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Influence of zinc ion concentration on structure, morphology, and optical properties of spray deposited ZnO thin films

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ABSTRACT

Zinc oxide (ZnO) thin films were deposited for five different molarity (M) of Zinc acetate hydrated (0.075, 0.1, 0.125, 0.15, and 0.175 M) using simple spray technique to study the effect of zinc ion concentration on structure, morphology, and optical properties. The XRD patterns of deposited ZnO thin films show hexagonal crystal structure with wurtzite symmetry. The effect of molarity on morphology was studied using scanning electron microscopy (SEM). The elemental analysis was studied by using energy dispersive X-ray analysis (EDX). The optical absorption was recorded by using systronics double beam spectrophotometer (2201). Crystallite size estimated from XRD data was in nanometre (nm) range; however, films deposited for 0.15 M zinc acetate show maximum crystallite size (66 nm) as compared to other samples. All the films show low absorption in wide range (340-999 nm) of electromagnetic spectrum. However, ZnO film deposited for 0.15 zinc acetate hydrated shows maximum blue shifting of absorption edge and higher band gap (3.8 eV) as compared to other samples.

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1. INTRODUCTION

Zinc oxide (ZnO) is a hexagonal crystal system, exhibit stable wurtzite crystal structure in which the oxygen ions are surrounded by four zinc ions forming tetrahedron. There exists covalent bonding with substantial ionic character between anion and cation and hence ZnO was classed into wide band gap semiconducting material [1]. The direct optical band gap of ZnO was in the range 3.2 to 3.37 elecron volt (eV), exhibit higher transmittance in the visible region of electromagnetic spectrum and large exciton binding energy of 60 meV due to these reasons, ZnO materials have numerous applications in solar cells and in optoelectronic devices as an optical wave guide [2], [3]. ZnO thin films in pure and doped forms have been used as photocatalytic activators, chemical and biological sensors [4], [5], besides these ZnO nanoparticles have been used as biomedical materials for synthesis of antiseptic and antibacterial creams, lotions [6].

Variety of methods has been employed for synthesis of ZnO thin films such as radio-frequency magnetron sputtering [7], chemical vapour deposition [8], and sol–gel method [9], [10] pulsed laser deposition [11]. Chemical spray pyrolysis (CSP) is an innovative technique suitable for large area thin-films deposition and very economic [12].

Significant work has been reported on zinc oxide nano particles and zinc oxide thin films from long period however, quality of micro structure, and crystallite size has been depending on the preparation

techniques, chemical and physical conditions of techniques. In this view, an attempt has been made to improve the structure and optical properties of ZnO by proper moulding of structure and morphology

There are several reports on synthesis of ZnO thin films using chemical spray pyrolysis technique [12]-[14]; however only a single report was available which is related to influence of zinc ion concentration on structural and optical properties of ZnO thin films [15]. Therefore, in present paper ZnO thin films were deposited to study the effect of Zinc ion concentration on structure, morphology and optical parameters by using simple spray technique.

2. RESEARCH METHOD

The ZnO films were deposited by using domestic spray pyrolysis technique. Instrumentation consists of hotplate (0 to 400 ^oC) of B. S. Instruments Ambala. The temperature of the hotplate was monitored by digital temperature controller. The substrate was heated at desired temperature. The precursor was sprayed manually on the substrates by locally available perfume atomizer. Initially soda lime glass substrates were cleaned ultrasonically using organic liquid such as acetone. Before cleaning glass substrates were kept immersed in dilute hydrochloric acid overnight then washed with distilled water. The washed substrates were kept in ultrasonic cleaner which was filled with mixture of distilled water and detergents for two hours. After two hours the substrates were rinsed by using distilled water and acetone. The cleaned substrate was dried by hair drier and used for deposition.

At the beginning of experiment various sources of Zn ions such as zinc Chloride (ZnCl), zinc sulphate ($ZnSO_4$), zinc nitrate and zinc acetate hydrated were used for deposition of ZnO thin films. Among variety of these zinc salts, the good quality ZnO thin film was obtained by using zinc acetate hydrated. Therefore, in present case zinc acetate hydrated was used as zinc ion source for deposition of ZnO thin films. Precursor solution was prepared by dissolving reagent grade (0.075, 0.1, 0.125, 0.15, and 0.175 M) zinc acetate hydrated (Zn (CH3COO) $_{2:2}H_2O$) in distilled water/methanol (70:30). Few drops of acetic acid were added to avoid formation of zinc hydroxide [13]. The solution was stirred by using magnetic stirrer for two hours. The clear precursors have been sprayed on pre-heated glass substrates at desire temperature. The distance of spraying nozzle form substrate is adjusted such that the whole surface of substrate was exposed to spray. The spray rate of 5 ml per second, precursor spraying time 45 second and substrate 275 ℃ were kept fixed [13]. The depositied substrates were allowed to cool at room temperature and removed from hot plate. The deposited samples were annealed at 300 ^oC for one hour in muffle furnace and characterized by using variety of techniques. In physical characterization the thickness (t) was estimated using weight and difference method [16] by (1).

$$t = \frac{m}{\rho A} \tag{1}$$

Where m = deposited mass in grams (gm), ρ = density of deposited material in gram per cubic centimetres (gm/cm^3) and A = area of film in cm^2.

The crystallite size was estimated from full width at Half Maximum of XRD peak and using following Scherrer's equation [17].

$$D = \frac{0.94\lambda}{\beta COS\theta} \tag{2}$$

Where λ is wavelength of X-ray, 1.504 A^o, β is full width at half maximum (FWHM) and θ is the peak position. The lattice parameters 'a' and 'c' have been estimated using (3), (4) and values of interplaner distance d, bond length 'u' parallel to the 'c' axis, in units of c was calculated by using (5) [18].

$$a = \sqrt{\frac{1}{3}}\frac{\lambda}{\sin\theta} \tag{3}$$

$$c = \frac{\lambda}{\sin\theta} \tag{4}$$

$$u = \frac{1}{3}\left(\frac{a^2}{c^2}\right) + \frac{1}{4} \tag{5}$$

The optical absorption has been recorded by using systronics double beam spectrophotometer 2201 in 290-1000 nm wavelength range. The statistical interpretation of absorption data was used to estimate the optical band gap of deposited material. The UV-visible absorption edge is directly linked to the optical band

gap and optical band gap can be estimated from the absorption edge by using Tauc relationship. The Tauc relation explains variation of the absorption coefficient α in the strong absorption range which is linked to the band gap Eg of the material by the following expression [19]:

$$\alpha h\nu = A(h\nu - Eg)^n \quad (6)$$

where A is an energy-independent constant, ν is the frequency of radiation and index n is theoretically equal to 1/2and 3/2 for allowed and forbidden direct transitions respectively; however, ZnO is direct band gap semiconductor therefore *n* set equal to 1/2.

3. RESULTS AND DISCUSSION

The deposited ZnO thin films have been characterized by using different techniques and physical structural, morphological, and optical properties were investigated and described as follows.

3.1. Physical characterization

Film thickness (*t*) of deposited ZnO thin films was estimated using (1) and displayed in Table 1. Film thickness was increased with increase in zinc ion concentration. However, beyond 0.15 M molarity of zinc acetate hydrated film thickness was observed consstant. ZnO film of maximum thickness 14.2 micro meter (μm) was obtained for 0.15 M of Zn (CH3COO) $_{2:2}H_2O$ by using locally designed present spray pyrolysis technique.

3.2. Structural study of ZnO thin films

Figure 1 shows XRD patterns of spray deposited ZnO thin films. XRD patterns exhibit hexagonal crystal structure of wurtzite symmetry. The wurtzite crystal structure was confirmed by comparing with XRD data of standard JCPDS card no. 75-1526. The similar crystalline structure of ZnO was reported in earlier literature [14]. The XRD pattern for 0.075 M zinc acetate hydrated represents the amorphous type structure this may be due to zinc hydroxide and zinc oxide crystallites of small grain boundaries present in the film. The crystallity of ZnO thin films was increased on increasing molarity of zinc acetate hydrated.

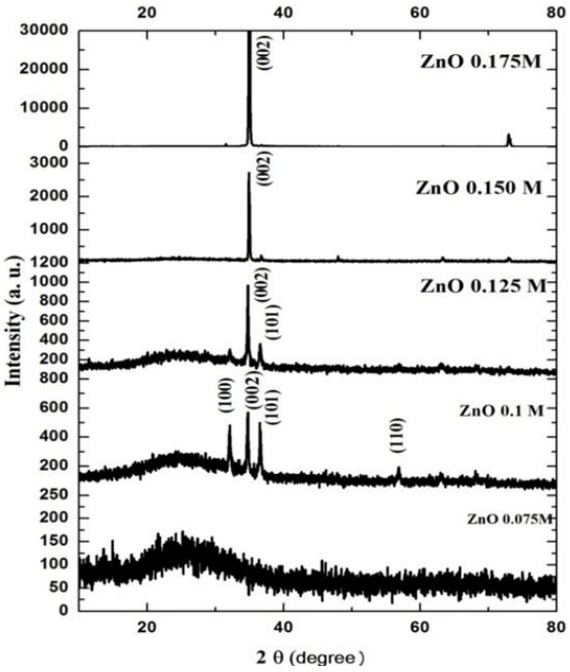

Figure 1. XRD spectra of ZnO thin films

The highly crystalline ZnO films were obtained for molarity ≥0.125 M. The 0.15 M and 0.175 M samples exhibit significant, single dominant peak along (002) direction. The material growing along (002)

direction provides the lattice matching to the chalcogenide component systems and may be used in solar cell application for getting better solar cell efficiency was reported in other literature [16]. Therefore, the presently prepared ZnO thin films have a novel importance in solar cell applications. The estimated crystallite size was displayed in Table 1. The crystallite size was increased with increase in zinc acetate molarity. The estimated lattice parameters were displayed in Table 1. The value of lattice constants were found to be similar as obtained from standard JCPDS card no. 75-1526 (a=3.242, c=5.194).

The calculated values of c/a ratios and the parameter u estimated from lattice constants were tabulated in Table 1. The c/a ratio for ideal wurtzite hexagonal unit cell was 1.633. The calculated c/a ratios were similar to be reported values which give the confirmation of wurtzite crustal structure of deposited ZnO thin films and the parameter *u* is defined as the length of the bond parallel to the *c* axis, in units of *c*. The calculated values of u were similar to be the values reported for ideal wurtzite structure of ZnO's [2]. This gives the confirmation of deposited Zno thin films exhibit stable wurtzite crystal structure.

Table 1. Film thickness, grain size, and lattice constants

Film sample	d	β	D	t	Lattice parameters a	Lattice parameters c	Ratio c/a	u
ZnO (0.075M)	2.590	0.433	35	12.8	3.223	5.178	1.6067	0.378
ZnO (0.1 M)	2.579	0.641	23	13.2	3.206	5.157	1.6085	0.378
ZnO (0.125M)	2.579	0.226	65	13.6	3.219	5.157	1.6020	0.379
ZnO (0.15 M)	2.568	0.199	66	14.2	3.203	5.135	1.6033	0.379
ZnO (1.75 M)	2.582	0.232	64	14.1	3.216	5.162	1.6053	0.379

d= interplaner distance, (A), β=full width at half maximum (radians), D=Crystallite Size (nm),
t= thickness of the film in (μm) and *u* is the bond length parallel to caxis in the unit of *c*

3.3. Surface morphology of ZnO thin films

The surface morphology of ZnO thin films deposited at different precursor concentrations was studied by SEM micrographs. Figure 2 shows SEM scans of four ZnO thn films deposited for four different zinc ion concentrations (0.75, 0.1, 0.125, and 0.15 M). Thin films deposited at 0.75 M and 0.1 M has similar wrinkled slab type structure morphology of 416 and 361 nm size respectvelly. Similar morphology was described in the report of others literature. ZnO film deposited at 0.125 M exhibit nanorods of 281 nm size while surface morphology of ZnO film deposted for 0.15 M zinc acetate hydrated shows systematic natework of nanowire of size 185 nm. Therefore, it was concluded that the surface morphology of ZnO thin films was improved from wrinkle type natework to nanowires on increasing zinc ion concentration.

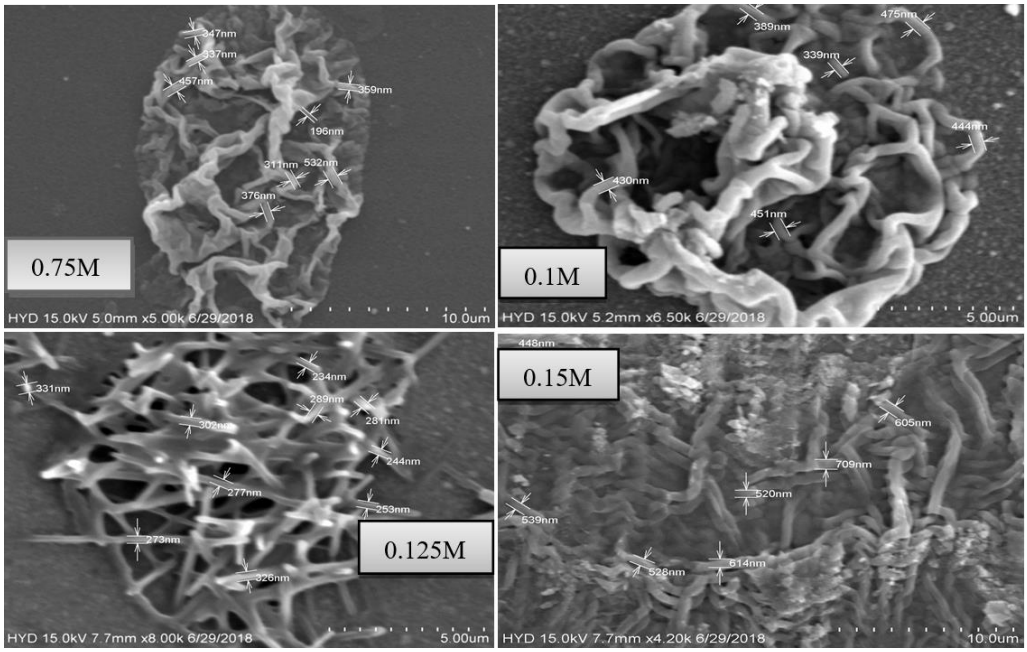

Figure 2. SEM micrographs of ZnO thin films

3.4. Elemental analysis of ZnO thin films

Figure 3 shows the EDX spectra of ZnO (0.15 M) thin film. The elemental analysis confirms that prepared sample composed by zinc and oxygen elements. There were no impurities present in the sample. Final atomic % was shown in Table 2. The atomic % shows that deposited films were oxygen reach however, above 0.125 M f zinc ion concentration was increased which leads increase in crystallity of ZnO thin films.

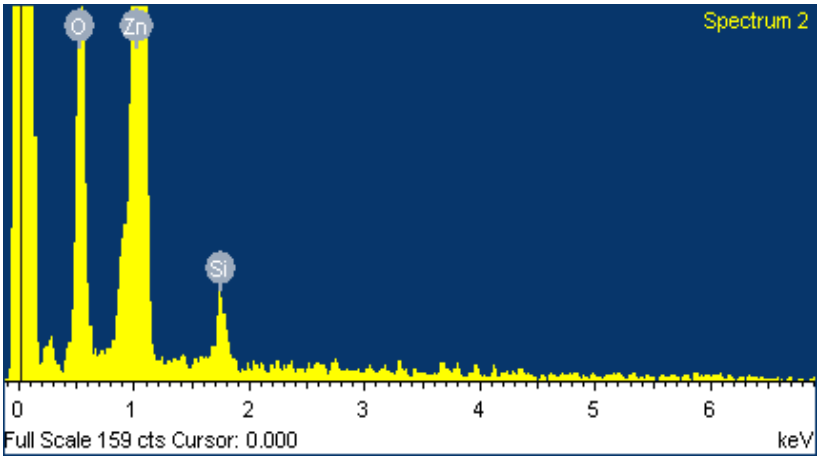

Figure 3. EDX spectra of of ZnO (0.15 M) thin film

Table 2. Atomic % of the film composition

Film Sample	ZnO (0.075 M)	ZnO (0.1 M)	ZnO (0.125 M)	ZnO (0.15 M)	ZnO (0.175 M)
Element	Atomic%	Atomic%	Atomic%	Atomic%	Atomic%
O K	68.31	66.03	53.77	54.78	59.76
Zn L	31.69	33.97	46.23	45.22	40.24
Totals	100.00	100.00	100.00	100.00	100.00

3.5. Optical properties of ZnO thin films

The optical absorption data was recorded by using systronic double beam spectrophotometer 2201 in the 290 to 999 nm range and presented in Figure 4. Figure 4 represents all the film samples show significant low absorption in the wide range of the electromagnetic spectrum from 340 to 999 nm and higher absorption in ultraviolet (290-340 nm) region. A region of high absorption corresponds to the fundamental absorption (λ<350 nm) in ZnO films. This absorption is due to the inter-band electronic transition. Similar finding has been reported in the earlier literature [17].

However, the absorption edge was gradually shifted towards the blue side of the electromagnetic spectrum with increase in molarity of zinc acetate hydrated. This is may be due to a greater number of ZnO grains are closely packed over the substrates. The film sample deposited for 0.15 M zinc acetate hydrated shows maximum blue shifting as compared to other samples. Low absorption in the wide range of the electromagnetic spectrum indicates that light energy over this broad region of spectrum may be useful for device application. The ZnO thin films exhibits low absorption in the wide region of the spectrum may be applicable in solar cell as a window layer material useful for transmitting the harvested light energy for conversion in usable form [17].

The energy band gap Eg was calculated by using Tauc's plots. Figure 5 shows the Tauc's plots of deposited ZnO thin films. The shifting of absorption edge to shorter wavelengths indicates that the optical band gap increases with increase in molarity of the zinc acetate hydrated. The band gap of ZnO thin films estimated were 3.7, 3.7, 3.72, 3.8, and 3.75 eV, for 0.75, 0.1, 0.125, 0.15, and 0.175 M film samples respectively. The observations confirm that the optical band gap increases with increase in molarity of zinc acetate hydrated or zinc ion concentration. The film deposited for 0.15 M zinc acetate shows maximum blue shifting and higher band gap (3.8 eV) as compared to other samples.

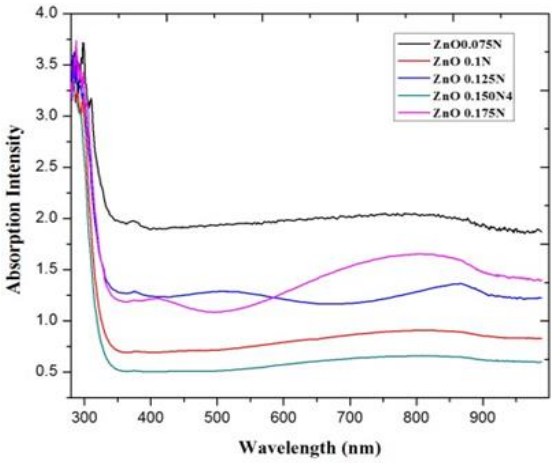

Figure 4. Absorption spectra of ZnO thin films

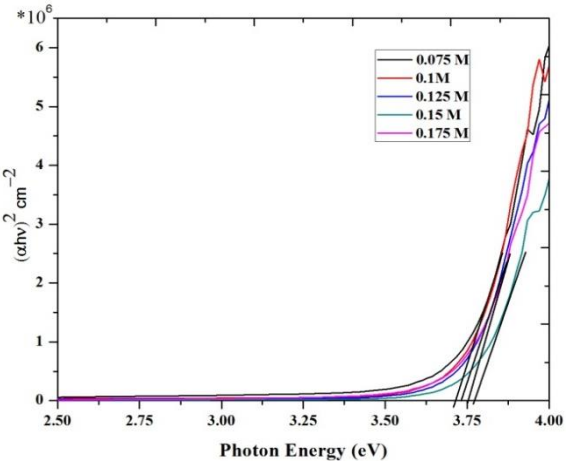

Figure 5. Tauc's plots of ZnO thin films

4. CONCLUSION

ZnO thin films were deposited by using chemical spray pyrolysis technique by varying molarity of zinc acetate hydrated. XRD pattern exhibits stable wurtzite hexagonal crystal structure of deposited ZnO thin films. The X-ray diffraction showed that films have grown along c-axis corresponding to the (002) crystallographic orientation. The intensity of this (002) peak and grain size were increasing, with increase in zinc ion concentration. SEM scans of ZnO thin films shows improvement in surface morphology of the films from wrinkle to nanowires morphology with increase in molarity of zinc acetate.

On the basis of results discussed in the report, the ZnO films deposited for 0.15 M zinc acetate shows maximum crystallite size and exhibits excellent network of nanowires, the maximum blue shifting and higher band gap 3.8 eV. Therefore, it is confirmed that optimal value of molarity of zinc acetate was 0.15 M to obtain good quality ZnO thin films using present chemical spray pyrolysis technique. The ZnO films growing in (002) direction are advantages for solar cell applications provided that PEC measurement of deposited ZnO thin films is to be needed and it is the scope of the work.

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