CHAPTER - IV

SYNTHESIS OF Zn$_{1-x}$Mg$_x$O NANOCRYSTALS BY LOW TEMPERATURE SOL-GEL METHOD AND ITS FUNCTIONAL PROPERTIES

ABSTRACT

This chapter deals with the structural and optical studies of sol-gel synthesized Zn$_{1-x}$Mg$_x$O nanocrystals. Zn$_{1-x}$Mg$_x$O nanocrystals with various compositions were synthesized by sol-gel process using tri ethanol amine (TEA) as a capping agent. The structural properties of the prepared materials were studied by X-ray diffraction analysis. Un-agglomerated nanocrystals with spherical morphology were observed by Scanning electron microscope (SEM). The presence of Mg in the Zn$_{1-x}$Mg$_x$O was confirmed by X-ray photoelectron spectroscopy (XPS). The photoluminescence studies demonstrated that the intensity of defect related deep level emission increases drastically with increasing the x value from 0.02 to 0.08 and decreases sharply on further increase of Mg from 0.08 to 0.1. The results are discussed.
CHAPTER IV

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4.1. Introduction

Zinc Oxide (ZnO) is one of the potential wide band gap semiconductor and good alternative for Gallium nitride (GaN) due to its larger exciton binding energy which leads to high UV emission efficiency at room temperature [Aoki et al., 2000; Yang et al., 2001; Xu et al., 2006]. Moreover, ZnO is an environmentally conscious semiconductor with bio-compatible nature which is highly desirable especially for bio-related applications [Ramamoorthy et al., 2004]. The band gap of ZnO can be controlled by adding Mg and thus Zn$_{1-x}$Mg$_x$O alloy has been extensively studied as the band gap tuning is a powerful tool to design a semiconductor with novel functional properties [Ohtomo et al., 1998; Chen et al., 2003; Minemoto et al., 2000]. Zn$_{1-x}$Mg$_x$O has the same material advantages of ZnO due to its wide-band gap, less lattice mismatch with ZnO as the ionic radius of Mg$^{2+}$ (0.57 Å) and Zn$^{2+}$ (0.6 Å) are quite similar [Minemoto et al., 2000]. In addition, it was reported that the energies of fundamental band to band transition of Zn$_{1-x}$Mg$_x$O were strongly increased with increasing Mg composition [Minemoto et al., 2000; Schmidt et al., 2003; Makino et al., 2000; Zhang et al., 2005].

Zn$_{1-x}$Mg$_x$O material was prepared normally by high temperature process such Metal Organic Vapour Phase Epitaxy (MOVPE) [Gruber et al., 2004],
Molecular beam epitaxy (MBE) [Fujita et al., 2005; Tsukazaki et al., 2007], pulsed Lased Deposition (PLD) [Heitsch et al., 2007; Liu et al., 2011] and by few other methods as well [Yang et al., 2009; Young et al., 2009]. For example, Gruber et al., (2004) grown the ZnMgO epilayers and ZnO-ZnMgO quantum well structures by MOVPE, and they reported the enhancement of the exciton binding energy up to ~ 96 meV in ZnO quantum well structures. In addition, Mg_xZn_{1-x}O with MgO/ZnO superlattices were grown by Fujita et al., (2005) using MBE method and they found that the quasi-ternary Mg_xZn_{1-x}O exhibited excellent ultraviolet emission and thus highly useful for UV light emission and/or detection applications. Tsukazaki et al grown ZnO/Mg_xZn_{1-x}O heterostructures by laser MBE and observed the quantum Hall effect in the heterostructures [Tsukazaki et al., 2007]. Liu et al., (2011) deposited pure ZnO and Mg_{0.1}Zn_{0.9}O thin films on sapphire substrate by PLD, and the Mg-doped ZnO thin films showed much higher H_2 sensing performance than the pure ZnO thin films. Polycrystalline Zn_{1-x}Mg_xO thin films were prepared by Yang et al., (2009) using filtered cathodic vacuum arc technique and UV lasing action with a tunable wavelength between 375 and 400 nm has been observed. As a consequence, most of the previous reports are dealt with Zn_{1-x}Mg_xO materials are thin films prepared at high temperature process. The solution route offers an elegant way of preparing high quality nanocrystals with relatively large area growth. Only very few works were reported on the preparation of Zn_{1-x}Mg_xO nanocrystals or thin films by low temperature solution routes like sol-gel process and wet chemical methods.
[Yang et al., 2009; Young et al., 2009; Ghosh and Raychaudhuri, 2006; Xu et al., 2013]. Ghosh and Raychaudhuri, (2006) prepared the Zn$_{1-x}$Mg$_x$O nanocrystals by low temperature process and studied their structural and optical properties. Xu et al., (2013) studied the structural and optical properties of the sol-gel processed ZnO/ZnMgO oxide thin films. Still, further investigations are needed on the various aspects of preparation and functional properties of Zn$_{1-x}$Mg$_x$O as it is one of the potential materials with technological importance. In this chapter, we attempted to synthesis Zn$_{1-x}$Mg$_x$O \((x=0 \text{ to } 0.1)\) nanocrystals alloy by sol-gel process and studied it structural and optical properties.

4.2 Synthesis of Zn$_{1-x}$Mg$_x$O nanocrystals

Nanocrystals of Zn$_{1-x}$Mg$_x$O with various compositions \((x=0, 0.02, 0.04, 0.06, 0.08 \text{ to } 0.1)\) were prepared by sol-gel process (samples a-f). Zinc acetate, Magnesium acetate and Sodium hydroxide (NaOH) were purchased from Aldrich and used as a source material to prepare the precursor solution without further purification. Tri ethanolamine (TEA) was used as a capping agent to avoid the agglomeration of the nanocrystals. The appropriate amount of constituents such as Zinc acetate and Magnesium acetate were weighed and added with de-ionised water followed by the addition of 0.3 M of NaOH. After that 0.2 M of TEA was added into the solution before the formation of white precipitates to control the size of the crystals and the stirring was continued for the next five hours. The Zn$_{1-x}$Mg$_x$O solutions with various x values (0 to 0.1) were prepared by varying the molar concentration of Zinc acetate and Magnesium acetate to obtain the nanocrystals with various Mg compositions.
for analysing the effect of Mg composition on structural and optical properties of \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) nanocrystals. In the present experiments, the value of \( x \) represents the initial mol percent of Magnesium acetate in the respective precursor solution. The precipitates were collected from the solution by centrifuge method and washed in ethanol before drying at 70 °C. Subsequently, the synthesised materials were annealed at 150 °C for two hours.

X-ray diffraction (XRD) of all the synthesised samples was recorded using a Rigaku diffractometer with Cu K\( \alpha \) radiation. Morphologies of the prepared samples were observed by SEM, FE-SEM, and TEM analysis. The composition of the constituents elements of the synthesised powders were analysed by X-ray photoelectron spectroscopy (XPS). The optical properties of the prepared nanocrystals were studied by optical absorption studies. The luminescence properties of the prepared materials were analysed photoluminescence studies.

4.3 Results and discussion

4.3.1 Structural analysis

Fig. 4.1 shows the XRD spectra of the samples a to f. The XRD patterns are identical for all the samples with pure ZnO (\( x=0 \)) and thus the samples contain a single phase of ZnO with hexagonal wurtzite structure. Moreover, all the diffraction peaks were indexed and well matched with the standard JCPDS data [Minemoto et al., 2006]. From the results, it is obvious that the Mg ions are incorporated substitutionally in the ZnO lattice by replacing the Zn ions.
Fig. 4.1: XRD spectra of the prepared Zn$_{1-x}$Mg$_x$O samples. (a) $x=0$ (b) $x=0.02$ (c) $x=0.04$, (d) $x=0.06$, (e) $x=0.08$, (f) $x=0.1$
Moreover, in the literature the two phases such as ZnO and MgO were identified only when the x ≥ 0.30, indicating that the limit of miscibility of Mg$^{2+}$ ions in the ZnO lattice is around 30% [Minemoto et al., 2006]. In the present investigation, the composition of Mg (x ≤ 0.1) is quite lower than the miscibility limit and thus single phase of ZnO was identified in the XRD spectra of the prepared samples. Further, the sharp and intense diffraction peaks illustrates the crystalline quality of the nanocrystals.

4.3.2 Morphological studies

Figs. 4.2 a, b and c shows the SEM images of the synthesised Zn$_{1-x}$Mg$_x$O (x = 0, 0.04 and 0.1) nanocrystals. All the three images illustrate that the synthesised materials are un-agglomerated with spherical morphology. In general, the growing nanocrystals are highly attractive by large surface energy due to their large surface to volume ratio. As a result, the nanocrystals are agglomerated by so called Ostwald ripening process. In order to control the size of a nanocrystal by suppressing the agglomeration process, organic molecules are generally introduced during the synthesis process as a capping agent. The organic molecules encapsulate the nanocrystals by chemical interaction with the surface layer [Navaneethan et al., 2012; Chandrasekaran et al., 2012] and control the agglomeration thereby size of the crystals. In the present synthesis process, TEA was introduced as a capping agent to suppress the agglomeration of the Zn$_{1-x}$Mg$_x$O nanocrystals.
Fig. 4.2a: SEM image of ZnO sample.

Fig. 4.2b: SEM image of Zn$_{1-x}$Mg$_x$O (x=0.04) nanocrystal.
Fig. 4.2c: SEM image of Zn$_{1-x}$Mg$_x$O (x=0.1) nanocrystals.

Fig. 4.3a: FE-SEM image of Zn$_{1-x}$Mg$_x$O (x=0.04) nanocrystals.
Fig. 4.3b: FE-SEM image of Zn$_{1.3}$Mg$_{0.7}$O (x=0.1) nanocrystals.
Figs. 4.3 a and b shows the FE-SEM images of the prepared Zn$_{1-x}$Mg$_x$O (x= 0.04 and 0.1) nanocrystals. As can be seen from Fig. 4.3 a and b, the nanocrystals are obviously monodispersed with spherical morphology. Moreover, the sizes of the particles are in the range of 20 to 30 nm and it is obvious that the TEA effectively suppressed the agglomeration by encapsulating the surfaces of the growing nanocrystals.

### 4.3.3 Elemental analysis

The compositions of the prepared Zn$_{1-x}$Mg$_x$O (x=0.02 and 0.1) samples were studied by XPS analysis. Figs. 4.4 a, b and c shows the XPS spectra of Zn, O and Mg of Zn$_{1-x}$Mg$_x$O samples. In Fig.4.4 a, the two peaks correspond to Zn2P$_{3/2}$ and Zn2P$_{1/2}$ was clearly observed. Moreover, the intensity of both the peaks was decreased for the sample which has higher Mg composition. As shown in Fig. 4.4 b, the 1s peak of oxygen (O) was observed at 532 eV with a shoulder peak at 530 eV. The peak at 530 eV corresponds to O bonded with either Zn or Mg in Zn$_{1-x}$Mg$_x$O lattice whereas the peak at 532 eV represents the unbonded O at the surface of the material. Furthermore, the intensity of the peak at 532 eV increased drastically for the sample with higher Mg composition.
Fig. 4.4a: XPS spectra of the Zn 2p of Zn$_{1-x}$Mg$_x$O (x=0.02), and Zn$_{1-x}$Mg$_x$O (x=0.1) samples.
Fig. 4.4b: XPS spectra of the O 1s of Zn$_{1-x}$Mg$_x$O (x=0.02), and Zn$_{1-x}$Mg$_x$O (x=0.1) samples.
Fig. 4.4c: XPS spectra of the Mg 2s of Zn$_{1-x}$Mg$_x$O (x=0.02), and Zn$_{1-x}$Mg$_x$O (x=0.1) samples.
From the result, it is obvious that more amount of O diffuses to surface (even at low temperature annealing) when the Mg content increases in the material due to low binding energy of Mg\textsubscript{-}O compared to Zn\textsubscript{-}O. Moreover, due to O diffusion, the number of O vacancies and unbounded surface O increases in the crystal. As a result, the defect related deep level emission was drastically increased in the Zn\textsubscript{1-x}Mg\textsubscript{x}O compared to pure ZnO material (discussed in the next section). Mg 2s of Zn\textsubscript{1-x}Mg\textsubscript{x}O (x=0.02) was observed at 95.7 eV and it was shifted to low energy side of 91.2 eV for the sample Zn\textsubscript{1-x}Mg\textsubscript{x}O (x=0.1) (Fig.4.4c). Moreover, the intensity of the peak is nearly four times larger for the Zn\textsubscript{1-x}Mg\textsubscript{x}O sample with x=0.1 when compared to that of Zn\textsubscript{1-x}Mg\textsubscript{x}O with x=0.02 and it confirms the rate of incorporation of Mg increases as the Mg concentration increases in the precursor solution. As a consequence, the incorporation of Mg in ZnO leads to strong green emission as evidenced from the photoluminescence studies.

4.3.4 Optical absorption studies

The optical properties of the nanocrystals were investigated by means of UV-visible optical absorption studies. Fig. 4.5 shows the optical absorption spectra of the synthesised Zn\textsubscript{1-x}Mg\textsubscript{x}O (x=0 and 0.1) nanocrystals. The absorption onset was observed at 363.5 nm for the ZnO sample while it was blue shifted to 359 nm for the Zn\textsubscript{1-x}Mg\textsubscript{x}O sample with x=0.1. The observed variation in the cut off wavelength is possibly due to the incorporation of Mg\textsuperscript{2+} ion in ZnO lattice as the incorporation of Mg increases the band gap [Schmidt \textit{et al.}, 2003].
Fig. 4.5: Optical absorption of (a) ZnO and (b) Zn$_{1-x}$Mg$_x$O (x=0.1) samples.
4.3.5 Photoluminescence studies

Luminescence properties of the prepared Zn$_{1-x}$Mg$_x$O (x=0 to 0.1) was investigated by photoluminescence analysis. Fig. 4.6 a and b shows the recorded photoluminescence spectra of the Zn$_{1-x}$Mg$_x$O samples. As shown in the Fig. 4.6 a, the near band edge emission was clearly observed at about 380 nm for the pure ZnO with weak defect level emission at 590 nm. When the Mg composition increases in the ZnO the defect related deep level visible emission increases drastically and the weak near band edge emission was overlapped. Low temperature annealing is the possible cause for the weak near band edge emission in the samples. Moreover, the deep level emission was increased when the x increases up to 0.08 and decreased slightly at x =0.1 (Fig. 4.7). It means that the intrinsic defect concentration increases when the Mg composition increases in the material up to the molar ratio of 0.08. In addition, the deep level emission showed a red shift for the samples with x value of ≤ 0.04. For example, the deep level emission of the Zn$_{1-x}$Mg$_x$O sample with x=0.04 was observed at 576 nm whereas the deep level emission for ZnO was observed at 545 nm. The visible emission observed in violet, green and orange-red regions are mainly due to the interstitial zinc (Zn$_i$), oxygen vacancy (V$_o$), anti-site oxygen (O$_{Zn}$) and interstitial oxygen (O$_i$) defect levels [Jeong et al., 2003; Lin et al., 2001; Reynolds et al., 2001; Garces et al., 2002; Andelman et al., 2005].
Fig. 4.6 a: Photoluminescence spectra of (a) Zn$_{1-x}$Mg$_x$O ($x=0$ to 0.1) samples.
Fig. 4.6b: Photoluminescence spectra of enlarged view of near band edge emission.
Fig. 4.7: Deep level emission intensity variation as a function of x value of Zn$_{1-x}$Mg$_x$O.
It is expected that, when the Mg composition increases in the material, the number of Mg-O bonds are likely to be increased. The length of Mg-O bond is longer than Zn-O bond due to variation in the ionic radius of Mg$^{2+}$ and Zn$^{2+}$. In general, if the bond length is longer, obviously the binding energy is decreases. As discussed in the XPS analysis the binding energy of O was decreased up to 0.3 eV when the Mg composition increases from 2 to 10 mol % in the precursor solution. Due to low binding energy, the rate of diffusion of O increases even at low temperature processing and thus the amount of O$_1$ and V$_o$ defects are increases in the sample. As a consequence, these defect related deep level emission peak in the range of 540 to 576 nm increases as a function of Mg incorporation. Similar kind of results was observed by Ghosh and Raychaudhuri, (2006) for the low temperature processed Zn$_{1-x}$Mg$_x$O samples. In addition, marginal quantity of Mg(OH)$_2$ is likely to be formed in the Zn$_{1-x}$Mg$_x$O sample with 10 mol % of Mg and it may suppress the deep level green emission [Ghosh and Raychaudhuri, 2006]. However, the Mg(OH)$_2$/MgO phase is possible to form only when the x value is greater than 0.3 [Minemoto et al., 2000; Ghosh and Raychaudhuri, 2006]. As a consequence the deep level emission mechanism in low temperature processed Zn$_{1-x}$Mg$_x$O must be investigated more in detail with wide range of Mg concentrations and such kind of research is under progress.