Effect of background gas and substrate temperature on ZnO:Zn PLD thin films

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Abstract. The dependence of the structural and optical properties of ZnO:Zn thin films deposited by Pulsed Laser Deposition at different preparation conditions have been investigated. All the films showed highly preferential c-axis orientation, and their crystallinities were improved with increasing the substrate temperature. The stress in the thin films has varied from -12.7 to -7.30 GPa depending on the background gas. The minimum value was obtained in the case of the oxygen background gas. The optical bandgap varied from 3.12 to 3.20 eV with the deposition background gas for Argon, Vacuum and Oxygen. The bandgap was also affected by the substrate temperature for the thin films deposited in oxygen gas. All the thin films exhibited ultraviolet emission. The thin films deposited in the oxygen atmosphere showed strong photoluminescence emission around the green and orange region (500 – 627 nm). These results suggest that the ZnO:Zn thin films may be used in the design, simulation and fabrication of optoelectronics devices such as white light emitting diodes.

1. Introduction

Recently, zinc oxide (ZnO) thin films have been studied extensively because of their excellent properties and various applications. The inherent defects in the ZnO matrix such as oxygen vacancies (V_o), oxygen interstitials (O_i), oxygen antisites (Zn_o), Zn vacancies (V_{Zn}), Zn interstitial (Zn_i) and Zn antisites (O_{zn}) play important roles in determining its optical and structural properties [1]. Various studies have predicted that oxygen vacancies, interstitial oxygen, zinc vacancies, and zinc interstitials are responsible for the luminescence in ZnO [2].The green emission from ZnO has been known at least since the turn of the century. The addition of dopants influences the ZnO defects as well as enhancing its optical properties [3].

A variety of techniques have been utilized to fabricate ZnO thin films, such as thermal deposition, sputtering, chemical vapour deposition, spray pyrolysis and pulsed laser deposition (PLD) [4,5]. In this study commercially available ZnO:Zn was used to fabricate thin films on Si(111) substrates by using the PLD technique. Photoluminescence (PL) using a He-Cd laser at 325 nm and UV-Vis spectroscopy were employed to elucidate the origin of the luminescence emission as well as determine the bandgap. It was found that orange and green emissions of ZnO were due to defects. The effect of background gas and the substrate temperature on the luminescence of ZnO:Zn PLD thin films were explored.

2. Experimental details

A commercial ZnO:Zn phosphor powder, obtained from Phosphor Technology, was pressed without binders using an in-house built sample holder to create an ablation target. The ablation target was

annealed at 250 ^{0}C for 24 h in air to remove all adventitious water containing species that might be present. The target was then placed inside the chamber of the PLD system on a rotating target holder that can also move linearly (up and down). Si (111) was used as a substrate, and was cleaned in an ultrasonic bath using acetone, then ethanol and finally deionized water, and then dried with N_2 gas. The 266 nm fourth harmonic of a Nd:YAG laser (40 mJ/pulse and 10 Hz pulse repetition rate) was used for the preparation of the ZnO:Zn thin films with PLD under different experimental conditions. The substrate temperature was fixed at 300 ^{o}C during the deposition of the thin films in vacuum and with argon background gas atmosphere, but varied for the thin films deposited in an oxygen atmosphere (50, 200, 300 and 400 ^{o}C). The laser deposition time was fixed at 25 min. The chamber was pumped down to a base pressure of 5×10^{-5} mbar and then backfilled with O_2 and Ar gases to a partial pressure of 5×10^{-2} mbar.

The structure of the thin films samples were characterized by X-ray diffraction (XRD) using a Bruker D8 Advance Diffractometer (40 kV, 40 mA) with Cu K_α x-rays (λ = 0.154 nm). Atomic force microscopy (AFM) using a Shimadzu SPM-9600 instrument was used to study the surface and roughness morphology. UV-Vis diffuse reflection spectra were measured using a Perkin Elmer Lambda 950 spectrophotometer. PL spectra were collected with a He-Cd laser PL system with a 325 nm excitation wavelength.

3. Results and discussion

3.1. XRD and structure analysis

Figure 1 shows the XRD patterns of the ZnO:Zn thin films deposited on the silicon substrates for (a) different background gasses and (b) different substrate temperatures, respectively. ZnO has a tetrahedral coordinated (wurtzite) structure in which the (0 0 2) plane has the lowest surface energy [6]. Hence, all the samples exhibited preferential (0 0 2) plane orientation, which is in line with the characteristics of the hexagonal wurtzite structure of ZnO where the c-axis lies perpendicular to the substrate surface. Crystallite size, stress and lattice parameters (a, c) of the thin films were calculated using the full width at half maxima of the (0 0 2) peak by using the Scherrer equation, biaxial strain model and the Miller indices formulas [7] and are tabulated in tables 1 and 2. The crystallite size was altered by increasing the substrate temperature or changing the chamber atmosphere (vacuum, oxygen and argon). The stress on the thin film varied as a function of lattice parameters, which were affected by the background gas. The crystallite size also increased when increasing the substrate temperature (table 2), this is probably due to the agglomeration of the grains or particles on the film. It can also be seen from figure 1 that the intensity of the (0 0 2) diffraction peak was affected by the background gas and the substrate temperature. The highest intensity was obtained from the thin film deposited in oxygen gas at a substrate temperature of 300 ^{o}C.

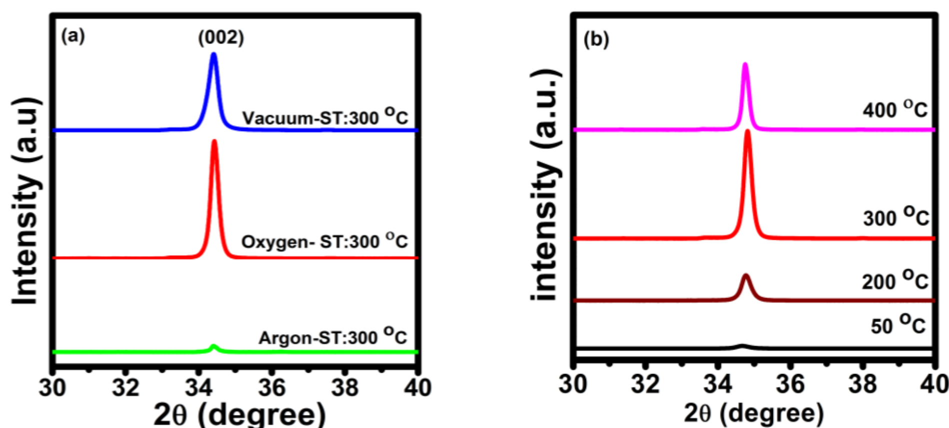

Figure 1. XRD patterns of ZnO:Zn thin films deposited (a) in different growth atmosphere and (b) for different substrate temperatures.

Atmosphere	Lattice constant (Å)		Stress (GPa)	Crystallite size (nm)	Surface roughness (nm)	Bandgap (eV)
	c	a				
Vacuum	5.123	2.958	-7.305	40	2.048	3.19
Argon	5.077	2.931	-11.481	46	7.085	3.12
Oxygen	5.063	2.923	-12.767	38	2.016	3.20

Table 1. Effect of growth atmosphere on ZnO:Zn thin films produced with a substrate temperature of 300 °C.

Table 2. Effect of different substrate temperature on ZnO:Zn thin films produced with oxygen background gas.

Substrate temperature (°C)	Lattice constant (Å)		Stress (GPa)	Crystallite size (nm)	Surface roughness (nm)	Bandgap (eV)
	c	a				
50	5.077	2.931	-11.481	24	3.023	3.16
200	5.063	2.923	-12.767	31	3.461	3.16
300	5.063	2.923	-12.767	38	2.016	3.20
400	5.063	2.923	-12.767	48	7.525	3.14

3.2. Surface morphology and roughness

The surface morphology of the ZnO:Zn films are shown as two and three dimensional AFM micrographs (3.00 × 3.00) μm^2 in figure 2. All the thin films showed distinguishable particles with a uniform distribution. The clear particle images were obtained from the thin films deposited in an argon atmosphere and oxygen (400 °C substrate temperature). The roughness of the thin films varied from 2.016 to 2.048 to 7.085 nm with the variation in background gas from oxygen, vacuum and argon, respectively (table 1). In reality, the roughness for the samples in vacuum or oxygen are almost the same, while that for argon is rougher. The roughness of the thin films obtained in an oxygen background gas also varied with increasing the substrate temperature as shown in table 2.

3.3. UV-Vis reflectance and photoluminescence properties

Figure 3 shows the UV-Vis reflectance curves of the ZnO:Zn thin films as deposited in different atmospheres, and at different substrate temperatures for an oxygen background gas. A sharp band edge observed between 353 and 376 nm (figure 3(a,b)) was assigned to the bandgaps absorption of ZnO due to electron transitions from the valence band to the conduction band ($O_{2p} – Zn_{3d}$) [7].
The optical bandgap was estimated by the extrapolation of the linear portion of the $[F(R_o)h\nu]^2$ versus hν plots and was calculated by the Kubelka – Munk equation using the Tauc method:

$$[F(R_o)h\nu]^2 = C_2(h\nu - E_g). \quad (1)$$

C_2 is a constant, E_g is the optical bandgap, h is Plank's constant and $F(R_o)$ is the absorption coefficient.

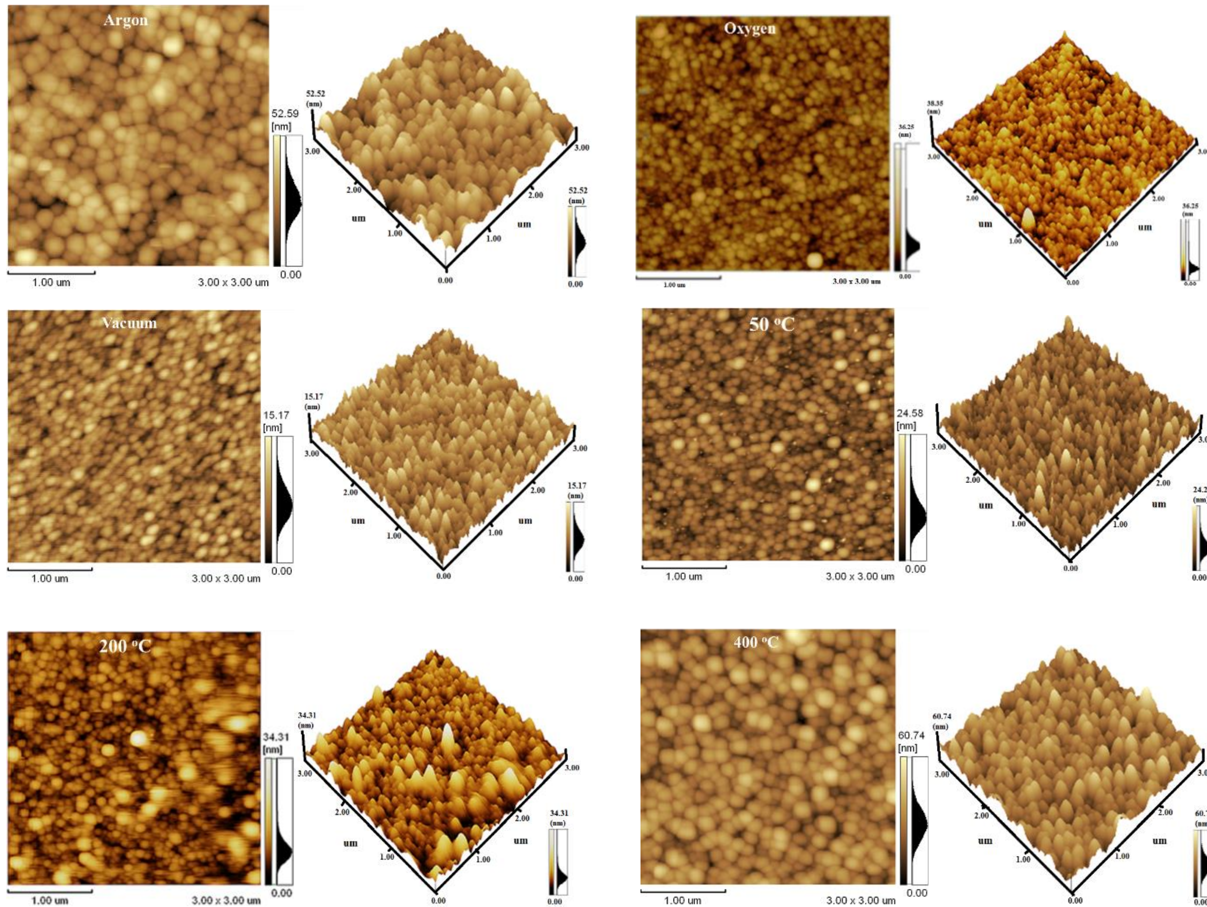

Figure 2. AFM images of ZnO:Zn thin films obtained in different growth atmospheres (300 ^{o}C substrate temperature) and for different substrate temperatures for an oxygen background gas.

The calculated optical band-gaps for the different background gas and substrate temperature for the thin films obtained at different background gas and temperature are tabulated in tables 1 and 2, respectively. The bandgaps of the thin films were strongly affected by the type of background gas and substrate temperature. In the case of the thin film obtained in an oxygen background gas shown in figure 3(c, d), the band marked with (*) is corresponding to the orange and green band in PL spectra figure 4(c).

The PL spectra are shown in figure 4. All the samples exhibited ultraviolet emission around 378 nm characteristic of band-to-band emission from ZnO, and their intensities were altered by the chamber background gas (fig. 4(a)). The weak emission band in some spectra near about 760 nm (e.g. for argon in fig. 4(a)) occurs when this ultraviolet emission is intense and is its second order. The thin films deposited in an oxygen atmosphere, which is deconvoluted in fig 4(c) showed green and orange bands. The green band was attributed to recombination of carriers bound at V_o and O_i defects, while the orange band was attributed to the recombination between carriers bound at Zn_i and O_i defects [8]. The oxygen vacancies were formed due to the excess of zinc atoms in the original ZnO:Zn PLD target and the oxygen interstitial defects were formed from oxygen in the oxygen atmosphere, respectively. Worth noting is that the green and orange bands correspond to the second absorption peak in the UV-

Vis curve (figure. 2(c)), which is labeled with an asterisk (*). The green and orange emission that appeared in the oxygen atmosphere due to the defects was completely diminished in the thin film deposited in the vacuum and argon gas atmospheres (figure 4(a)). This confirmed that there was a low defect concentration in the samples prepared using these two atmospheres.

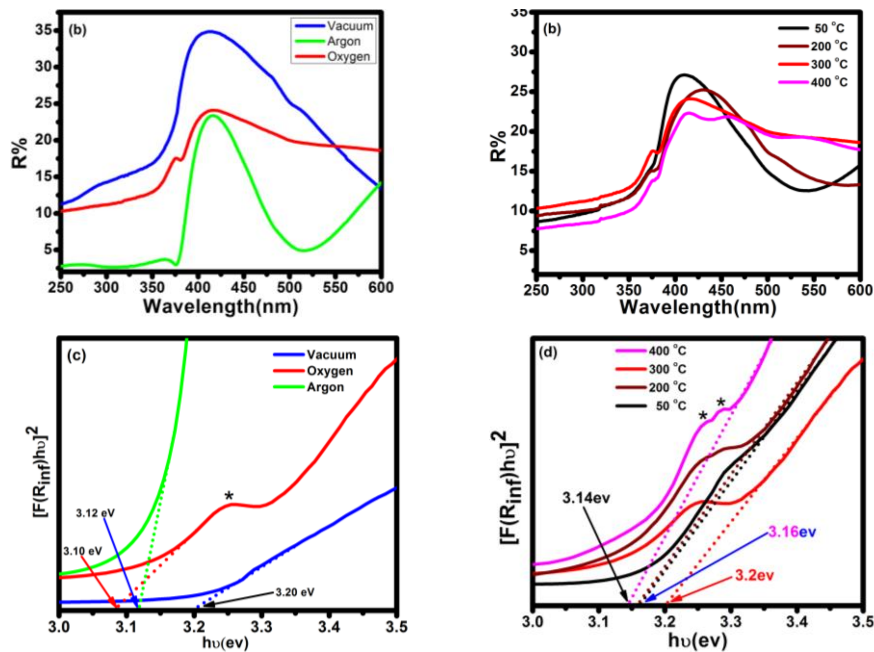

Figure 3. Reflectance curves (a,b) and Tauc plots (c,d) used to calculate the band-gaps for ZnO:Zn thin films deposited in different growth atmospheres (a,c) and different substrate temperatures (b,d).

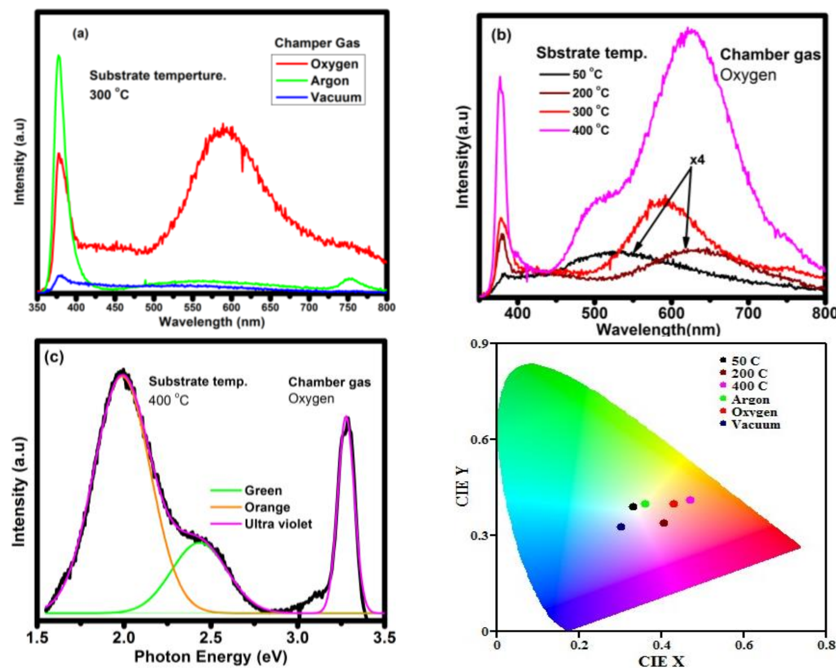

Figure 4. PL spectra of ZnO:Zn thin films deposited for (a) different growth atmospheres (300 °C substrate temperature), (b) for different substrate

temperatures for an oxygen background gas, (c) Deconvoluted peak of oxygen atmosphere at 400 ^oC substrate temperature and (d) CIE diagram of all samples. Data was averaged over three scans and spikes caused by the photomultiplier tube detector, detected in only one of the three scans, were removed.

4. Conclusion

C-axis oriented ZnO:Zn thin films were deposited on Si (111) substrates in different growth atmospheres by the PLD technique. The PL results showed a broad emission around 500 and 600 nm, which confirmed the presence of oxygen related defects in the thin films deposited in the oxygen atmosphere. The crystallite size and PL emission intensity depended on the growth atmosphere and substrate temperature. The results suggested that ZnO:Zn thin films may be a suitable candidate material for white light emitting diode applications.

Acknowledgment

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