO crystals grow along the (100) direction when excess amount of Mg coated on silicon substrate. This result agrees well with previous results [7].

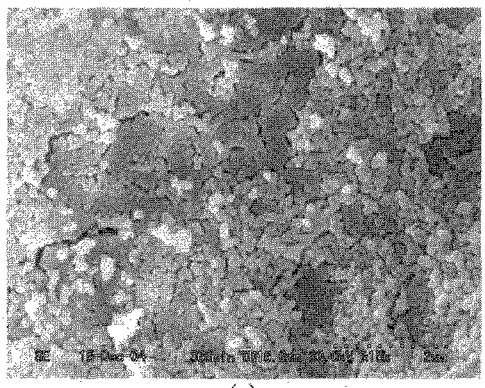


(a)

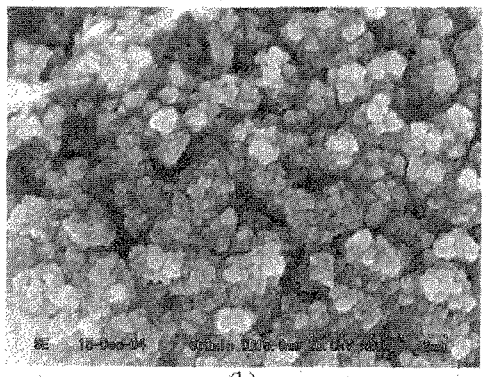
(b)

(c)

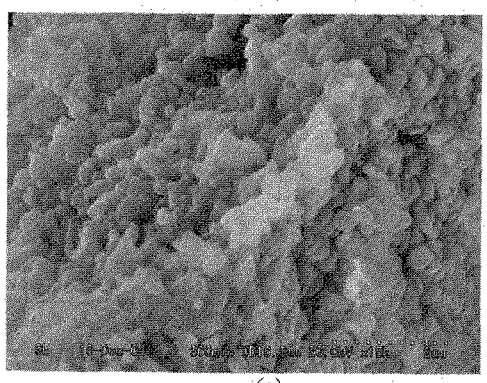
Fig 6 SEM images (a) Pure Zno, (b) $Zn_{1-x}Mg_xO$ (x=0.05) and (c) $Zn_{1-x}Mg_xO$ (x=0.02) on Si substrate.



(a)



(b)



(c)

Fig.7 SEM images (a) Pure Zno, (b) $Zn_{1-x}Mg_xO$ (x=0.05) and (c) $Zn_{1-x}Mg_xO$ (x=0.02) on corning glass substrate.

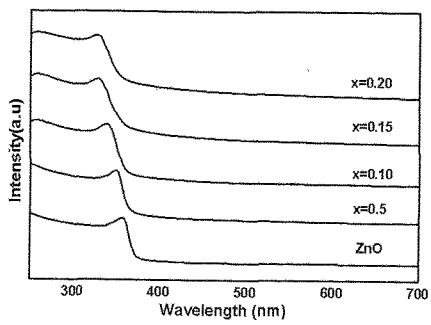


Fig.8 Absorbance spectra of the $Zn_{1-x}Mg_xO$ thin films on glass substrates with different x.

Fig.8 shows the absorbance spectra of ZnO and $Zn_{1-x}Mg_xO$ thin films on corning glass substrate with different concentration of Mg with the drying temperature 350 °C and the annealing temperature 650°C. A clear absorbance edge is slightly shifted towards the smaller wavelength when increasing the concentration of Mg.

4. CONCLUSION

The ZnO and $Zn_{1-x}Mg_xO$ thin films were prepared on corning glass and silicon substrates by sol gel method. $Zn_{1-x}Mg_xO$ thin films were dried and annealed at different temperatures. The ZnO and $Zn_{1-x}Mg_xO$ thin films dried at 350°C and annealed at 650°C showed an extremely sharp (002) peak in the XRD patterns. The C-axis lattice constants of the ZnO and $Zn_{1-x}Mg_xO$ thin films on silicon substrate were larger than those of the glass substrates. SEM image gives the surface morphology of the samples and it depends on the concentrations of Mg in ZnO and type of substrates. From this experiment we observed that c-axis orientation is most prominent for high crystalline quality and this crystalline quality can be obtained on right substrates with maintaining suitable drying and annealing temperature using low cost materials.

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