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The changes in structural and optical properties of (ZnO:AlN) thin films fabricated at different RF powers of ZnO target

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Abstract

AlN doped ZnO thin films were prepared on glass and Si (100) substrates by RF sputtering. The ratio of nitrogen (N_2) to Argon (Ar) used to prepare the films was 80:20. The films were deposited at different RF powers of 150 W, 175 W, 200 W, 225 W and 250 W for ZnO target and 200 W for AlN target. XRD results revealed the existence of (002) ZnO phase for RF power of ZnO target above 175 W. However, at the RF power of 150 W, the film exhibited amorphous properties. The prepared films showed transmission values above 70% in the visible range. The average calculated value of energy band gap and the refractive index were 3.43 eV and 2.29 respectively. The green and UV emission peaks were observed from PL spectra. Raman Peaks at 275.49 cm^{-1} and 580.17 cm^{-1} corresponding to ZnO:N and ZnO:AlN were also observed.

Keywords: B. X-ray methods; C. Optical properties; D. ZnO

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1. Introduction

ZnO is well-known for various applications, which include gas sensors, transparent conductors for thin film transistors and solar cells. ZnO also attractive for the fabrication of light emitting diodes (LEDs), laser diodes (LDs) and light detectors. These applications are essentially due to unique properties of the material with a wide and direct band gap (3.37 eV) and a high exciton binding energy (60 meV). An abundance of defects is another important characteristic that has a direct impact on the electrical and optical properties of the material [1–3].

Several techniques have been used to fabricate ZnO thin films such as thermal oxidation, direct current (DC) and radio frequency (RF) sputtering, chemical vapor deposition, molecular beam epitaxy and pulsed laser deposition. The RF sputtering technique has drawn considerable attention since the resulting films properties can be controlled by changing the sputtering conditions. The structural and optical properties of ZnO films are affected by the preparation conditions such as substrate temperature, types of substrate, deposition pressure, annealing temperature, RF power and doping material. Among these factors, the effect of AlN doping on ZnO film characteristic was less reported [4–8].

In this work AlN doped ZnO thin films were deposited by RF sputtering on Si (100) and glass substrates and their structural and optical properties were investigated.

2. Experimental

AlN doped ZnO films were prepared by RF sputtering using high purity ZnO target (99.99%) and high purity AlN target (99.99%). The substrates used were n-type Si with (100) orientation and microscope slide glass. The substrates were initially cleaned with acetone and isopropanol in an ultrasonic bath for 15 min and then rinsed with deionize water before being fixed to a rotating substrate holder inside the Edwards A500 RF sputtering unit at a distance of 10 cm above the ZnO target. Mechanical rotary pump and turbo pump were used to evacuate the sputtering chamber of the unit to its ultimate pressure of about 5×10^{-5} mbar. Argon (Ar) of high purity (99.99%) and N_2 of high purity (99.99%) were used to sputter the target. The ratio of nitrogen (N_2) to Argon (Ar) used to prepare the films was 80:20. The pressure inside the chamber was maintained at 2×10^{-2} mbar during the sputtering process.

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The films were deposited at different RF powers of 150 W, 175 W, 200 W, 225 W and 250 W for the ZnO target and 200 W for the AlN target for 50 min for all the samples. Table 1 shows the deposition conditions of AlN doped ZnO cosputtered films.

The optical properties of AlN doped ZnO thin films were investigated by UV–visible spectrophotometry, photoluminescence (PL) and Raman spectroscopy. The filmetrics F20 was used to determine the thickness (*t*) of the prepared films. An X-ray diffractometer (source Cu Kα with $\lambda = 1.5406$ Å) was used to characterize the structural parameters while atomic force microscope (AFM) was used to study the surface morphologies of the fabricated films. Energy dispersive X-ray (EDX) was used to identify the element present in the films.

3. Results and discussion

Fig. 1 shows the increased thickness (*t*) of the prepared films with the increasing RF powers on ZnO target, indicating that the number of atoms sputtered from the target was proportional to the applied RF power.

Table 1
Deposition conditions of AlN doped ZnO films.

Working pressure	2×10^{-2} mbar
Cosputtering gases	$(N_2{:}Ar) = (80{:}20)$
RF power supplied on targets	ZnO target≡175 W, 150 W, 200 W, 225 W and 250 W; AlN target≡200 W samples (AZO4, AZO9, AZO10, AZO11 and AZO12 respectively)
Deposition temperature	Room temperature
Deposition time	50 min
Target–substrate distance	10 cm

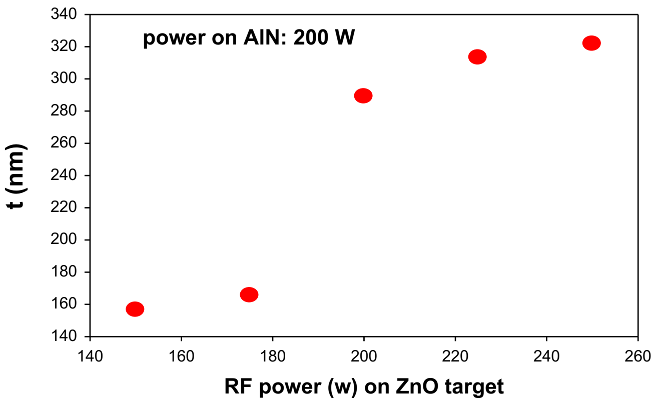

Fig. 1. Thickness of the AlN doped ZnO films on Si substrates as a function of the RF power of ZnO target.

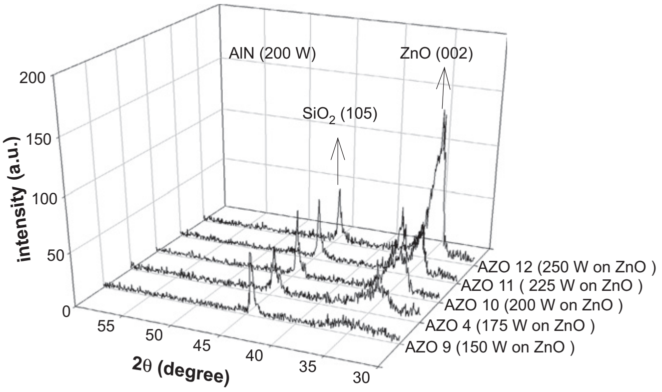

Fig. 2. XRD spectra of AlN doped ZnO films on Si substrates prepared at various RF powers of ZnO target.

Table 2
X-ray diffraction data summary of AlN doped ZnO films.

Sample	2θ (deg.)	FWHM (deg.)	d (Å)	c (Å)	D (nm)
AZO 4	34.1750	1.1510	2.6216	5.2431	7.55
AZO 9	–	–	–	–	–
AZO 10	33.9391	0.5904	2.6414	5.2829	14.7
AZO 11	33.7965	0.3936	2.6523	5.3044	22.04
AZO 12	33.8664	0.5904	2.6469	5.2938	14.70

Fig. 2 shows the XRD spectra of the prepared AlN doped ZnO films in which the (002) ZnO phase was observed for samples with RF power (ZnO target) at and above 175 W. However, for the RF power of ZnO target at 150 W, the film was amorphous. The full width at half maximum (FWHM) of (002) ZnO peak can be used to estimate the crystallite size (*D*) in the grown films using Scherrer's formula:

$$D = (0.94\lambda)/(\mathrm{FWHM}\cos\theta) \tag{1}$$

Table 2 summarizes the values of d, c, 2θ, FWHM and D for (002) phase of AlN doped ZnO films.

Table 3 shows EDX analysis of AlN doped ZnO films in which the traces (0.6–2.7%) of nitrogen was observed. The surface morphology of the films was measured by AFM (Fig. 3) with the resulting root mean square (rms) of 4.26 nm, 5.78 nm, 10.93 nm, 9.34 nm and 8.36 nm for the respective films.

Fig. 4 shows the transmittance spectra of the AlN doped ZnO films, which revealed a good optical transmittance of above 70% in the visible range. The absorption coefficient (α) and the photon energy (E) is given by:

$$\alpha E = A\left(E - E_g\right)^{1/2} \tag{2}$$

where E_g is the energy band gap of the semiconductor and A is a constant. Therefore a plot of $(\alpha E)^2$ versus photon energy E yields a straight line that cuts the photon energy axis at the energy band gap value. Fig. 5 shows the plot of $(\alpha E)^2$ versus E for the prepared samples with values of band gap of 3.49 eV, 3.48 eV, 3.39 eV, 3.32 eV and 3.47 eV for the films prepared at RF powers (ZnO target) of 150 W, 175 W, 200 W, 225 W and 250 W respectively. Refractive indexes of the films were calculated using the following equation [9]:

$$\left[\left(n^2-1\right)/\left(n^2+2\right)\right] = 1 - \left(E_g/20\right)^{0.5} \tag{3}$$

where n the refractive index of AlN doped ZnO thin films and E_g the energy band gap of the prepared films. The calculated refractive indexes were 2.276, 2.279, 2.299, 2.315 and 2.280 for the films prepared at RF powers (ZnO target) of 150 W, 175 W, 200 W, 225 W and 250 W, respectively.

Table 3
EDX analysis of AlN doped ZnO films.

Sample	NK (at%)	O K (at%)	Al K (at%)	Zn L (at%)
AZO4	1.24	53.68	6.71	38.36
AZO9	2.71	53.99	7.29	36.01
AZO10	1.41	51.96	2.89	43.74
AZO11	0.61	51.41	3.64	44.33
AZO12	–	50.81	2.45	46.74

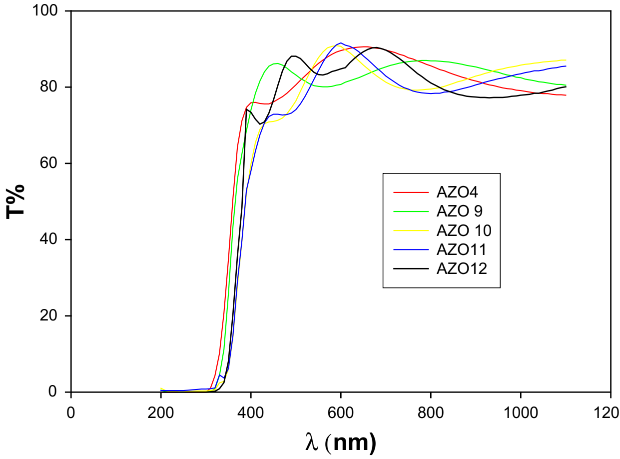

Fig. 4. Transmittance spectra of the prepared AlN–ZnO thin films on glass substrates at different RF powers of ZnO target.

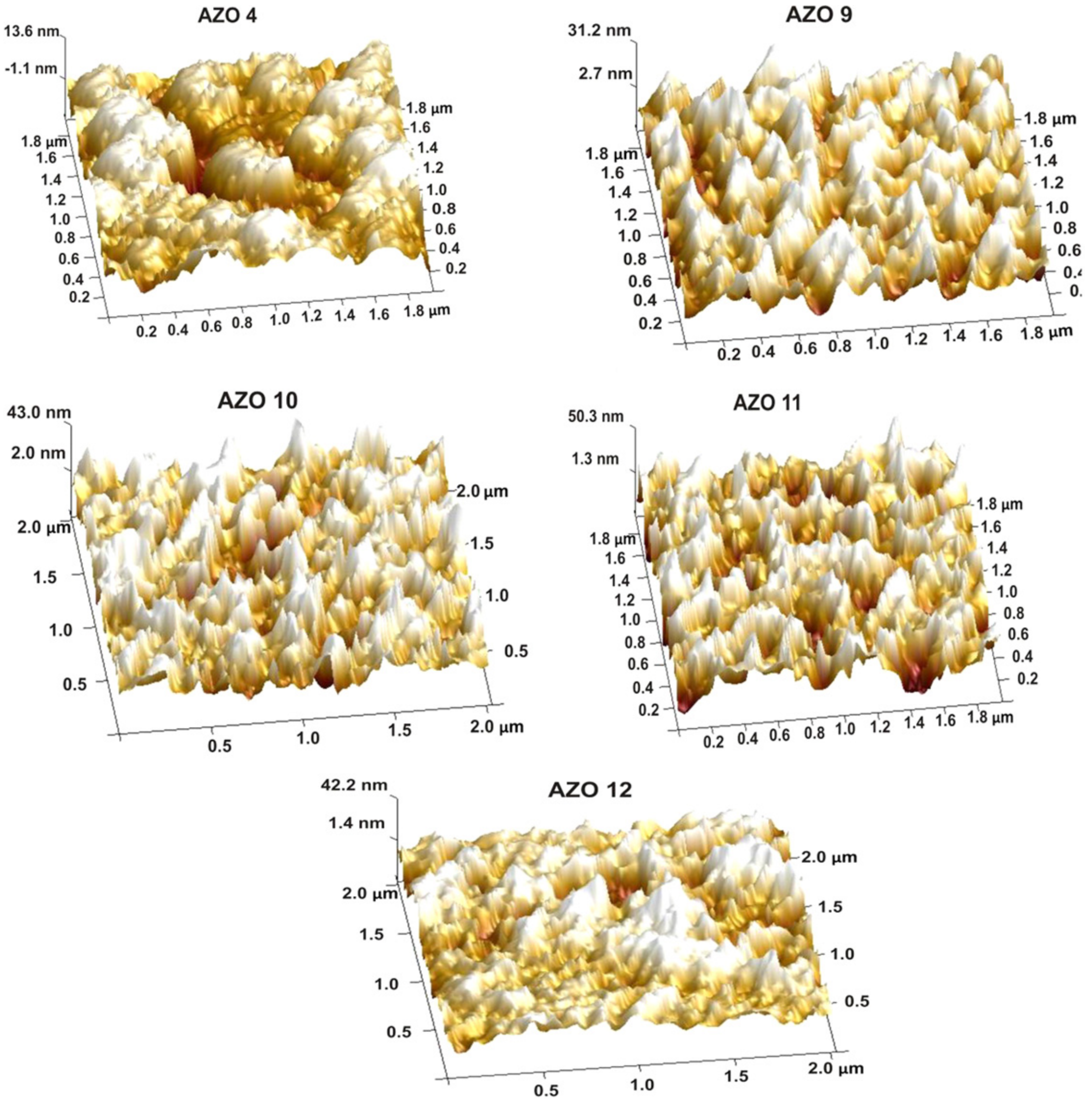

Fig. 3. AFM image of AlN doped ZnO films on Si substrates prepared at various RF powers of ZnO target.

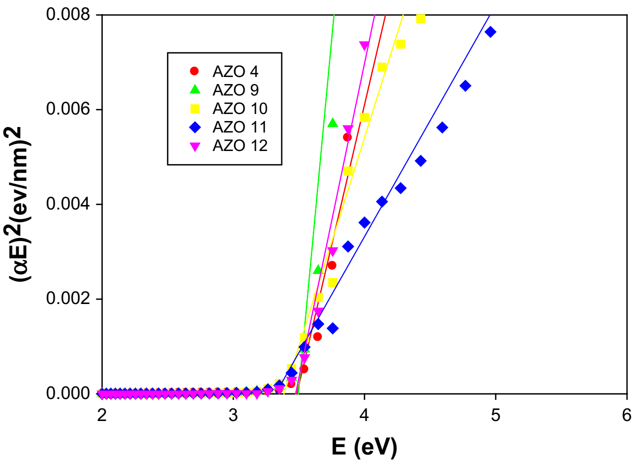

Fig. 5. $(\alpha E)^2$ versus E of AlN–ZnO thin films on glass at different RF powers of ZnO target.

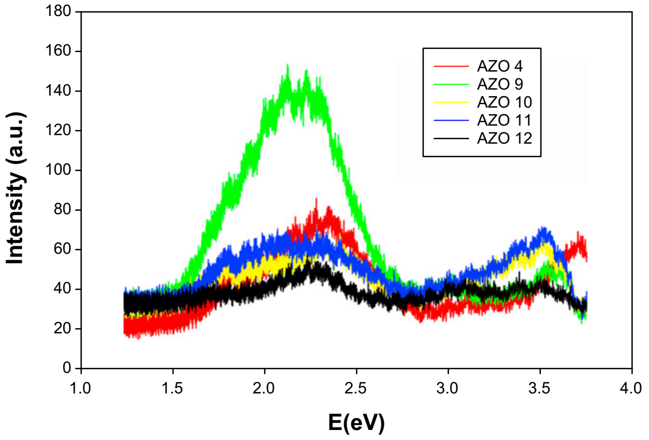

Fig. 6. PL spectra of AlN doped ZnO films on Si substrates prepared at various RF powers of ZnO target.

The PL Spectra of AlN doped ZnO thin films are shown in Fig. 6. All the films showed a visible emissions peaks in the range 2.18–2.30 eV, which was assigned as green emissions attributed to dopant induced defect or intrinsic defect in ZnO [10]. The observed UV emissions peaks at 3.53 eV was attributed to the recombination of free excitons [11].

Fig. 7 shows Raman spectra of AlN doped ZnO thin films. The observed peak at 275.49 cm^{-1} for all samples was attributed to nitrogen in the films [12,13] while, the peak at 580.17 cm^{-1} was attributed to A_1 (LO) mode of the AlN doped ZnO films [14,15]

4. Conclusion

The structural and optical properties of AlN doped ZnO deposited at different RF powers of ZnO target were investigated. XRD results revealed the formation of (002) ZnO phase for the films sputtered at RF power of 175 W and above. Good transmittance of above 70% in the visible range had been observed for the prepared films with the average calculated value of energy band gap of 3.43 eV. The green and UV emission peaks of PL spectra were attributed to the defects and free excitons respectively. The observed peaks at 275.49 cm^{-1} and 580.17 cm^{-1} of the Raman spectra were believed to be associated with the incorporation of N and AlN in the ZnO films, respectively.

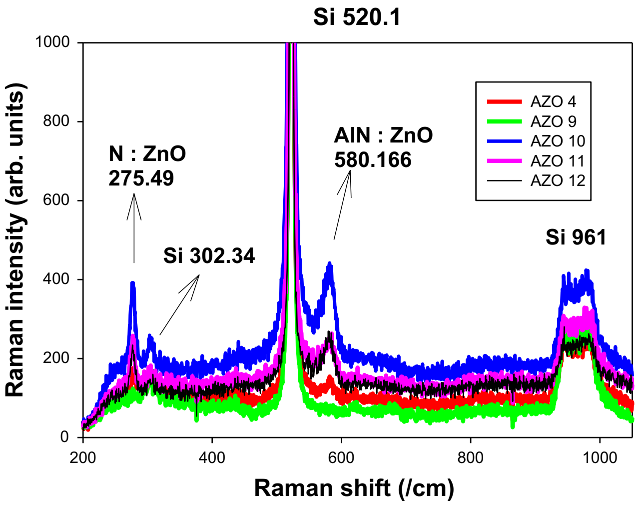

Fig. 7. Raman spectra of AlN doped ZnO films on Si substrates prepared at various RF powers of ZnO target.

Acknowledgments

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