CHAPTER - 9
NANOCRYSTALLINE Zn_{(1-x-y)}Be_x Mg_y O THIN FILMS SYNTHESIZED BY
SOL-GEL METHOD: STRUCTURAL AND NEAR INFRARED
PHOTOLUMINESCENCE PROPERTIES

9.1 Introduction

Zinc Oxide (ZnO) is a semiconductor with a wide direct band gap of 3.37 eV and a large
exciton binding energy of 60 meV, which is widely used in various applications [423]. ZnO
is one of the II-VI compound semiconductors composed of hexagonal wurtzite crystal
structure [424]. To achieve effective excitonic recombination at room temperature in optical
devices, a quantum well structure, composed of an active thin layer sandwiched between the
two high band gap barrier films is desirable. To minimize the defect density in the structure,
lattice constants of all layers should be as close as possible. Hence, the band gap modulation
in ZnO becomes important. Ohtomo et al. [425] have proposed a common approach for the
fabrication of ZnO-based alloys with a band gap larger than that of ZnO. They have reported
that the band gap of Zn_{1-x}Mg_xO goes up to 3.99 eV at room temperature as the content of Mg
is increased to x = 0.33 [426]. However, crystal phase separation between ZnO and MgO was
observed at x > 0.36, which is due to different crystal structures and hence a large lattice
mismatch between ZnO and MgO, for example MgO is cubic with 4.22 Å, and ZnO is
hexagonal with a = 3.234 Å and c = 5.206 Å [427].

To avoid such problems a new metal oxide along with ZnO and MgO is proposed. Keeping that in mind beryllium (Be) has been codoped here with the ZnO and MgO
combination to avoid this mismatch. That both BeO and ZnO have the same hexagonal
structure is the main reason for the incorporation of Be as a codopant.
A hexagonal BeO has been newly proposed as a strong candidate due to its good solubility and a large band-gap value of 10.6 eV experimentally at room temperature [428]. Yang et al [429] have reported that the single phased wurtzite ZnO based oxide system $\text{Zn}_{1-x-y}\text{Be}_x\text{Mg}_y\text{O}$ has been successfully prepared with a band gap ranging from 3.7 to 4.9 eV. Moreover it seems to be more crystalline and exhibits better optical properties when compared with those of ZnMgO and BeZnO. Ryu et al. [430] reported results for a series of $\text{Zn}_{1-x}\text{Be}_x\text{O}$ alloys in the form of thin films, which can be used alone or in combination to form active layers for semiconductor photonic devices that can emit and detect light at single wavelength or multiple wavelengths over a wide range of values.

Different techniques, such as: hybrid beam deposition [431-433], RF magnetron sputtering [434] and pulsed laser deposition [435-437] have been used to deposit thin films of doped ZnO. Sol–gel method [96] has been receiving attention due to its manifold advantages such as low cost, simple deposition procedure, easier composition control, low processing temperature and easier fabrication of large area films [438]. Therefore, in this chapter, we report the deposition and characterization of Be, Mg doped and (Be, Mg) codoped ZnO thin films on sapphire by sol–gel spin-coating method. Two powerful optical characterization techniques, photoluminescence (PL) and Raman spectroscopy are commonly employed for fast and nondestructive studies on carrier recombination and transport processes. To further understand the effects of extrinsic defects caused by codoping on the optical and vibrational properties of doped ZnO, investigations on PL and micro Raman measurements in BeMgZnO thin films have been carried out at room temperature. Obvious changes in the properties of BeZnO, MgZnO and BeMgZnO and the underlying mechanisms accounting for the effects of doping on the optical and vibrational properties of ZnO have been discussed in detail.
9.2 Experimental details

9.2.1 Sol-gel synthesis of Zn\((1-x-y)\)Be\(_x\)Mg\(_y\)O thin films

Be doped and (Be, Mg) codoped ZnO thin films have been deposited by sol-gel spin coating method on sapphire (Al\(_2\)O\(_3\)) substrates. Zinc acetate dihydrate Zn(CH\(_3\)COO)\(_2\).2H\(_2\)O, (99.9%), magnesium acetate dihydrate (CH\(_3\)COCH(O)CH\(_3\))\(_2\)Mg·2H\(_2\)O, (98%) and beryllium acetylacetonate (CH\(_3\)COCH=C(O-CH\(_3\))\(_2\) Be, (97%) are used as the starting materials procured from Sigma Aldrich and 2-methoxyethanol (CH\(_3\)OCH\(_2\)CH\(_2\)OH) and monoethanolamine (NH\(_2\)CH\(_2\)CH\(_2\)OH) are used as solvent and stabilizer, respectively. Zinc acetate dihydrate is first dissolved in the mixture of 2-methoxyethanol and monoethanolamine (MEA). The molar ratio of MEA to total metal cations is maintained at 4.0. The total concentration of solution is kept at 0.5 mol/L and the concentration of dopants at 6 mol%, with respect to zinc. Then, the resulting mixture is stirred at 60°C for 2 hours. Finally, a clear and transparent homogeneous solution is formed. The sol is aged for 24 hours at room temperature. Earlier procedure has been followed in cleaning and coating of the films as in chapter-3. The procedure from coating to drying is repeated ten times. The grown film is then kept in a furnace and annealed in air at 600°C for 1 hr.

9.2.2 Characterization

X-ray diffraction (XRD) studies of the films were performed using monochromatic CuK\(_{α1}\) radiation. The surface morphology studies of the films were done using scanning electron microscope (SEM-NanoNova). The core level electrons of the deposited films were characterized by high resolution X-ray photoelectron spectroscopy (XPS). The \(μ\)-photoluminescence (PL) and Raman measurements were carried out using a Horiba Jobin Yvon HR-800 UV micro-PL-Raman set up. A 325 nm line of a He–Cd laser was used as the
excitation source with a 2400 grooves/mm grating in the backscattering geometry. A 500-µm confocal pinhole is used to obtain high-resolution Raman spectra.

9.3 Results and Discussion

9.3.1 XRD analysis

XRD spectra of the BeZnO, BeMgO and BeMgZnO layers grown under optimized conditions are presented in Fig.9.1.

![XRD pattern of a nanocrystalline film annealed at 600°C for 1 hr](image)

**Fig. 9.1** XRD pattern of a nanocrystalline film annealed at 600°C for 1 hr (a) ZnO film (b) 6% Mg doped ZnO film (c) 6% Be doped ZnO film (d) 6% Be and Mg doped ZnO film.

All the peaks of the doped ZnO thin film in the present study are in accordance with the peaks of the standard ZnO (JCPDS 89-0510) [439] and all the films exhibited a hexagonal wurtzite structure with (100), (002) and (101) peaks. The presence of diffraction peaks can be used to evaluate the structural order at long range or periodicity of the material [440]. The main diffraction band of BeZnO, MgZnO and BeMgZnO is shifted towards a slightly higher diffraction angle than that of ZnO. The patterns arising due to this shift correspond to the
diffraction bands of BeZnO (002), MgZnO (002) and BeMgZnO (002). Also, the films are strongly c-axis oriented and epitaxially crystallized under constraints created by the substrate. The full width at half maximum (FWHM) of the (002) band is 0.273° for ZnO, 0.333° for BeZnO, 0.466° for MgZnO and 0.463° for BeMgZnO, respectively. The lattice constants of ZnO film is \(a = 3.2282\, \text{Å} \) and \(c = 5.1783\, \text{Å}\) and that of BeMgZnO film is \(a = 3.2306\, \text{Å}\) and \(c = 1.7306\, \text{Å}\). Value of lattice constant ‘a’ is increased while ‘c’ is decreased in the co-doped film compared to ZnO film and is closely coincide with the previous literature values [441]. The increase/decrease in the values of lattice parameters indicate a change in the preferential growth directions. Evaluating the mean grain size (D) of the films based on the XRD results, we have applied the Scherrer formula [442]. The calculated mean grain size of the undoped ZnO, BeZnO, MgZnO and BeMgZnO samples annealed at 600°C for 1hr is 30.48, 24.97, 17.84 and 17.97 nm respectively. The compressive stress was found to change into tensile stress after Mg incorporation [443]. In the present study we also found a similar result when Mg and Be are incorporated in the ZnO host lattice. The calculated structural parameters are listed in Table 9.1.

Table 9.1 Calculated structural parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>ZnO</th>
<th>BeZnO</th>
<th>MgZnO</th>
<th>BeMgZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a (\text{Å}))</td>
<td>3.2282</td>
<td>3.2303</td>
<td>3.2306</td>
<td>3.2306</td>
</tr>
<tr>
<td>(c (\text{Å}))</td>
<td>5.1783</td>
<td>5.1765</td>
<td>5.1580</td>
<td>5.1730</td>
</tr>
<tr>
<td>Particle Size (nm)</td>
<td>30.48</td>
<td>24.97</td>
<td>17.84</td>
<td>17.97</td>
</tr>
<tr>
<td>Stress ((\sigma))</td>
<td>1.209</td>
<td>1.297</td>
<td>0.859</td>
<td>1.432</td>
</tr>
</tbody>
</table>

9.3.2 Surface and XPS analysis

The deposited films surface has been analyzed by scanning electron microscope (SEM) images and is shown in Fig.9.2 (a-d). Undoped and doped ZnO film surfaces consist of irregular shaped grains with different size and the morphology changes on doping the host
ZnO lattice. It can be seen that the surface is closely packed and the grain size is decreased with respect to doping as observed from the SEM images. The average grain size has been found to be in the order of 30 – 60 nm matches with the XRD results.

![SEM Images of ZnO and Doped ZnO Compounds](image)

**Fig. 9.2** Scanning electron microscope images (a) ZnO, (b) BeZnO, (c) MgZnO, (d) BeMgZnO

**Fig. 9.3** shows the XPS spectra of the ZnO: (Be, Mg) films. The core level bands of Zn 2p, O 1s, Mg 2p and Be 1s are observed. They can be well fitted by Gaussian functions. The binding energies of Zn 2p3/2, Mg 2p and Be 1s are located at 1020.84 eV, 48.9 eV and 108.35 eV, respectively, as shown in **Fig. 9.3(a)** and **9.3(c & d)**, suggesting a single Zn$^{2+}$ ion component in the films. Fig.9.3(b) shows stronger band at 529.97 eV which may be attributed to O$^{2-}$ ions in Zn–O, Be–O and Mg–O bonds, while another at 531.61 eV is usually associated with the loosely bound oxygen (e.g., adsorbed O$_2$, –OH) chemisorbed on the surface and/or grain boundary of polycrystalline film [444-446].
Fig. 9.3 XPS spectra of a 6% Be and Mg codoped ZnO nanocrystalline film.

9.3.3 Photoluminescence

Fig. 9.4 shows the $\mu$-PL spectrum of ZnO, BeZnO, MgZnO and BeMgZnO excited by 325-nm UV light from a He–Cd laser at room temperature.

Fig. 9.4 Room temperature $\mu$-PL spectra of the undoped and doped ZnO nanocrystalline films.
The room temperature μ-PL spectra of ZnO, BeZnO, MgZnO and BeMgZnO all contain a strong UV band (bands at 3.28, 3.3, 3.26 and 3.4 eV, respectively) and a very weak, broad green band spreads from 2.1 to 2.8 eV. The UV emission originates from the excitonic recombination corresponding to the near band edge emission (NBE) of the film and it was blue shifted. The reason for the shift might be due to the incorporation of (Be, Mg) codopants in ZnO lattice. Also the shift of NBE emission peak in the doped film was believed to be a cause of Burstein–Moss effect [176]. The NBE peak intensity of BeZnO and BeMgZnO films are increased compared to ZnO and MgZnO and it is due to the density of free excitons [274]. It could have been taken place possibly through the non-radiative recombination process.

A broad weak green emission peak observed in the region 2.1–2.8 eV in all the films correspond to the oxygen vacancy related defects of ZnO [275]. The near infrared (NIR) band is found at ~1.64 eV in all the films except MgZnO corresponds to NIR emission. This band intensity increase the shift towards the higher energy side with the doping of Be and codoping (Be and Mg) in ZnO. The transition between zinc vacancy and oxygen vacancy states give rise to the 1.64 eV NIR emission [348]. We previously reported the NIR emission in Cs doped ZnO sol gel thin films [308]. It is also observed in Be doped ZnO film however it is enhanced after codoping Mg into BeZnO lattice, the increased NIR emission intensity is four orders of magnitude which confirms the defects formation. The NIR emission intensities are much less when compared to all the other intensities of emission. In Mg doped ZnO the intensities of NBE and green emission itself has lesser magnitude when compared to the other doping and hence NIR emission is not pronounced. The NIR emission is shown in the inset of Fig.9.4.
The effect of Be, Mg doped and (Be, Mg) codoping in ZnO film has been studied using micro-Raman spectroscopy. For all samples, the observed multiphonon bands range lies from 200 to 2500 cm\(^{-1}\). Although the multi-phonon scattering processes have been observed in ZnO thin films, micro Raman spectra of BeZnO and BeMgZnO thin films have not been reported until now to the best of our knowledge.

9.3.4 Raman analysis

![Raman spectra of the undoped and doped ZnO nanocrystal line in back scattering geometry.](image)

Fig. 9.5 Raman spectra of the undoped and doped ZnO nanocrystalline in back scattering geometry.

Fig. 9.5 shows the typical Raman spectra of BeZnO, MgZnO and BeMgZnO films. The Raman spectra of BeZnO, MgZnO film are composed of four sharp bands at 575.49, 1149.276, 1727.701 and 2319.6 cm\(^{-1}\), which arise from the emission of 1, 2, 3, and 4 longitudinal optical (A\(_1\)LO) phonons of ZnO wurtzite structure. This result is consistent with
previously reported Raman shift of ZnO bulk crystal and thin films [217, 447, 448]. For BeMgZnO thin films, a typical Raman spectrum is observed up to 3rd order. The second order E₂(low) phonon mode observed around 220 cm⁻¹ due to the substitution of the Mg and Be atom on the zinc site in the lattice. The strong band at about 442, 443,442 and 446 cm⁻¹ is assigned to the E₂(high) mode of ZnO, BeZnO, MgZnO and BeMgZnO, respectively, which is a Raman active mode in the wurtzite crystal structure.

The strong E₂ (high) mode indicates very good crystallinity. The additional band could be assigned to the combination of modes such as E₁ (TO) + E₂(low), E₁ and E₂ (TA+ LO). A very small Raman active band near 320 cm⁻¹ can be assigned to the multi-phonon process, E₂ (high)–E₂ (low), in which an E₂ (high) mode is emitted and an E₂ (low) mode is absorbed. The 1LO phonon band intensities have increased with respect to the increase of Mg concentration in Be doped ZnO thin films. This has led to an increase in the number of phonons in (Be, Mg) codoped ZnO thin films, promoting electron–hole nonradiative recombination process. FWHM and the band intensity of 1LO were found to increase in the codoped films with the decrease of crystalline size. This has led us to the conclusion that a broadening of LO phonon band followed by an increase in its intensity may lead to an increase in scattering cross-section. The possible reason for this could be the presence of the interband Frohlich contribution as per the following discussion. The contribution from the impurity-induced mechanism is significant for 1LO phonon scattering, but it can be neglected for scattering by two and more LO phonons [215], which is only due to the intrinsic intraband Frohlich mechanism. An impurity-induced enhancement of 1LO phonon mode scattering results in for the following reason. Serious breakdown of the wave vector conservation caused by scattering by random impurities allows phonons with larger wave vectors to participate in the Raman scattering. These larger wave vectors greatly enhance the intraband
Frohlich contribution and therefore increase the corresponding scattering cross-section [216].

Deformation energy of undoped, Be, Mg doped and (Be, Mg) codoped ZnO films are calculated using the relation, \( n\omega_{LO} \) where, ‘\( n \)’ is the number of LO phonons and ‘\( \omega_{LO} \)’ is the first LO phonon frequency. The calculated deformation energies are plotted as a function of number of LO phonons and it is shown in Fig.9.6.

![Deformation Energy Plot](image)

**Fig. 9.6** Deformation energy of ZnO, BeZnO, MgZnO and BeMgZnO films.

It increases with the number of LO phonons which indicates the increase of LO phonons orders could lead to the structural stability. Compared to other two films Mg doped ZnO:Be has lesser deformation energy and hence a reorientation of its structure which coincides with the XRD results.
9.4 Conclusions

In summary, wide band gap BeZnO, MgZnO and BeMgZnO nanocrystalline films have been successfully grown on sapphire substrate by sol-gel method. XRD results revealed that the average particle sizes are in the range of 17-50 nm for undoped and doped ZnO nanocrystalline films. The modified values of lattice parameters suggest that the preferential growth directions are altered. The introduction of tensile stress due to the incorporation of the dopants has altered the host ZnO lattice. The SEM images revealed that the film surface is closely packed and the grain size is decreased with the incorporation of dopants. The μ-PL spectra of ZnO, BeZnO, MgZnO and BeMgZnO show a strong UV emission band tuned from 3.26 to 3.4 eV and also a very weak visible emission associated with the singly ionized oxygen vacancy. The observed NIR band has been enhanced and shifted in the doped and codoped films when compared to pure ZnO. The blue shifts of optical band gap, quenching off the near-band-edge photoluminescence and multi-phonon Raman scattering originating from ZnO like A1(LO) phonons are observed. The position of ZnO like LO phonons are blue shifted in the 6% Be, 6% Mg and 6% (Be, Mg) codoped ZnO films. The broadening of the 1LO phonon scattering bands indicate the increase of lattice disorder and deformation due to the incorporation of Be²⁺, Mg²⁺ into the ZnO lattice. Structural stability is confirmed by deformation energy calculations. Based on the results we conclude that this wide band gap semiconductor is useful for photonic and optoelectronic applications.