

Optical properties of post-annealed zinc oxide (ZnO) thin films synthesized by pulsed laser deposition (PLD)

Bhawana Joshi^{1*}, Santanu Ghosh², Pankaj Srivastava²

¹Department of Applied Physics, Gautam Buddha University, Greater Noida 201310, India

²Nanotech Laboratory, Department of Physics, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

*Corresponding author, Tel: (+91) 120-2344355; E-mail: bjoshi_physics@yahoo.com

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Abstract

In the present work, ZnO thin films deposited by pulsed laser deposition (PLD) technique have been characterized structurally and optically after post-deposition annealing. As-deposited thin films were annealed in the ambient atmosphere for different annealing temperatures of 200°C, 400°C, 600°C and 800°C. X-ray diffraction (XRD) technique was used for structure analysis and elucidated that both as-deposited and annealed films were of good structural quality and highly oriented towards c-axis. UV-Vis spectrophotometer was used to study the transmittance and optical band gap of as-deposited and annealed films. Photoluminescence (PL) technique was used to investigate the photoluminescent properties of all the films. It was found that ZnO thin films were highly transparent in nature and showed two emissions in PL spectra. One was attributed to near band edge (NBE) emission and the other was the broad deep-level (DL) emission. There was a significant change in the photoluminescent properties of the films and it was observed that the intensity of the DL emission increased significantly with the increase in the annealing temperature. The change in DL emission is attributed to the change in defect states inside the band gap of the annealed films. From the present work, it is inferred that the properties of the ZnO films can be tuned by post-deposition annealing for various applications such as optical and optoelectronic devices. Copyright © 2017 VBRI Press.

Keywords: ZnO thin films, pulsed laser deposition, optical properties, photoluminescence, deep level defects.

Introduction

Zinc oxide (ZnO) is a promising material with wide band gap (~ 3.37 eV) and large excitonic binding energy (~ 60 meV) at room temperature and other unique physical properties [1]. These properties make this material a promising candidate for the next generation optical and optoelectronic devices. Particularly these properties are required to produce efficient and lasting blue and ultraviolet light emitting diodes (LED) and laser diodes (LD) and have attracted much attention among different research groups [2-9]. For this purpose, luminescent properties of ZnO have gained a lot of interest and many efforts have been paid for improving the luminescence efficiency in the ZnO materials. Instead of many reports on luminescence in ZnO materials, the cause and mechanisms responsible for the observed luminescence properties is still a matter of controversy. Furthermore, the emission of photons from sub-band gap is particularly interesting because it can give the information about the near band edge (NBE) defects. These defect states strongly influence the quantum efficiency of the overall luminescence from the material.

In a recent study, NBE PL features are observed in epitaxial film of ZnO which is found to decrease with the temperature and are very sensitive to the thermal annealing conditions [3]. Xu *et al.* prepared ZnO films by sol-gel method on Ag/Si substrates and annealed the films at different temperatures. It is concluded that the variation in the emission of different visible lights is due to the change in the defect density in ZnO [4]. Shi *et al.* studied the annealing effects on the light emissions from ZnO thin films in various atmospheres for a temperature range and found that the intensity of both UV light emission and visible emission depends on the ambient atmosphere during annealing of the films [6]. In another study, ZnO thin films were deposited on silicon substrate for surface acoustic wave (SAW) device for UV sensors and investigated diverse luminescent characteristics by PL measurements. Different peaks are reported to be due to oxygen and zinc vacancies in ZnO [5]. Kang *et al.* also studied the variation in the properties of UV and green emissions of ZnO thin films after annealing the films in oxygen and vacuum environment at 300°C and 800°C. It is found that the variation in the optical properties highly depends on the ambient atmosphere and annealing

temperature [10]. Several physical and chemical techniques have been employed to synthesize high quality ZnO thin films [7-12] and it is found that the properties of the films are dependent on the technique of deposition. Electrically ZnO is an insulator in its stoichiometric form. However, experimentally it is observed that the ZnO thin films are n-type semiconducting in nature and this behavior is attributed to the presence of different kinds of defects in the thin films [10-12]. These intrinsic defects work as luminescence centers also and are mainly responsible for the visible light emission from the film [10-14]. The nature and intensity of these defects change with thermal treatment of the material which changes the luminescence properties and hence the properties of the fabricated device. In this paper, we are reporting the variation in the structural and optical properties of ZnO thin films deposited by PLD and annealed at different temperatures in the air atmosphere. The objectives of the study are to (i) study the change in the structural and optical properties of ZnO thin films after post deposition annealing; (ii) to explore the reasons behind the variation in visible light emission from ZnO thin films after post deposition annealing in air atmosphere. The novelty of the present work is that the contributions of different defects in the luminescence properties of air-annealed ZnO thin films are presented, which in turn is important for optical and optoelectronic applications.

Experimental

ZnO target and thin films preparation

The polycrystalline laser target of ZnO for ZnO thin film deposition was prepared by using powder chemical route before the deposition of thin films. In this process, 8 g of polycrystalline ZnO powder (purity 5N5) is ball milled, cold pressed, and sintered at 1100°C for 12 hours in air.

The ZnO thin films were then deposited by PLD using the synthesized target in Germany [15]. During the deposition, KrF excimer laser (LAMBDA PHYSIK LPX 305) operating at 248 nm wavelength was used. The deposition is done on c-plane sapphire (0001) substrates of (10×10×0.5) mm³ dimension. During the deposition, the base pressure of the deposition chamber was about 10⁻⁷ mbar, the target to substrate distance was 52 mm and deposition rate was adjusted around 1 Å per laser pulse. Oxygen pressure during deposition of the films was around 5 × 10⁻² mbar. The substrate temperature was kept around 750°C by controlling the heater power to obtain good quality ZnO thin films. The PLD regime was optimized by introducing a ZnO nucleation layer to be deposited first on the bare substrate and a final epitaxial strain reducing top layer. For ZnO thin films this two-step PLD process was applied using a thin nucleation layer of about 30 nm thickness deposited at reduced (5 × 10⁻⁴ mbar) oxygen partial pressure on the bare sapphire surface to improve epitaxial film quality of the following thicker ZnO film of about 800 nm thickness. This two-step PLD process was performed for getting the good structural quality of the deposited ZnO thin films.

All parameters of the PLD process are controlled by sophisticated PC software [15].

Post deposition annealing of the films

The deposited ZnO films were annealed in ambient atmosphere (Air) in a high temperature tube furnace (METREX) at the temperatures of 200°C, 400°C, 600°C and 800°C for 6 hours. The as-deposited film is named as A and annealed films as B, C, D and E corresponding to annealing temperature 200°C, 400°C, 600°C and 800°C respectively.

Characterizations of as-deposited and annealed thin films

The crystalline structure of the as-deposited and annealed films was studied by using a PHILIPS 'XPerT' PRO model diffractometer using CuK α line with wavelength $\lambda = 1.5406$ Å. The operating voltage was kept at 45 kV and the tube current was 40 mA during the study. The 2 θ range is kept as 20°-80° and the scanning speed was 0.05 2 θ /s. The optical transmission and band gap of the films was measured by using a HITACHI 3300 double beam spectrophotometer in the wavelength range of 200-800nm. The photoluminescence studies were performed by using MECHELLE 900 spectrograph under 325 nm excitation He-Cd laser (KIMMON). The power of the laser was 32 mW. The PL system had a cooled charged coupled device (CCD) array based detection system. The laser light was made to fall on the thin film samples and the photoluminescent light was collected using a collector assembly attached to the spectrograph through optical fibre for detection and analysis of the data. The electrical resistivity measurements are done in Vander Pauw geometry both at room temperature and variable temperature by using the KEITHLEY current source and voltmeter.

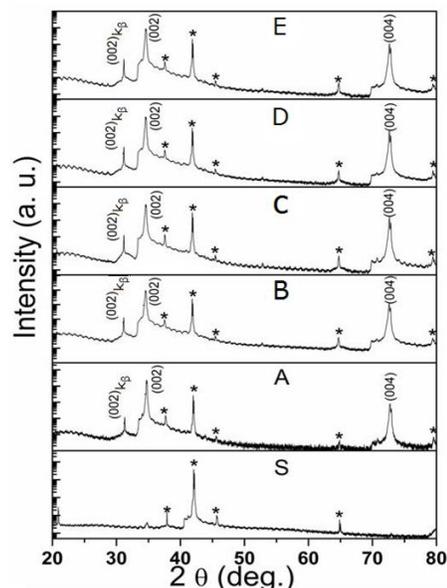


Fig. 1. X-ray diffraction patterns of the as-deposited and annealed films (A-E). 'S' stands the XRD pattern of sapphire substrate and the corresponding peaks are marked with (*) in all the films.

Results and discussion

X-ray diffraction studies

The diffraction patterns (logarithmic scale) of bare sapphire substrate (named as S), as-deposited and annealed films are shown in Fig. 1. The diffraction peaks are indexed using the standard JCPDS data for thin films and substrate. It is observed that the annealed films (Films A-E) are highly oriented along the c-axis (002) of wurtzite ZnO.

Along with the (002) K_{α} peak at 2θ value of 34.7° , a peak corresponding to K_{β} at a position of 31.44° is also found in the patterns. This peak is considered to be due to the incomplete filtering of the Cu K_{β} x-ray beam during the experiment. It is evident from the figure that the peaks indexed by an asterisk (*) corresponds to the crystalline peaks of the substrate (as shown in S also). The relative intensity of crystalline peaks are found to be same in all the thin films. However, it is observed that the peak position of (002) orientation in the films is shifted from $\sim 34.7^{\circ}$ to $\sim 34.5^{\circ}$ after annealing treatment. This variation indicates the shift of the peak orientation towards the bulk value of ZnO (which is $\sim 34.4^{\circ}$) after annealing. In literature, this shift in the peak position is understood to be due to the strain between the substrate and the deposited films.

It should be noted that the selection of the substrate is important for the growth of thin film. Moreover, the matching of crystal structure and lattice parameters between the film and substrate is the deciding factor and strongly affects the growth of film. It is reported in the literature that the lattice mismatch between ZnO (lattice parameters, $a = 3.250 \text{ \AA}$ and $c = 5.213 \text{ \AA}$) and c-plane sapphire (lattice parameters, $a = 4.754 \text{ \AA}$, $c = 12.990 \text{ \AA}$), varies from $\sim 18\%$ to $\sim 32\%$ [16]. Although the mismatch is significant but this range is lesser as compared to the mismatch between silicon and ZnO which is approximately 40%. It is to elucidate here that this mismatch is significant to create structural defects (such as vacancies and interstitials) in the films during the growth. The generated defects later affect the physical properties of the films. The calculated values of lattice parameter of the films along c-axis indicate an increase due to annealing which is attributed to a built in tensile strain in the films due to this mismatch [17]. Moreover, this strain in the films can be relaxed by providing sufficient thermal energy in the forms of annealing temperature. Therefore, there is a small shift in the diffraction peaks towards the bulk values with increase in the annealing temperature, as discussed earlier. From the above discussion, it can be concluded that the structural quality of all the films is nearly same after annealing. The electrical resistivity measurements are done in Vander Pauw geometry and the films are found to be resistive in nature. The temperature dependent resistivity measurements also confirm the high resistivity values and the variation of resistivity with temperature shows that the as-deposited and annealed films are semiconducting in nature. It is speculated that the charge carriers are

localized in the defects site and are not contributing to the electrical conductivity even at room temperature. In a different study by our groups, the similar result on electrical properties is observed in the ZnO thin films deposited by PLD [18].

Optical studies

Fig. 2 shows that transmittance of the films in the Visible and Ultraviolet (UV) region of electromagnetic spectrum. All the films are found to be transparent (Average transmittance $> 80\%$) for the visible photons with a minor change in the average transmittance value with annealing temperatures. The oscillations present in the transmittance spectra is due to the higher thickness ($\sim 800 \text{ nm}$) of the films.

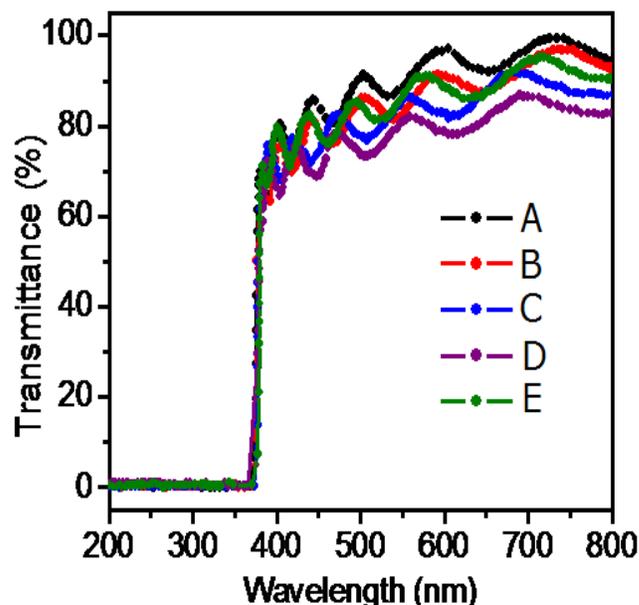


Fig. 2. Optical Transmission spectra of as-deposited and annealed films (shown by different colors and named as A, B, C, D and E respectively). It is found that all the films were highly transparent in the visible region with sharp decrement in the band edge.

The thickness of the films can also be calculated using the oscillations present in the transmittance spectra and given by the following equation:

$$d = \frac{1}{2n} \left(\frac{\lambda_2 \lambda_1}{\lambda_2 - \lambda_1} \right) \quad (1)$$

where, d is the thickness, n is the refractive index of the film, λ_2 , λ_1 are the wavelengths corresponding to the consecutive maxima and minima in the transmittance curve.

In the UV region of electromagnetic spectrum, the photons are absorbed by the ZnO thin films being a wide band gap material and due to which the transmittance of the films decreases to almost zero value. The absorption edges of all the films are found to be very sharp, which indicates good optical quality of these films. The optical

band gaps (E_g) of the films are calculated by Tauc's plot (not shown here). The calculated values of band gap, as shown in **Table. 1**, shows that there is a very small change due to annealing. This result indicates that the band edges of all the films are almost same within the detecting ability of the instrument. The similar optical band gap nature is also supported by the NBE emission of PL spectra of all the films and is discussed in the subsequent sections.

In **Fig. 3**, the PL spectra of as-deposited and annealed films are shown. The broad and intense emission spreading from 450 nm to 900 nm along with a less intense band at around 385 nm can be seen in the figure. The 385 nm peak is attributed to NBE emission, excitonic luminescence or UV emission in the literature and its nature depends on the band structure of ZnO [19-22]. The broad band in the visible region is recognized as the deep level (DL) emission and is generally believed to be associated with intrinsic defects in nominally undoped ZnO [9, 23-25].

It is clear from **Fig. 3** that the NBE emission from the films shows a high thermal stability as the intensity and peak position remain intact in both as-deposited and annealed films. This important observation is understood to be in accordance with the optical band gap variation in the films [Table. 1].

Theoretically, the intensity of light emission from any material is determined by the radiative and nonradiative transition and the efficiency of luminescence of the light emission can be determined by the following formula [5]:

$$\eta = \frac{p_R}{p_R + p_{NR}} \quad (2)$$

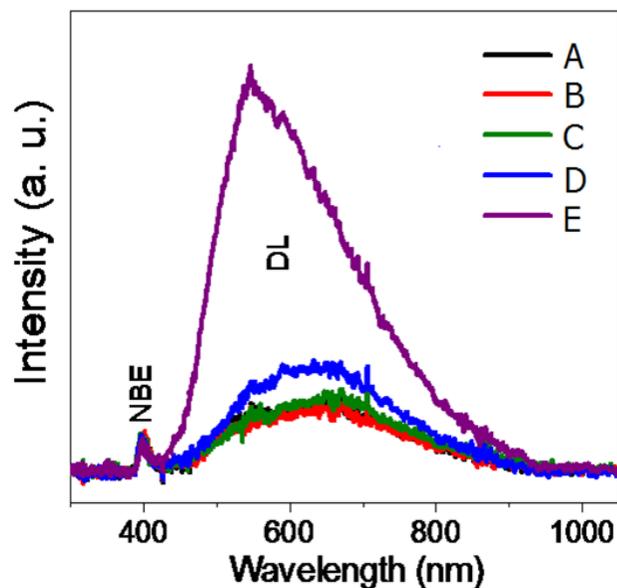


Fig. 3. Photoluminescence spectra of as-deposited and annealed films (shown by different colors and named as A, B, C, D and E respectively). The position and intensity of Near Band edge (NBE) emission is found to be almost same while the deep level (DL) emission changes with the annealing temperature.

Here η is defined as overall luminescence efficiency, p_R and p_{NR} are respectively radiative and non-radiative transition probabilities. As mentioned earlier, the as-deposited ZnO films are nonstoichiometric in nature and have lattice and surface defects. Moreover, these defects create radiative as well as non-radiative luminescence centres in the band structure of the ZnO [9, 11]. Some defects work as radiative centers while others work as non-radiative centres. Hence, there is a competitive phenomenon between any two kinds of defects which decides the overall efficiency of luminescence from the films. It can be elucidated that the intensity of visible light emission from the films can be increased or decreased by increasing or decreasing the concentration of radiative defects centers. In the case of NBE emission, the intensity and peak position remains same in all the films and is correlated with the constant optical band gap of the films. However, from **Fig. 3**, it can be seen that the intensity of visible light emission changes significantly with the change in annealing temperature from 600°C to 800°C. The cumulative variation of overall relative area of this DL peak with annealing temperature is shown in **Fig. 4**.

As mentioned earlier, the intensity variation in this light emission can be attributed to the reduction or restructuring of point defects or radiative centers like oxygen vacancies (V_o), zinc interstitials (Zn_i) and oxygen interstitials (O_i) [14]. This is understood on the basis of energy band diagram of a ZnO material with different defects states which is theoretically calculated and experimentally verified by different luminescence measurements in this material [16, 17, 19-21].

The correlation between observed PL variation with annealing temperature and the defects states is presented in the subsequent sections. It is important to mention here that the lattice mismatch between ZnO thin film and sapphire substrate is considered to be one of the reasons for the generation of defects in the ZnO matrix [16].

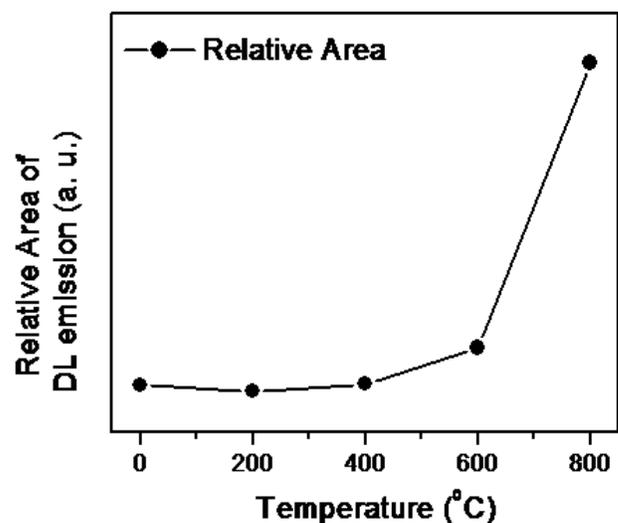


Fig. 4. Relative area of the overall DL emission with annealing temperature. It is almost same for A-C while increases in D and further enhanced significantly in E.

In films A-C, relative area is found to be almost same. It increases in film D, and further enhanced significantly in film E. As mentioned earlier, this DL peak corresponds to visible light emission and is generally accepted to be due to the defects present in ZnO matrix [23-26]. Therefore, it can be stated that the defect density increases with increase in annealing temperature. To understand the reason behind the asymmetric nature of the peak, this broad peak is deconvoluted into two Gaussian peaks having centre positions at 545 nm and 665 nm respectively. It is found that the origin of these two bands are opposite in nature, a competitive evolution of the two emissions is likely to occur and is discussed in the subsequent text.

The broad and asymmetric DL emission peak is deconvoluted into two Gaussian peaks as shown in Fig. 5.

In these two peaks, one peak is centered at around 545 nm and the other is centered at around 665 nm. The first peak (Centered at 545 nm) corresponds to green emission in the films [19, 23-26] and the other peak (Centered at 665 nm) corresponds to the orange-red emission from the films [19]. Although the Fig. 5 is plotted in arbitrary units, the relative areas under the peaks are given in Table 1 for films A-E. It can be deduced from table that the relative intensities of both the peaks (Area under the corresponding peaks) changes with change in the annealing temperature. Both the emissions intensities first decrease at low annealing temperature (200°C and 400°C) and start increasing at 600°C while both increase significantly at the highest annealing temperature of 800°C.

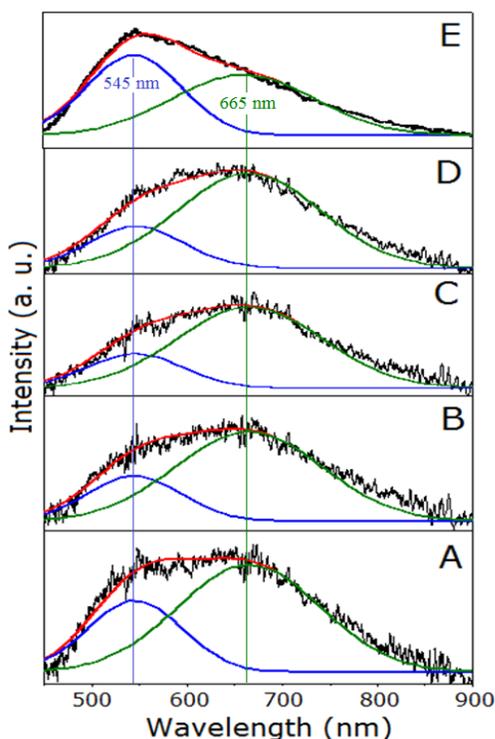


Fig. 5. De-convolution of the DL emission into two different emissions [545 nm (Green emission), 665 nm (Orange-red emission) respectively]. The relative intensity of both the components changes with change in the annealing temperature.

It is reported in the literature that the origin of green emission arises due to the presence of defects like V_o and Zn_i in the films [9, 23-26] while the origin of orange-red emission is due to both V_o and O_i [19].

Table 1. Optical band gap and area under the curve of green (Centered 545 nm) and orange-red (Centered 665 nm) peaks in as-deposited (A) and annealed (B-E) ZnO thin films

Thin Films	Band gap (eV)	Intensity of Green Emission (~ 545 nm)	Intensity of Orange-red emission (~665 nm)
A	3.29	7900	17859
B	3.28	5845	17928
C	3.28	5644	20466
D	3.27	8690	29675
E	3.27	62532	70929

Fig. 6 shows the energy band diagram of a non-stoichiometric ZnO material with NBE and different defect states in forbidden energy gap due to the presence of different surface and bulk defects.

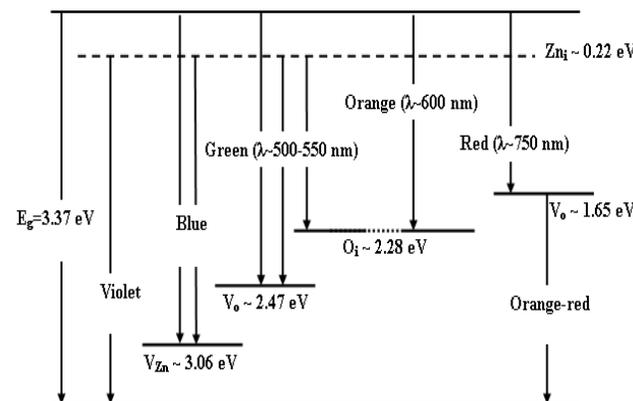


Fig. 6. Schematic band diagram of the Deep Level (DL) emission in ZnO materials

The variation of the visible emission is understood on the basis of these defects as follows. At lower annealing temperatures (upto 400 °C here) O_i are filled up and Zn_i react with environmental O, thereby reducing green luminescence as evidenced in PL. At 600°C, the oxygen in the films starts desorbing out of the film due to higher thermal energy and the concentration of V_o increases. Due to this, the intensity of the peak corresponding to the green emission enhances. With further increase in annealing temperature, the concentration of V_o enhances and hence the green luminescence peak. In the case of orange-red emission peaked at 665 nm, the intensity of the peak increases with increase in the annealing temperature because of the adsorption of oxygen atoms and thereby enhancing O_i to increase the concentration of oxygen interstitials in the film. It is worth to mention here that the process of adsorption and desorption of oxygen atoms from the air environment is a competitive phenomenon. At the highest annealing temperature this process plays a great role in deciding the overall peak

intensity of the green as well as orange red emission from the annealed film. Oxygen leaving the lattice site at this temperature either make an oxygen interstitial or leave the surface of the film because of which both oxygen interstitials and oxygen vacancies increase in the film at 800°C simultaneously which in turn increases the intensity of both the deconvoluted peaks. Moreover the intensity of the overall peak also increases. Further studies to confirm the changes in the defects levels in the annealed films are required for the better understanding of annealing effects of these films under different annealing environments.

Conclusion

The variation in the structural and optical properties of the air-annealed ZnO thin films deposited by PLD is presented in this study. The structural quality of both as-deposited and annealed films is found to be good and almost similar before and after annealing. Films are found to be highly transparent in the visible region and band gap of films are almost same. The variation in the luminescence properties of the films is studied. The PL spectra are found to have two peaks; one corresponding to NBE and other corresponding to the visible light emission from all the films. The cause of visible light emission from the films is understood on the basis of defects in the films. It is found and concluded that the defects increases in the films with increase in the annealing temperature and are maximum in the film annealed at a temperature of 800°C. It can be concluded that the physical properties of the films can be modified by post-deposition annealing for particular applications.

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