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Effect of Nitrogen on optical properties of ZnO film deposited by sol gel method

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Undoped and nitrogen-doped ZnO (NZO) films have been prepared by the sol gel spin coating method. The nominal volume ratio of the N/Zn was 0%, 1%, 3%, 5%. and 10%. The influence of doping on the optical, structural and morphological properties of all films was investigated. The values obtained from both XRD and SEM showed that the average crystallite size is about between 50 and 60nm. The optical transmittances of all films are studied using spectrophotometer. All the films are highly transparent with average transmission (>85%) in the visible region. Optical band values were calculated as approximately 3.27eV and it was observed no significant effect on the band gap depending on the N doping. Also, the optical constants of these films were determined.

Keywords: N doped ZnO, optical constants, sol gel

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1. Introduction

Zinc oxide (ZnO) is a wide band gap (E_g~3.37 eV) semiconductor with large free excitation binding energy (~60 meV). Because of wide band gap, ZnO is transparent material in the visible region. ZnO is a very versatile semiconductor material for optoelectronic applications. ZnO thin films can be obtained by different methods; molecular beam epitaxy [1], chemical vapor deposition [2], pulse laser deposition [3], spray pyrolysis [4], sol gel processing [5]. In this work, undoped and nitrogen-doped ZnO (NZO) films were deposited by sol gel method. The sol gel process has some advantage when compared with other methods such as; low cost and easy of fabrication, low annealing temperature and the possibility of large area deposition. The doped semiconductor materials have studied intensively because of their unique properties. Doping materials can change electrical, optical and structural properties of main materials. Among these materials, the doped ZnO films have investigated intensively to improve its properties [6].

In previous studies on nitrogen doped ZnO films, A. B. Lavand and Y. S. Malghe [7] prepared pure and N doped ZnO nanospheres using microemulsion method. X-ray diffraction (XRD) results indicated formation of nanosized N-doped ZnO with wurtzite phase. They reported that spherical morphology of pure and N doped ZnO samples. Also, UV–visible spectra results showed that N doping enhanced the light absorption capacity of ZnO in the visible region. R. Kumari et al. [8] studied influence nitrogen doping on structural and optical properties of ZnO nanoparticles. The result of TEM and EDAX indicated that the partical size of undoped ZnO was 11 nm and 0.5–10% N doped ZnO (N:ZnO) were 18-22 nm. T. K. Pathak et al. [9] deposited N doped ZnO films on ITO coated glass substrate by sol gel method. Ammonium nitrate was used as a dopant source of N with varying the doping concentration 0, 0.5, 1.0, 2.0 and 3.0 at% in their work. X-ray diffraction pattern showed the preferred (002) peak of ZnO. The ZnO films with increasing N dopant showed high transmittance (~ 88%) and band gap of films increased from 3.28 to 3.70 eV.

In the present study, we have deposited undoped and N doped ZnO films by sol gel spin coating method. And then the optical, structural and morphological properties of ZnO films have been studied with respect to N doping.

2. Experimental details

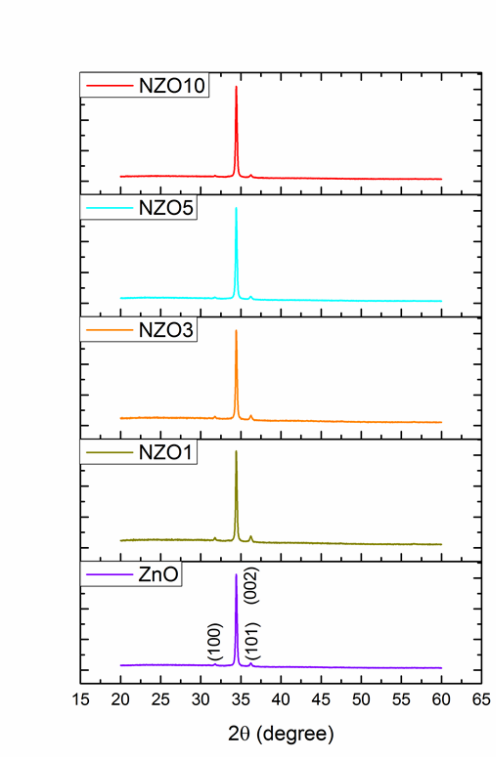
The sol-gel spin coating method was used for preparing undoped and N doped ZnO films. To obtain the sol, zinc acetate dihydrate ($ZnCH_3COO)_2.2H_2O$) (ZnAc), 2-methoxyethanol and monoethanolamine (MEA) were used as starting, solvent and stabilizer materials, respectively. Ammonium acetate ($CH_3CO_2NH_4$) (NAc) was used as dopant material. The molar ratio of MEA to ZnAc (or NAc) was kept at 1.0 with 0.35M ZnAc and NAc concentration. Firstly, ZnAc and NAc were prepared at 60 ℃ for 2 h to obtain a clear and homogeneous solution. Then, the prepared solutions were mixed at different volume ratio from 1% to 10%. The

prepared solutions at different ratio were kept 24 hours in the dark before deposition. Finally, the solutions were dropped on glass substrates and rotated with 3000 rpm for 30 s to obtain films. This process was repeated 10 times for each sample. The dried temperature was maintained at 300℃ for 10 min into a furnace in air to evaporate the solvent and remove organic residuals. The deposition temperature was set at 550℃ into a furnace for 1 h in air ambient.

3. Results and discussion:

Figure 1 shows X-ray diffraction (XRD) patterns of all films. XRD measurements are carried out using the BRUKER D8 Advance Diffractometer with CuK_α radiation (λ= 1.54059 Å). All patterns illustrate wurtzite phase (JCPDS:36-1451) structures and (002) preferential orientation. The average crystallite size estimated from Scherrer's Formula [10] and the lattice constants calculated using analytical method [11] are given in table 1. Although crystallite size is not affected by N doping, lattice constants show a decreasing trend with increasing doping. Also, to determine the preferential growth orientation (*TC*(*hkl*)), the following relation was used [11]:

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{N^{-1}\Sigma_n I(hkl)/I_0(hkl)} \qquad (1)$$



1. Figure XRD patterns of the undoped and N doped ZnO films

where *I*(*hkl*) is the measured relative intensity of a plane (*hkl*) and I_0(*hkl*) is the standard intensity of the plane (*hkl*) taken from the JCPDS data. The obtained values for *TC*(*hkl*) have confirmed that the preferential growth orientation is (002). Some data of XRD and texture coefficient values are also presented in table.

Table 1. Structural parameters and lattice constants of the undoped and N doped ZnO films.

Film	(hkl)	2θ	FWHM	Grain size (nm)	TC	a (Å)	c (Å)
ZnO	100	31.749	0.151	58	0.1193	3.25176	5.21036
	002	34.397	0.150		2.8102		
	101	36.219	0.232		0.0705		
NZO1	100	31.736	0.197	58	0.1731	3.25313	5.20786
	002	34.414	0.150		2.7020		
	101	36.210	0.231		0.1248		
NZO3	100	31.728	0.157	58	0.1780	3.25392	5.20818
	002	34.411	0.151		2.7133		
	101	36.207	0.233		0.1086		
NZO5	100	31.754	0.082	56	0.1212	3.25124	5.20960
	002	34.402	0.154		2.8036		
	101	36.199	0.305		0.0752		
NZO10	100	31.742	0.183	52	0.1068	3.20764	5.20764
	002	34.415	0.169		2.8248		
	101	36.205	0.231		0.0684		

For investigation of the surface morphology ZEISS Ultraplus field emission scanning electron microscopy (FESEM) was used. As illustrated in figure 2, all the films have homogeneous surface and round-grained structure. Especially crystallites about 50 nm like estimated from XRD results can be seen with together N doping and the decrease in crystallite size at high doping is also observed in SEM image.

Double beam SHIMADZU UV 2450 spectrometer was used to investigate optical properties of films. Figure 1 shows the transmittance spectra of all films. Observed average transmittance values in visible region are given Table 2. As seen from figure 3, all films show high transparent properties (>85%). Figure 4 shows reflectance spectra of all films. The average reflectance values of the films in visible region are about 7%.

To determine band gap (E_g) of films absorption spectra can be used. For direct transition, the equation can be expressed by following relation [12]

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \qquad (2)$$

where *A* is a constant, $h\nu$ is the photon energy and E_g is the optical band gap. Figure 5 indicates plots of $(\alpha h\nu)^2$vs. $h\nu$. The E_g values of the films were obtained from these plots and given in Table 2. As can be seen from Table 2, the optical band gap of films was not altered excessively with increasing N dopant.

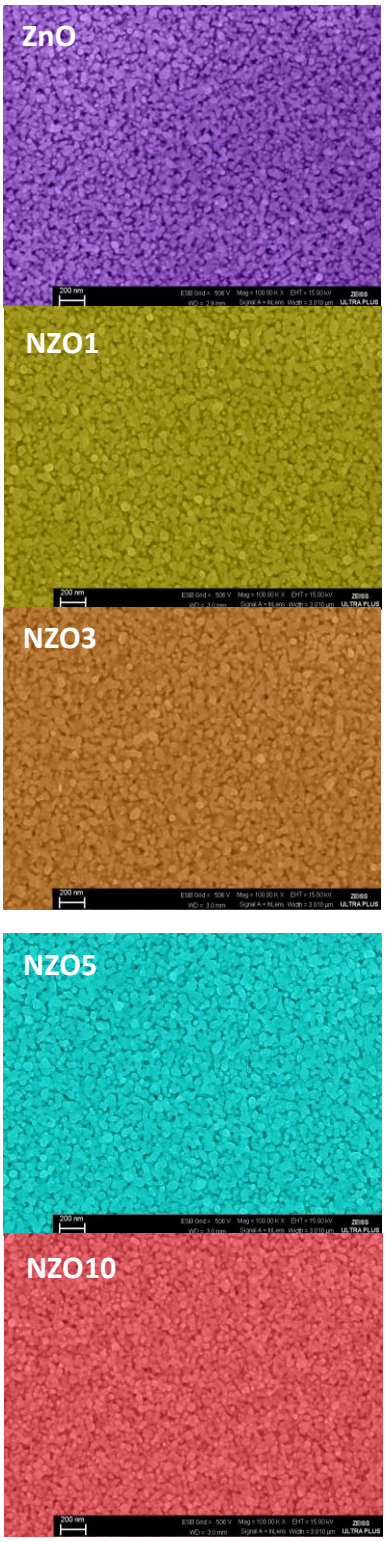


Figure 2. shows the FESEM images of undoped and N doped ZnO films.

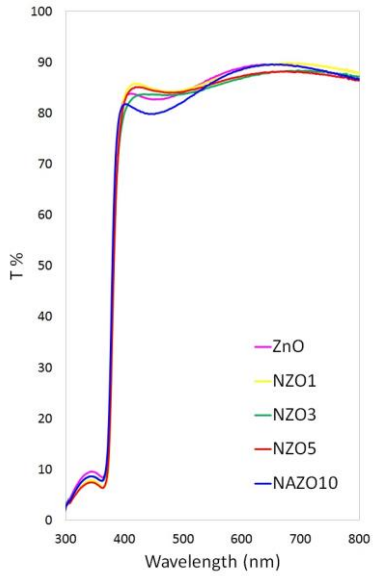


Figure 3. The transmittance of the undoped and N doped ZnO films

Table 2. E_g, transmittance and reflectance values of the undoped and N doped ZnO films

	E_g (eV)	T%	R%
ZnO	3.27	87	6.9
NZO1	3.27	87	6.8
NZO3	3.27	86	6.3
NZO5	3.27	86	7.8
NZO10	3.28	86	6.7

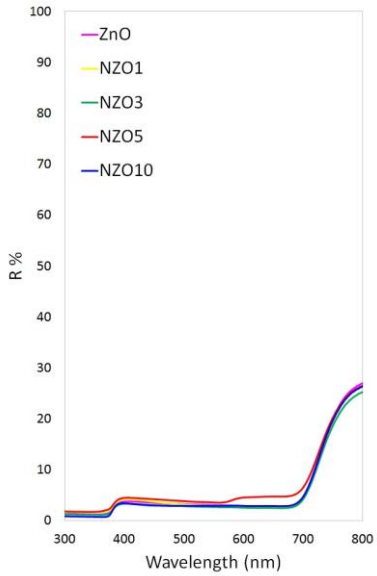


Figure 4. The reflectance spectra of the undoped and N doped ZnO films

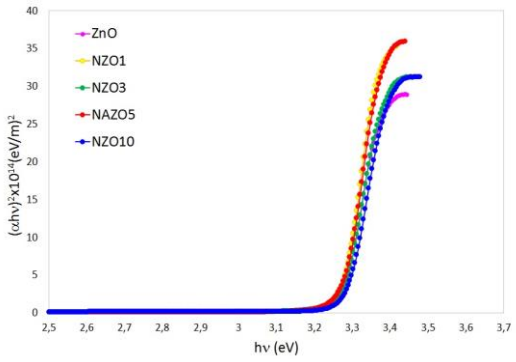


Figure 5. The plots of $(\alpha h\nu)^2$ vs. $h\nu$ of undoped and N doped ZnO films

The study of refractive index (n) for materials is provided useful information to design of electro-optic devices and to enhancement their optical parameters for electronic world. The complex optical refractive index (n') of the films is significant parameter to study optical properties of materials. The imaginary (k) and real parts (n) of n' are referred extinction coefficient and refractive index. This is defined through the equation [13]

$$n' = n(\lambda) + ik(\lambda) \qquad (3)$$

The refractive index of the films were defined from the following relation [14],

$$n = \left[\frac{1+R}{1-R}\right] + \sqrt{\frac{4R}{(1-R)^2} - k^2} \qquad (4)$$

Where k is equal to $\alpha\lambda/4\pi$. The n_{ave} and k_{ave} values in the visible range are given in Table 2.
The complex dielectric constant is described as,

$$\varepsilon(\lambda) = \varepsilon_1(\lambda) + i\varepsilon_2(\lambda) \qquad (5)$$

and real and imaginary parts of the dielectric constant are related to the n and k values. The ε_1 and ε_2 values were calculated using the formulas [15],

$$\varepsilon_1(\lambda) = n^2(\lambda) - k^2(\lambda) \qquad (6)$$

$$\varepsilon_2(\lambda) = 2n(\lambda)k(\lambda) \qquad (7)$$

The ε_1 and ε_2 values in the visible range are given in Table 3.

Table 3. Optical parameters of the undoped and N doped ZnO films

	n_{ave} (400 nm-800 nm)	$k_{ave}x10^{-2}$ (400 nm-800 nm)	ε_1 (400 nm-800 nm)	$\varepsilon_2 x10^{-2}$ (400 nm-800 nm)
ZnO	1.70	1.31	3.17	4.62
NZO1	1.69	1.25	3.12	4.33
NZO3	1.65	1.39	2.97	4.71
NZO5	1.77	1.38	3.38	5.03
NZO10	1.68	1.39	3.10	4.79

Conclusions

Undoped and N doped ZnO films have been successfully grown by sol gel spin coating method. N incorporation into the ZnO lattice does not cause a significant effect on crystal structure and surface morphology. The band gap values all of the films were calculated to be ~3.27 eV using absorbance spectra. The obtained films exhibited highly transparent behavior in the visible region. Refractive index, optical dielectric constants and extinction coefficient of doped and undoped films were calculated by transmittance and reflectance data. The results of this study shows that optical parameters were not affected greatly with increasing N doping.

References:

[1]W. Xiao Dan, Z. Hua, W. Hui Qiong, R. Fei, C. Xiao Hang, Z. Hua Han, Z. Ying Hui, K. JunYong, CHINESE PHYSICS B, 24, 97106 (2015).
[2] M.F. Melendreza, F. Solis-Pomar, C.D. Gutierrez-Lazos, P. Flores, A.F. Jaramillo, A. Fundora, E. Perez-Tijerina, Ceramics International 42, 1160–1168 (2016).
[3]C. Cachoncinlle, C. Hebert, J. Perriere, M. Nistor, A. Petit, E. Millon, Applied Surface Science 336, 103–107, (2015).
[4]S. Ilican, Y. Caglar, M. Caglar, F. Yakuphanoglu, Physica E 35, 131–138, (2006).
[5] S. Aksoy, Y. Caglar, S. Ilican, M. Caglar, Journal of Alloys and Compounds 512, 171–178, (2012).
[6]S. Ilican, Journal of Alloys and Compounds 553, 225–232 (2013).
[7]A. B. Lavand, Y.S. Malghe, Journal of Asian Ceramic Societies 3, 305–310 (2015).
[8]R. Kumari, A. Sahai, N. Goswami, Progress in Natural Science: Materials International 25, 300–309 (2015).
[9]T. K. Pathak, V. Kumar, L.P. Purohit, Physica E 74, 551–555 (2015).

[10]B.D. Cullity, S.R. Stock, Elements of X-ray Diffraction, (third ed.) Prentice Hall (2001
[11]C.S. Barret, T.B. Massalski, Structure of Metals, Pergamon Press, Oxford, 1980.
[12]J.I. Pankove, Optical Processes in Semiconductors, Prentice-Hall Inc.,
Englewood Cliffs, NJ, 1971.
[13]T.S. Moss, G.J. Burrell, B. Ellis, Semiconductor Opto-electronics, John Willey &
Sons, New York, 1973.

[14]F. Abeles (Ed.), Optical Properties of Solids, North-Holland Publishing
Company, London, UK, 1972.
[15]A.K. Wolaton, T.S. Moss, Proc. R Soc. 81 (1963) 5091.