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Structural and optical properties of Cd and Mg doped zinc oxide thin films deposited by pulsed laser deposition

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Structural and optical properties of Cd and Mg doped zinc oxide thin films deposited by pulsed laser deposition

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Abstract. The 7 wt % Cd doped and 15 wt % Mg doped ZnO thin films were deposited on quartz substrate by pulse laser deposition system. The structural and optical properties of the prepared ZnO, Cd:ZnO and Mg:ZnO films were investigated by X-Ray diffraction (XRD), photoluminescence and UV-Vis spectroscopy techniques. XRD results indicate that the doped ZnO films maintain wurtzite crystal symmetry without any defects and are oriented along c-axis. Photoluminescence studies show a sharp band edge emission peak at 384 nm for pure ZnO film. This peak is blue shifted to 381 nm with Cd doping and red shifted to 395 nm with Mg doping. UV visible absorption studies reveals a decrease in band gap with Cd doping and an increase in band gap with Mg doping.

1. Introduction

The increasing demand, of low power optoelectronic devices, such as white LEDs, photo detectors and UV emitters, has been stimulated the research on wide band gap semiconducting materials [1]. Silicon Carbide, Aluminum Nitride, Diamond and Gallium Nitride are very much popular among the researchers. Among these (high brightness white LED and blue laser), GaN has gain lots of interest due to its commercial success in optoelectronic devices [2]. More than 100 billion GaN based white and blue LED's were fabricated in 2013. These LED's were use in backlight of the LCD display, traffic lighting, solid state lighting and other's general lighting applications [3]. Use of this material at commercial level is limited, due to its high cost, maintenance and sophisticated/expensive growth process. ZnO is a low cost wide band gap material, which is easily available, non toxic and environmental friendly [4]. ZnO contains similar hexagonal wurtzite crystal structure as that of GaN materials, and has direct band gap of 3.34 eV. In ZnO the fundamental absorption spectra shows, comparatively higher excitonic binding energy (~ 60 meV) than GaN (~25 meV) at room temperature [5]. These properties of ZnO made it an attractive material for the optoelectronic devices and applications. For fabrication of optoelectronic devices from ZnO, quantum wells structures play an important role. In ZnO quantum well structures can be formed by tailoring the band gap with doping II group element like Cd and Mg [6].

Cd doped ZnO layers in multilayer structures acts as quantum well and undoped ZnO layers acts as barrier [7]. These barrier and quantum well layers can be used for fabrication LEDs and laser diode from ZnO. Mg doped ZnO films can be used as a electron blocking layer in these devices. In this work we have used Cd and Mg dopants successfully for reducing and widening the band gap of ZnO.

2. Experimental

For thin film synthesis, dense bulk targets of ZnO, $Zn_{0.93}Cd_{0.07}O$ and $Zn_{0.85}Mg_{0.15}O$ were prepared by standard solid state reaction route. Thin film from these bulk targets were grown on quartz substrate by Pulsed laser deposition (PLD) technique using KrF (λ=248 nm) excimer laser source. Prior to deposition the quartz substrates were cleaned in ultrasonic bath, first by acetone for 5 minutes, followed by cleaning in methanol for 5 minutes. The background pressure of deposition chamber was ~ 10^{-6} torr. For the deposition, laser pulse rate was kept at 10 Hz with energy density of laser beam at the target surface 2J/cm and the distance between substrate and target was adjusted to 5cm. About 150 nm thick films were grown on 650^0C substrate temperature at Oxygen partial pressure of $1x10^{-4}$ Torr. For X-ray diffraction Cu-$K_\propto$ radiations (λ=1.5414A^o) were used. The optical properties of the films were studied by photoluminescence and UV-Vis spectroscopy.

3. Results and discussion

The X-ray diffraction results of ZnO (a), $Zn_{0.93}Cd_{0.07}O$ (b) and $Zn_{0.85}Mg_{0.15}O$ (c) thin film samples grown on quartz substrate are shown in Fig. 1. The X-ray study indicates that the grown films are oriented along c-axis with wurtzite phase. Apart from (002) and (004) peaks, no impurities peaks are observed in these samples. X-ray diffraction results revealed that Cd and Mg atom replaces the Zn atom in wurtzite crystal lattice and there are not apparent changes in crystal lattice structure, of the doped films. We noticed a slight variation in position of reflection peak, corresponding to (002) plane of ZnO, towards lower and higher 2θ values for Cd and Mg doping respectively. The shift occurs due to the change in the lattice parameters of ZnO film with Cd and Mg doping (mismatch in ionic radi of Zn, Cd and Mg ions). The calculated lattice parameters from the XRD data are shown in Table 1and these are in agreement with reported values for ZnO, Cd:ZnO and Mg:ZnO.

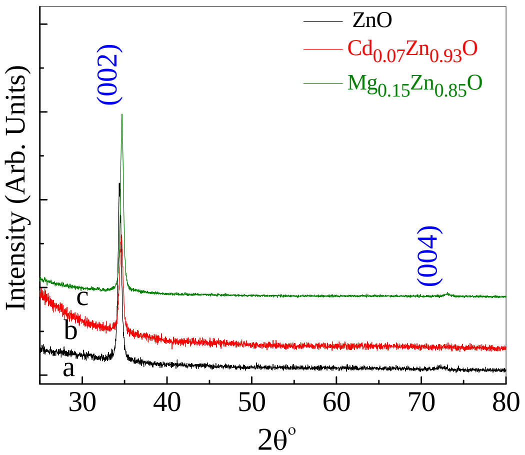

Figure 1. X-ray diffraction pattern of all the studied samples.

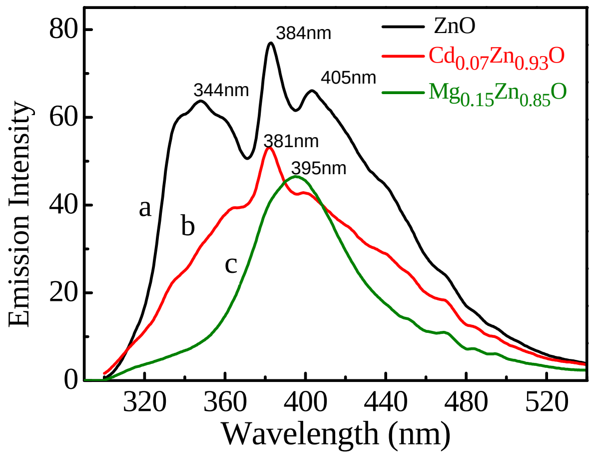

Figure 2. Photoluminescence spectra of doped and undoped ZnO thin film samples.

Room temperature photoluminescence (PL) results for undoped and doped samples are shown in Fig. 2. The strongest peak lines are obtained near band edge UV emission at 384 eV for ZnO with somewhat weaker lines at 344 eV and 405 eV. The main band edge peak is blue shifted towards lower wavelength of 381nm in case of Cd doped ZnO while in Mg doped ZnO; red shifted peak towards longer wavelength (395nm) is seen. For better explanation of red and blue shift in the doped samples requires, the band gap calculation. Therefore, these samples were characterized further by UV-Vis spectroscopy.

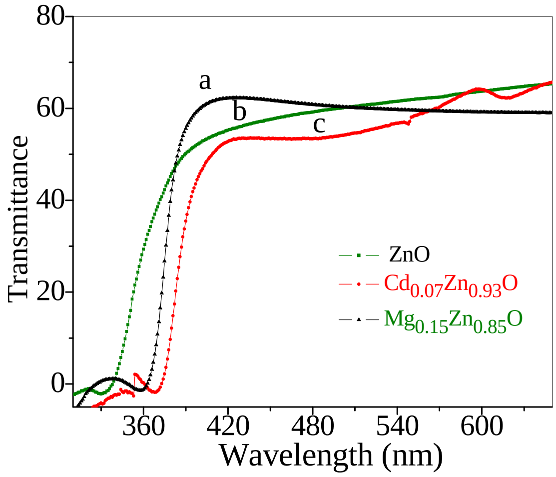

Figure 3. Transmission spectra of doped and undoped ZnO thin film samples.

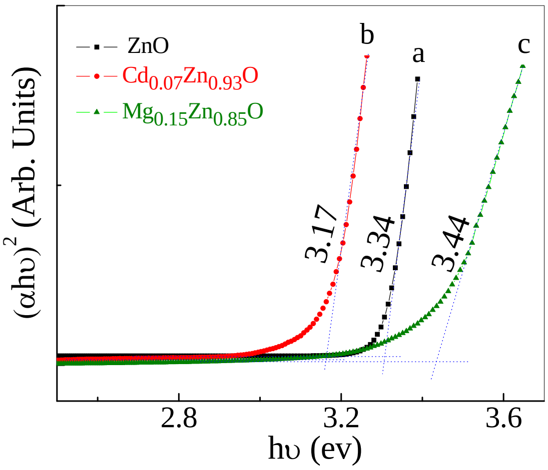

Figure 4. Taut plots calculated from the transmission spectra of studied samples.

Fig. 3 depicts UV-Vis spectra of undoped ZnO along with Cd and Mg doped thin films samples. Fig. 4 shows the taut plot for calculating of band gap of the samples. The band gap of pure ZnO is estimated to 3.34eV. For 7 wt% Cd doped ZnO, the band gap of film is decreases by 0.17eV. This narrow band gap material, can be used in fabricating quantum well devices. However for Mg doped film, the band gap is increase by 0.10eV. This widen band gap material can be used as barrier/ blocking layer in these quantum well structures. The calculated band gaps of $Zn_{093}Cd_{0.07}O$ and $Zn_{0.85}Mg_{0.15}O$ are 3.17eV and 3.44eV respectively. This observed shift in band gap could be responsible for the red and blue shift of band edge emission peaks of photoluminescence (PL) spectra as discussed above. The different important parameters deduced from the present study are summarized in table 1.

Table 1. The significant findings obtained from different thin film samples:

Sample Name	**ZnO**	**Cd:ZnO**	**Mg:ZnO**
Doping(x)	0%	7%	15%
XRD(2θ value for 002 plane)	34.62^0	34.56^0	34.68^0
Lattice Parameter(c)	2.710 nm	2.714 nm	2.706 nm
PL emission Peak	384 nm	381 nm	395 nm
Band Gap	3.34eV	3.17eV	3.44eV

4. Conclusion

Structural and optical properties of ZnO, $Zn_{0.93}Cd_{0.07}O$ and $Zn_{0.85}Mg_{0.15}O$ thin films grown by PLD were studied by XRD, PL and UV-Vis spectroscopy. X-ray diffraction study shows that Cd and Mg doped film are oriented along c-axis. No peak widening is observed in any of these samples. Photoluminescence study shows, blue and red shift of band edge emission peak for Cd and Mg doped ZnO sample, respectively. UV-Vis spectra shows that, by Cd doping the band gap of film is narrowed by 0.17eV and by Mg doping band gap is widen to 3.44eV. This red shift, blue shift of energy gap can be used for fabrication quantum wells and barriers in optoelectronic devices.

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