Structural and Surface Modifications by Varying Precursor Concentrations on Spray Deposition of Zno Thin Films

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Short Report

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Abstract

Zinc Oxide thin films have been deposited on glass substrates using zinc acetate as starting precursor at different concentrations 0.05–0.3 M in steps of 0.05 M by spray pyrolysis method at the constant substrate temperature of 350º C. Lattice structure of the prepared ZnO films were characterized by X-Ray diffraction analysis (XRD). Diffraction pattern revealed hexagonal wurtzite structure with cell edges a = 3.2530 Å, c = 5.2092 Å and density 5.66 g/cm^3, which is almost equal to the standard values a = 3.2556 Å, c = 5.2070 Å and 5.6525 g/cm^3 (COD No: 96-900-4180). Structural parameters such as dislocation density, lattice stress, unit cell volume, number of crystallites per unit area have been calculated and its dependency with thickness was studied. As the film thickness increases, the crystallite size also increases. Through FTIR, chemical bonds and their stretching vibrations confirmed the metal-oxide phase formation. Scanning electron microscope images showed the formation of good quality film with regularly distributed spherical shaped grains. Roughness values of the films were attained from the Atomic force microscope images. In overall observations, precursor concentration has significant effect on film thickness which in turn modified the structural, optical and morphology properties of the prepared ZnO thin films.

1. Introduction

Zinc oxide is one of the promising transparent material conducting oxides (TCOs) because of its typical properties such as thermal stability, high resistance to chemical attack, stability in hydrogen plasma, wide bad gap and large exciton binding energy of 60 meV [1–5]. It has wide applications in transparent electrodes, gas sensors [6], light emitting diodes (LEDs) [7] laser systems, hetero-junction solar cells [5, 6, 8, 9], liquid crystal displays (LCDs) [6], heat mirrors [6], multilayer photo thermal conversion systems, flat panel displays etc [1–3, 6, 10–13]. Its abundance in nature and non-toxicity [14], low dielectric constant, good photoelectric and piezoelectric activities compared with other possible materials such as ITO, Cd_2SnO_4 or SnO_2 [4, 11, 15, 4, 16]. ZnO thin films have been prepared by various methods such as RF magnetron sputtering [17], ion beam sputtering [18], molecular beam epitaxy (MBE) [19] metal organic chemical vapor deposition (MOCVD [20), pulsed laser deposition [21, 22], spray pyrolysis [3, 4, 8], hydrothermal method [23] and sol-gel process [2, 5]. ZnO thin films prepared by spray pyrolysis method have been especially paid attention owing to its advantages such as low cost [4, 16], simple deposition procedure [6, 4, 9, 24], easier composition control, regular particle shape [7], low processing temperature, easy introduction of doping elements [25] etc. The other advantage of the spray pyrolysis method is the production of large area films. Moreover, in spray pyrolysis technique, the deposition and the thickness of the films can be easily controlled over a wide range by changing the spray parameters. The spray pyrolysis technique is basically a chemical deposition technique where the most important deposition parameters are the precursors, solution concentration and deposition temperature. Many authors have described the preparation and characterization of ZnO thin films by spray pyrolysis with high *c*-axis preferred orientation. In this research, we deal with the influence of precursor concentration on ZnO thin films prepared by a simple spray pyrolysis technique under six specific conditions. Finally, the structural, phase formation, morphological properties were analyzed using X-ray diffraction (XRD) techniques (XPERT-PRO), FTIR (Thermo Electron Nicolet 5700), Scanning Electron Microscopy (SEM JEOL JSM-6390LV)) and.Varian Cary 5000 spectrometer and Atomic Force Microscope respectively.

2. Experimental Details

ZnO thin films were deposited on glass substrates for different concentrations (typically 0.05, 0.1, 0.15, 0.2, 0.25, 0.3 M) by spray pyrolysis technique. Zinc acetate was taken as the primary precursor salt dissolved in 25ml ethanol and 25ml distilled water The substrate deposition temperature was maintained at 350 ºC. Compressed dry air at a pressure 0.4 kg/cm^2 acted as a carrier gas to transform the precursor solution into a fine mist. When the fine droplets reached the preheated substrates, solvent species were evaporated and formed the desired ZnO as thin nanostructures. After deposition, prepared films were characterized using different instruments for deciding the nature and quality of the film.

3. Results And Discussion

3.1 Structural Analysis

Structural properties of spray deposited ZnO thin films as a function of precursor concentration was analyzed using XRD. Figure 1 shows the XRD patterns of ZnO thin films obtained at various precursor concentrations 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3M.

The diffraction peaks are observed at angular positions 31.73, 34.42, 36.22, 47.51, 56.53, 62.83 and 67.89 corresponding to the refraction planes (1 1 0), (0 0 2), (0 1 1), (0 1 2) (1 1 0) (0 1 3) and (1 1 2) respectively. These peaks are indexed based on the Crystallographic Open Database, COD (96-900-4180). The (0 0 2) and (1 0 1) peaks of the ZnO films prepared using 0.05 M solution are less intense. When the molarity is increased to 0.1 M, the peaks corresponding to the planes (1 0 2), (1 1 0) and (1 0 3) are observed well. Further increase to 0.3 M results intense peaks in all planes observed before. Predominantly crystallites are oriented alone the (0 0 2) because the number of Zn^{2+} ions incorporation and growth rate [5, 26]. It is observed that the intensity of (0 0 2) peak increased with increasing precursor concentration, indicating their higher crystallinity. The peak intensity is high for solution concentration of 0.3 M, showing the influence of precursor molarity on surface (orientation) of the ZnO films [2]. Thickness of the film also increases with increasing precursor concentration, 0.18 µm, 0.94 µm, 1.18 µm; 1.21 µm, 2.51 µm, and 2.75 µm for the precursor concentrations 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3M respectively. The similar trend has been observed by J.L. van Heerden for ZnO fimls prepared using the same technique [27].

The crystallographic parameters like lattice constant (a and c), unit cell volume, crystallite size, microstrain, dislocation density and number of crystallites per unit area (N) are calculated from the 2θ position of (0 0 2) plane and are tabulated in Table 1.

Table 1
Calculated lattice parameters of ZnO thin films deposited using precursors of different concentrations

Precursor Concentration	Lattice Parameter (Å)		Unit Cell Volume (Å) ^{3}	Crystallite Size (nm) ($x10^{-9}$)	Microstrain ($x10^{-4}$)	Dislocation Density ($x10^{14}$) Lines/m^2	Thickness (µm)	No of Crystallites ($x10^{14}$)	Density (g/cm^3)
	a	c							
Standard Value	3.2530	5.2070	47.72						5.66
0.05 M	3.2478	5.2146	47.63	40.276	8.203	6.1645	0.8	4.93	5.6738
0.1 M	3.2517	5.211	47.71	40.273	8.2024	6.1655	0.94	5.79	5.6641
0.15 M	3.2555	5.2093	47.80	40.272	8.2022	6.1658	1.18	7.27	5.6527
0.2 M	3.2556	5.2092	47.81	40.274	8.2026	6.1652	1.21	7.45	5.6525
0.25 M	3.2569	5.2058	47.82	53.6932	6.15133	3.4686	2.51	8.7	5.6517
0.3 M	3.2581	5.204	47.84	53.6931	6.15132	3.4687	2.75	9.53	5.6494

It was found that the lattice constants, crystallite size, unit cell volume, microstrain, dislocation density and density changes with increasing precursor concentration. Obtained lattice parameter, unit cell volume and density values are similar to previously reported values by Aryanto et al [28]. Attained crystallite size of ZnO thin films is around 40 nm for the film deposited using 0.05 M solution which increased to 53 nm when the precursor concentration is to 0.3 M. The crystallite size values of ZnO thin films increasing with increasing precursor concentration, because of the electrostatic interaction between the solute particles and also due to thickness [29]. In contrast to the crystallite size tendency, the values of strain decrease with increasing precursor concentration. This may come from the retarded crystal growth due to the stretched lattice that can increase the lattice energy and diminishes the driving force of the growth [38]. Similarly dislocation density (δ) values decrease as the precursor concentration increases. The obtained results are in well agreement with previous reported results [2]. Adel H. Omran Alkhayatt et al. also reported the dislocation density value of ZnO films as nearer to of 10^{14} lines / m^2 [31].

3.2 Metal-oxide phase Analysis - FTIR

FTIR spectrum provides the information about the presence of various functional groups and the elemental constituents in the material. Figure 2 shows series of absorption peaks in the range of 400 cm^{-1} to 4000 cm^{-1}, attributed to different groups and chemisorbed species in ZnO thin films prepared using precursors of different concentration.

Table 2
Vibrational Frequencies of ZnO Compounds

Wavenumber (cm^{-1}) Reported values	Wavenumber (cm^{-1}) Present study	Assignment
505	471	ZnO Streching
1632	1640	O-H deformation
3465	3450	O-H stretching

The peak at 471 cm^{-1} due to the stretching vibrations of Zn-O bonds which confirmed the formation of ZnO [3]. A broad peak at 3460 cm^{-1} which matches to the vibration mode of O-H bond indicated the coordination with hydroxide. This may be due to absorption of moisture as imperfection content [32]. One more peak at 1641cm^{-1} was due to deformation vibration of H_2O or O-H group.

3.4 Morphological studies

Surface morphology of the ZnO thin films deposited with various precursor concentration was recorded in SEM. Figure 3 shows SEM images of ZnO thin films recorded at the magnification of 80,000.

As observed, precursor concentration and thickness of the film has dominant effect on surface morphology of films. It is observed from the SEM images, all the ZnO films exhibit smooth and spherical grain structure. Many researchers reported ZnO films with spherical like structures by changing temperature, concentration and dopant ratio [26, 33]. For the film deposited with precursor concentration 0.05 M the average diameter of the spherical structures is 0.18 µm, when the film precursor concentration is increased to 0.3 M, the diameter of the spherical grains are increased to 0.98 µm. Hence the surface morphology modifies according to precursor concentration of the films. As precursor concentration increases, gradual evolution of the grain size and shape. Similar observations were reported by Vinoth Kumar Jayaraman et al [34]. These variations will surely alter the physical and chemical properties. The overall nature reveals a continuous film on the substrate surface without holes or cracks with smooth and the substrates are fully covered with material.

Atomic force microscopy (AFM) 2D and 3D images of the ZnO thin films have been recorded for two ZnO films prepared using precursor concentrations 0.2 M and 0.3 M. Figure 4 shows the columnar structure, which is contrast from SEM images.

The crystallite size seems to be increased with increasing precursor concentrations. AFM investigations show is smooth and homogeneous. Surface roughness values are found in the range from 22nm to 61nm. The surface roughness increased with the increasing precursor concentrations. The values of the grain size calculated using AFM were found to be 75.8 nm, 80.8 nm for the films deposited using of different concentration precursors 0.2 M and 0.3M respectively. Particle size obtained from AFM analysis are far higher than crystallite size obtained from XRD. Similar results were reported by Chaithra et al [35].

3.5 Conclusion

ZnO thin films were successfully synthesized by spray-pyrolysis method using precursors of different concentrations. Spray system with optimized deposition condition allowed obtain ZnO films. Prepared samples were wurtzite hexagonal structured and their mean particle sizes and crystallinity were gradually improved on increasing morality. The structural, optical properties of the ZnO thin films have been found to be influenced by precursor concentration during deposition. XRD studies revealed improved crystalline character on by increasing the precursor concentration. The ZnO phase formation was also identified from the FTIR studies. The crystalline quality of the films gets better and the grain size increases as the precursor concentration increases. The high resolution FE-SEM

images showed uniform distribution of spherical grain. Surface roughness parameter determined by AFM imaging increases from 22nm to 61nm for increasing precursor concentration.

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Figures

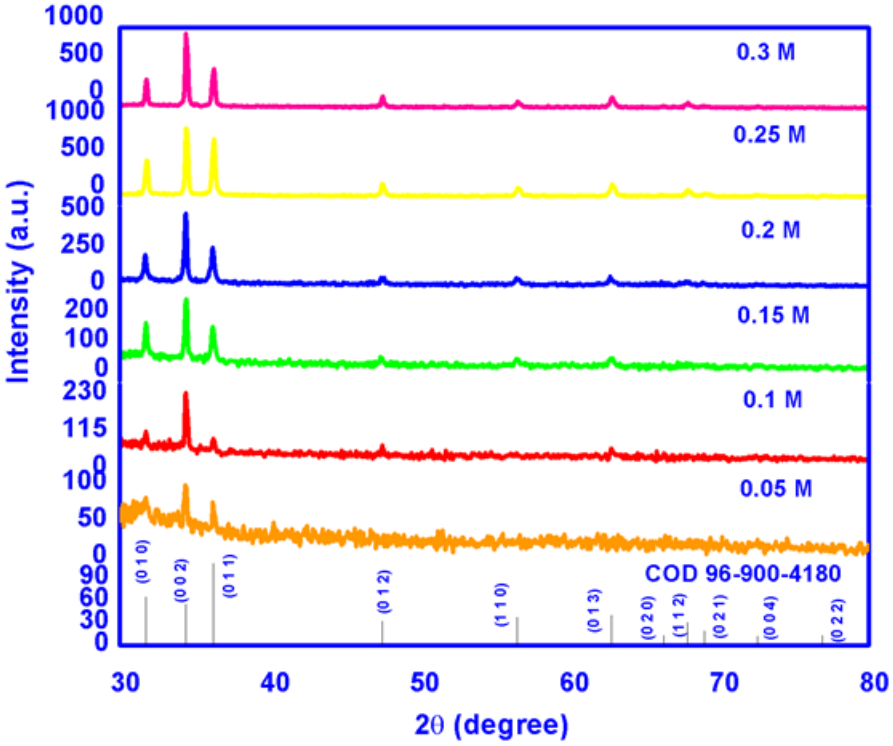

Figure 1

XRD patterns of ZnO thin films deposited using precursors of different concentrations.

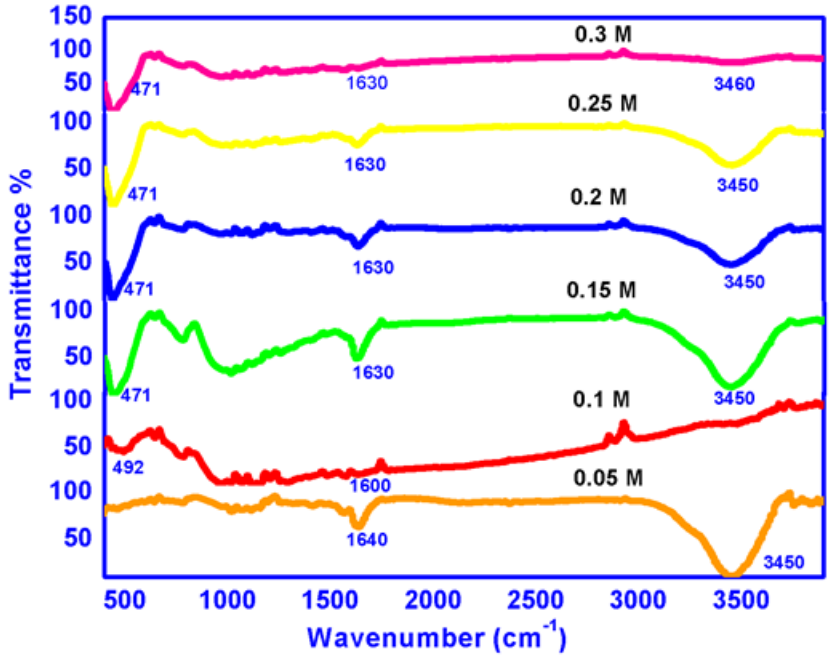

Figure 2

FTIR spectrum of ZnO thin films deposited using precursors of different concentrations.

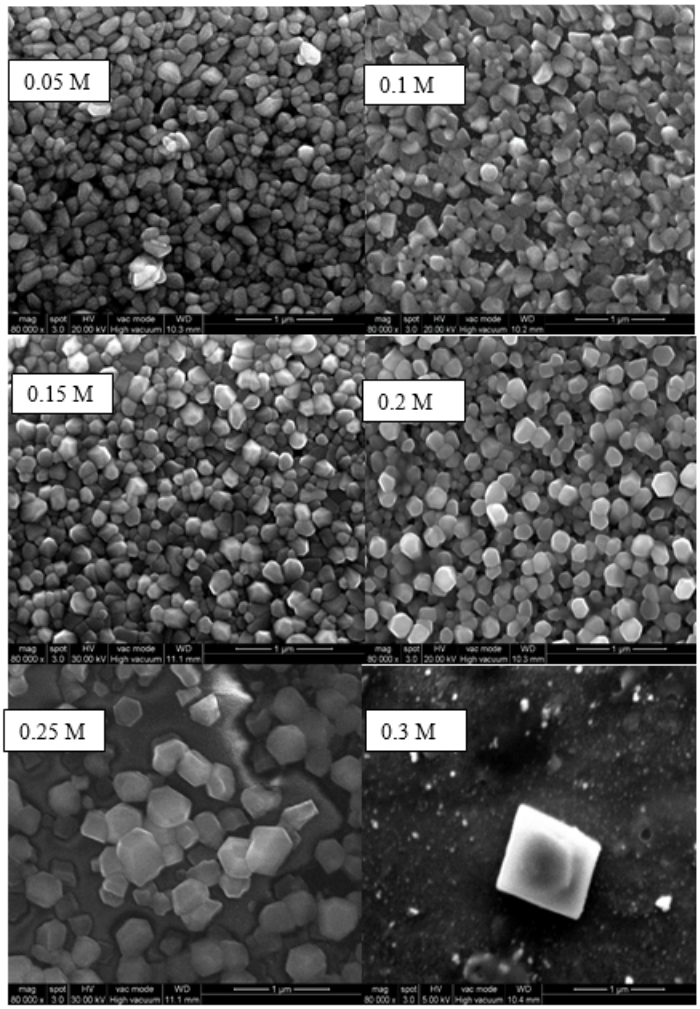

Figure 3

SEM micrographs of ZnO thin films prepared using precursors of different concentrations.

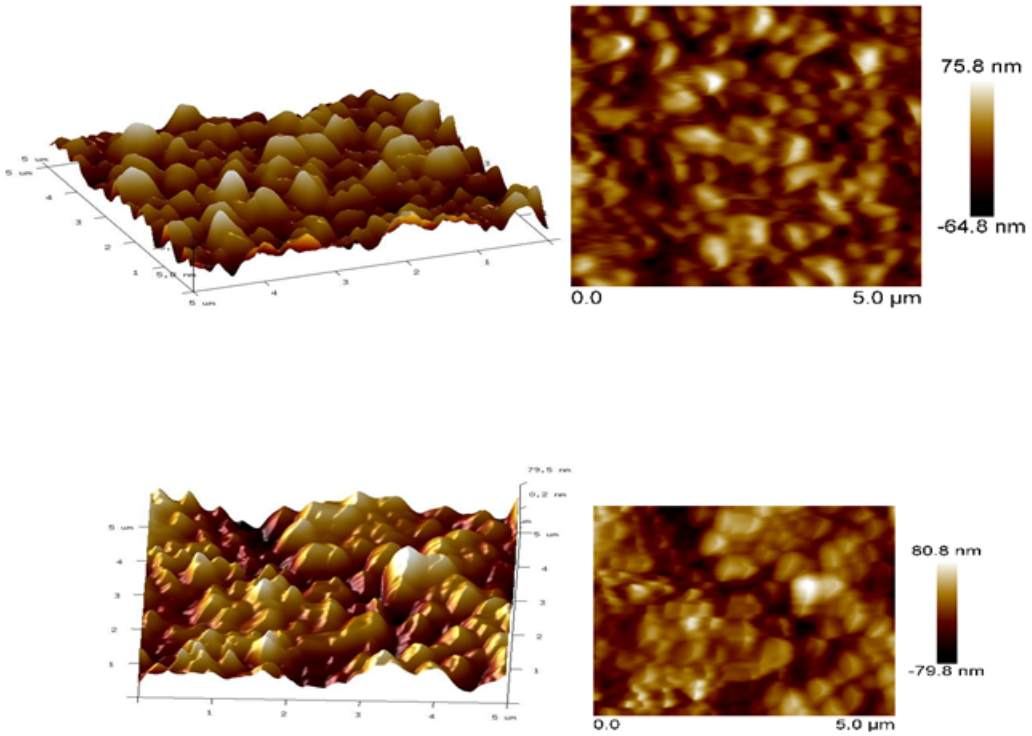

Figure 4

AFM images of ZnO thin films prepared using precursors of different solution concentrations.