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A Study on Structural and Optical Properties of $Mg_xZn_{1-x}O$ thin films using Pulsed Laser Deposition (PLD)

Ahirwar Vishnu Prasad[1], Misra P.[2] and Ahirwar G.[1]
[1]School of Studies in Physics, Vikram University, Ujjain MP, INDIA
[2]RRCAT, Indore MP, INDIA

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Abstract

We have study of grown high quality MgZnO thin films on sapphire (0001) substrates at ~ 400^{0}C temperature, using pulsed laser deposition (PLD) technique. The spectral position of the photoluminescence and optical band gap were successfully tuned from 3.3 to 4.2 eV by adjusting the Mg content. Throughout this tuning range the crystal quality was sufficiently preserved to maintain the exciton nature of the material resulting in very efficient ultraviolet emission. The transmittance spectra showed that MgZnO thin films are highly transparent with sharp absorption edges. Through Tauc's plot fitting of the absorbance spectra, the band gap energy Eg photoluminescence of the thin films was calculated. It is found that the Eg increases with increasing doped concentration, which coincides with the results from the measurements of photoluminescence. Growth of high quality MgZnO alloy films opens up numerous possibilities for the development of ultraviolet optoelectronic devices.

Keywords: Pulsed laser deposition, zinc oxide, X-ray diffraction, optical absorption spectroscopy, photoluminescence.

Introduction

Zinc oxide (ZnO) is an II–VI compound semiconductor with a direct and wide band gap of~ 3.3 eV[1-2] at room temperature. It has a large free exciton binding energy of ~60 meV[3-4]. This arge exciton binding energy which is larger than the thermal energy at room temperature (~25 meV) indicates that efficient exciton emission in ZnO can persist at room temperature and higher temperatures. Most of the group II–VI binary compound semiconductors crystallize in either cubic zinc blende or hexagonal wurtzite structure where each anion is surrounded by four cations at the corners of a tetrahedron, and vice versa. This tetrahedral coordination is typical of sp^3 hybridized covalent bonding. It has a polar hexagonal axis, the c axis, chosen to be parallel to z. This is a hexagonal lattice, with lattice parameters a = b = 0.3296 and c = 0.52065 nm, and is characterized by two interconnecting hexagonal sub lattices of Zn^{2+} and O^{2-}, such that each Zn ion is surrounded by tetrahedral of O ions and vice versa. This tetrahedral coordination gives rise to polar symmetry along the hexagonal axis. This polarity is responsible for a number of the properties of ZnO, including its piezoelectricity and spontaneous polarization, and is also a key factor in crystal growth, etching and defect generation. The density is 5.605 g cm^{-3}. ZnO thin films and nanostructures are widely used in various applications which include light emitting diodes (LED), UV photo detectors, transparent conducting oxides (TCOs), transparent thin film transistors (TTFTs), solar cells windows, piezoelectric transducers, Gas Sensors etc.[5-6]. The large exciton binding energy makes ZnO a promising material for optical devices that are based on exciton effects. Due to a strong luminescence in the green–white region of the spectrum, ZnO is also a suitable material for phosphor applications.

Material and Methods

$Mg_xZn_{1-x}O$ thin films were synthesized by pulsed laser deposition system using a KrF Excimer laser. Thin films were grown in a high vacuum chamber with background pressure of ~ 5×10^{-6} mbar. The KrF laser was operated at the wavelength of 248 nm with the repetition rate of 10 Hz and pulse duration of 25 ns. MgO-ZnO composite targets with MgO contents from 0 % to 21 % were used during the deposition. The composite targets were obtained by the standard pressing and sintering method as described earlier. Sapphire was used as substrates for growing these Mg_xZn_{1-x} O thin films. The substrates have the thickness of 0.5 mm and are c-axis oriented. Before loading into the vacuum chamber, substrates were cleaned with standard chemical method, by which the substrate was first cleaned in acetone and then in methanol for 10 min each in ultrasonic bath. Thin films were grown in oxygen environment with O_2 partial pressure of 2×10^{-5} mbar at substrate temperature of 400°C. Laser energy density focused on the target was about 1.5 J/cm^2. The deposition time was typically 40 min. After the deposition, thin films were cooled down to room temperature at a rate of ~ 20 °C/min in ~ 760 mbar of oxygen pressure.

Results and Discussion

The X-ray diffraction (Structural properties): The XRD patterns of ZnO thin films with different Mg concentrations (0, 6 and 12 at. %) on the (0001) sapphire substrates as shown in

figure (1). The [ω- 2θ] XRD pattern showed only (0002) ZnO reflections in ZnO and MgZnO thin films. It clearly reveals that the ZnO and MgZnO thin films grow in highly c-axis oriented hexagonal wurtzite structures on (0001) sapphire substrates as reported in existing literatures.

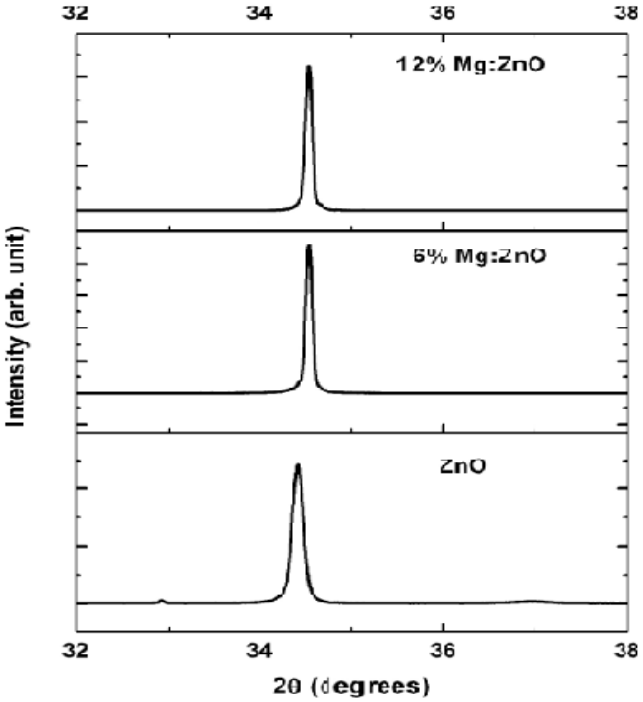

Figure-1
Shows XRD patterns of ZnO with different Mg concentrations

The positions of the (0002) ZnO peak have been found to be shifted to higher angle in the alloy MgZnO thin films. This shift of the (0002) peak to higher angle is proportional to the Mg contents in the films. The shift is due to decrease in the lattice constant in the growth direction (i.e. c axis) due to smaller size of Mg^{2+} ions as compare to the Zn^{2+} ions. It can be clearly understood from the Bragg's law,

$2d \sin\theta = n\lambda$ (1)

Here d is the plane spacing along the c axis, θ is the diffraction angle, λ is the wavelength of X-rays. As Mg concentration in the films increases, c axis length decreases resulting in the decrease of *d*. Hence from Bragg's law to keep the LHS of the equation equal to the RHS, θ increases shifting the position of the (0002) ZnO peaks to higher angles with increasing Mg doping. Hence the change in the lattice constant of the MgZnO films can also be calculated from the above mentioned shift. The c-axis lattice constant c is related to d by the equation,

$$c = 2d \quad (2)$$

Combining (1) and (2) we get,

$$c = n\lambda / \sin\theta \quad (3)$$

Using this equation and the w-2q diffraction patterns of the MgZnO films, c values were calculated for the films with different concentrations of Mg. They are shown in table-1.

Table-1

Mg concentration	2 θ (degrees)	c (angstrom)
0	34.417	5.2114
6	34.5272	5.1953
12	34.5301	5.1949

Optical absorption spectroscopy (Optical properties): The absorbance of the MgZnO thin films with different Mg concentrations (x=2%, 4%, 6%, 12 %, 15% and 21%) as shown in figure (2). The variation of the maximum absorbance is due to the variation in MgZnO films thickness. The figure reveals that with increasing Mg doping the band edge of ZnO shift to lower wavelength side (blue shift). As grown pure ZnO films has a band edge at ~ 380 nm. It monotonously blue shifted with increasing Mg doping, finally reaching a value of ~280 nm at ~21 % Mg doping concentration. The peak in the absorption spectra near the absorption edge is due to excitonic absorption. From figure 8 it is apparent that all the films, except the one with highest Mg doping, shows this excitonic absorption feature in the absorption spectra. The exciton peaks are broadened in MgZnO films due to alloying and the details of the individual excitons cannot be distinguished. However, the excitonic feature in the absorption spectra is still extremely significant. This is a consequence of the high binding energy (~60 meV) of the exciton in ZnO and its alloys and the high crystalline quality of the films.

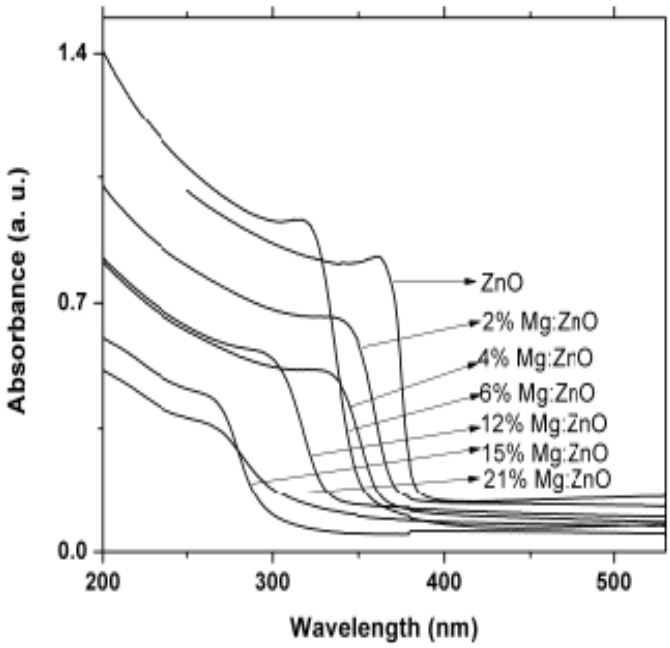

Figure 2
Shown the absorbance of the $Mg_xZn_{1-x}O$ thin films with different Mg Concentrations

In a direct bandgap semiconductor such as ZnO and its alloys the absorption co-efficient is related to the incident photon energy by the following relation,

$$\alpha = A\,(h\nu - Eg)^{1/2} \quad (4)$$

Where, *h* is the Plank constant, ***ν*** is the frequency of the incident photon; A is a constant depending on the electron-hole mobility and E_g is the optical band gap energy. So the band-gap of the MgZnO films can be calculated from the absorbance data by plotting α^2 as a function of hν (Tauc's plot) and extrapolating the linear portion of the graph to the x axis. The x-axis intercept made by a particular graph will give value of band gap of the corresponding film. The Absorption coefficient of MgxZn1-xO thin film versus photon energy (hv) as shown in figure(3) and Band gap energy was calculated for all the films and are shown in figure-4.

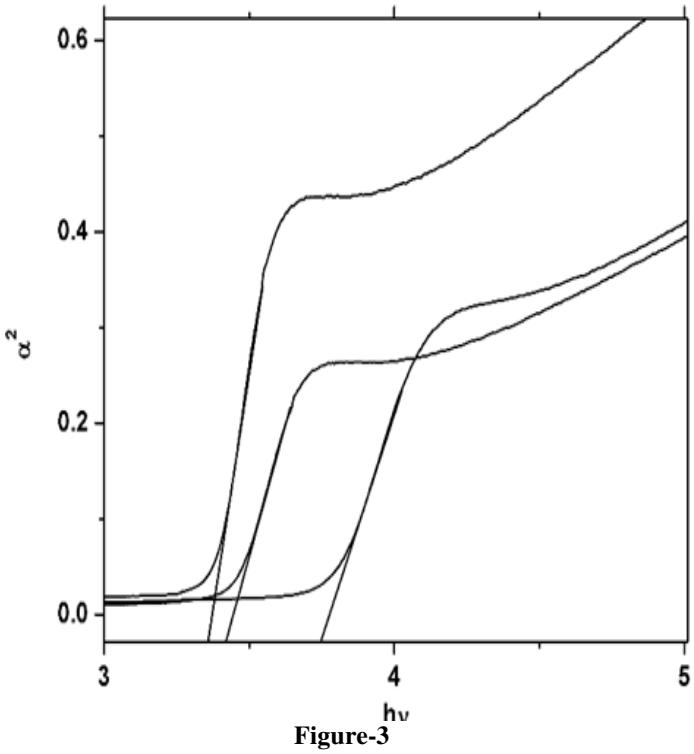

Figure-3
Shown the Absorption coefficient of MgxZn1-xO thin film versus photon energy (hv)

The band gap of the MgZnO thin films increases as the Mg content is increased. For 0 at. % of Mg content which is identical to pure ZnO thin film, the optical band gap energy was 3.3eV. On increasing Mg concentration to 15 % in the ZnO thin films the bandgap increased almost linearly to ~ 4.2 eV. Beyond 15% the bandgap remains practically constant, probably due to Mg segregation along the grain boundaries. It is also supported by the tailing of the absorption edge of the 21% MgZnO thin film. An increment of at least 0.9 eV in the band gap energy was obtained on increasing Mg content from 0 to 15 at. %.

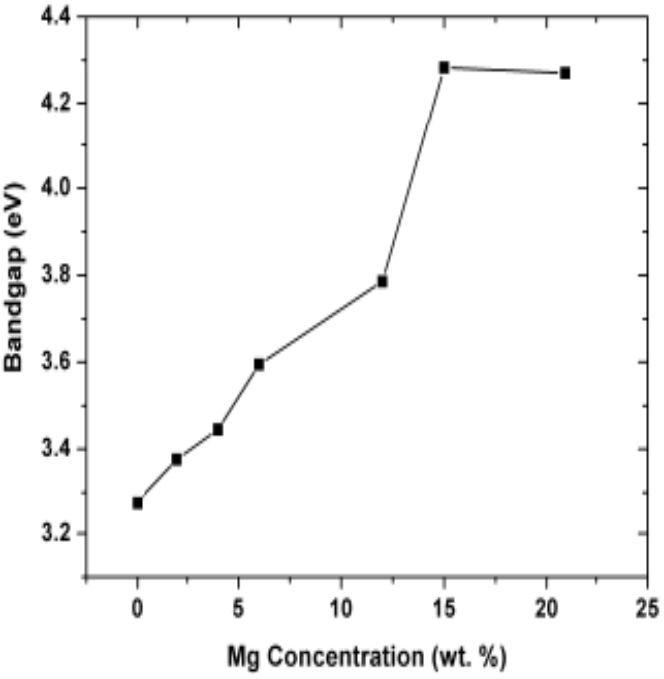

Figure 4
Optical band gap energy of $Mg_xZn_{1-x}O$ thin film calculated by using Tauc`s plot.

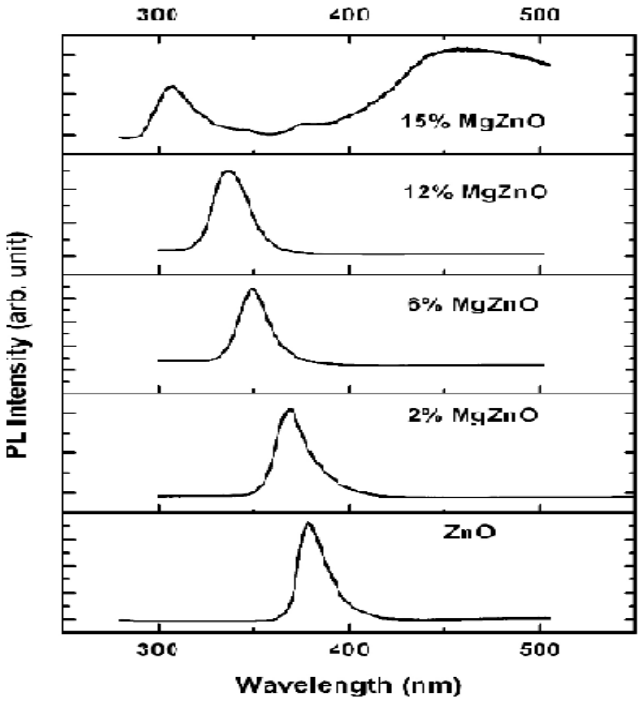

Figure-11
Shows room temperature PL spectra of Mg doped ZnO with different doping concentrations deposited at 400^0C on the sapphire (0001)

Photoluminescence: The room temperature photoluminescence spectra of the MgZnO thin films with different Mg concentrations grown on Sapphire substrates as shown in (5). In this figure, the spectra have been normalized for clarity in discussion. The sharp exciton emissions in UV spectral region were observed in all the MgZnO thin film samples. The peak position of the exciton emission bands shifted to the higher energy side as Mg concentration in the film increased. The reason is simply enhancement of the bandgap energy of ZnO due to Mg doping.

It was also seen that the PL peak positions are slightly red shifted as compared to the corresponding absorption edges due to Stokes shift normally found in polar ZnO samples. The Pl from the 15% Mg doped sample contain an extra peak centred at ~ 450 nm probably due to some mid gap defects introduced due to excessive Mg doping. However, the presence of exciton emission in the all the films shows the superior crystalline quality of the MgZnO thin films grown by PLD suitable for optoelectronic applications.

Conclusion

In conclusion, we have grown high quality MgZnO thin films on sapphire (0001) substrates at ~ 400^0C temperature, using pulsed laser deposition (PLD) technique. The spectral position of the photoluminescence and optical band gap were successfully tuned from 3.3 to 4.2 eV by adjusting the Mg content. Throughout this tuning range the crystal quality was sufficiently preserved to maintain the excitonic nature of the material resulting in very efficient ultraviolet emission. The transmittance spectra showed that MgZnO thin films are highly transparent with sharp absorption edges. Through Tauc's plot fitting of the absorbance spectra, the band gap energy Eg photoluminescence of the thin films was calculated. It is found that the Eg increases with increasing doped concentration, which coincides with the results from the measurements of photoluminescence. Growth of high quality MgZnO alloy films opens up numerous possibilities for the development of ultraviolet optoelectronic devices.

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