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IMPACT OF BLENDING OF SOLVENTS ON CRYSTAL STRUCTURAL AND SURFACE MORPHOLOGICAL CHARACTERISTICS OF WET CHEMICAL SOL-GEL SYNTHESIZED ZnONANO-THIN FILMS

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ABSTRACT
The nature of the solvent used to synthesize nanomaterial is one of the key factors that can influence the properties of nanomaterials. In this study, seed solutions containing various solventsblending were prepared at 0.2M concentration to fabricate Zinc oxide (ZnO) nano-thin films by the dip coating technique. Organic solvents such as methanol, ethanol and 2-Methoxyethanol were used to prepare the solvent blending. Various characterization techniques such as XRD diffraction, surface morphology studies using an electronic microscope (FESEM), Raman spectrum analysis, and double beam optical spectrum analysiswere adopted to investigate the influence of solvent blending on nanomaterials' properties. X-diffraction studies confirmed the formation of the wurtzite hexagonal crystal structure of ZnO. Electronic microscopic images evaluated the surface morphology and particle size. The presence of $E_2^{(High)}$ optical vibrating mode in Raman spectra of all the deposited thin films showed that ZnO has a hexagonal crystal structure. Finally, the UV-VIS spectra of the deposited films showed that the optical bandgap varied with the size of the particle clusters.
Keywords: ZnO, Nano Thin-Films, Blending of Solvents, Particle Cluster, XRD, SEM.
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INTRODUCTION

Nano thin film technology has gained popularity owing to its wide variety of applications, including optoelectronic, photovoltaic, piezoelectric, gas sensor, and thin film memory devices. Thin film technology helps in fabricating transparent conducting metal oxide thin film coatings.[1] Tin dioxide (SnO_2) and indium oxide (In_2O_3) are the two compounds that have shown the most promising TCO coatings.[2]However,researchers are looking for alternatives due to the increased need for optically transparent conducting coatings, especially in display devices. ZnO thin films were deemed an excellent candidate for optically transparent conducting films due to their broad optical bandgap (3.37eV) and 60meV of excitation energy.

Several variables might affect the quality of ZnO thin films, including solution pH, deposition duration, bath temperature, Etc. According to Cenayda Lopez *et al.,* the nature of the solvent influences the crystal growth of ZnO.[3]Spiros H. Anastasiadis*et al.* reported the growth of ZnO nanostructures with different sizes and shapes depending on the solvents used.[4]Jia-Yi Yin*et al.* showed that the solvent's boiling point significantly affects the surface morphology.[5]In this study, the impact of solvent blendson the crystal structural and morphological characteristics of ZnO nano-thin film coatings was investigated. The observed findings indicate that the crystal structure and the rise in formed ZnO nanoparticle cluster are solvent blending-dependent.

EXPERIMENTAL

Thin Film Deposition Procedure

Zinc acetate ($ZnC_4H_6O_4$)and monoethanolamine(C_2H_7NO) were the primary ingredients, i.e. metal salt and stabilizer, while methanol, ethanol, and 2-Methoxyethanol were used as solvent blending. Zinc acetate dihydrate is dissolved in a mixture of two solvents to make a zinc complex solution which is then stirred for 1 hour at 60^0C. Finally, the solution was kept for 24 hours for aging. Thin films were synthesized by dipping pre-cleaned glass substrates into the prepared solution for 2 minutes, removed at 2cm/sec speed, and dried for 5 minutes. Finally, the coated substrates were heated at 500^0C for 2 hours.

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Nano-thin films made with methanol, methanol, and ethanol, methanol and 2-Methoxyethanol, and ethanol and 2-Methoxyethanol were named Z1, Z2, Z3, and Z4, respectively. Figure-1[6]shows the likely chemical mechanism for ZnO synthesis.

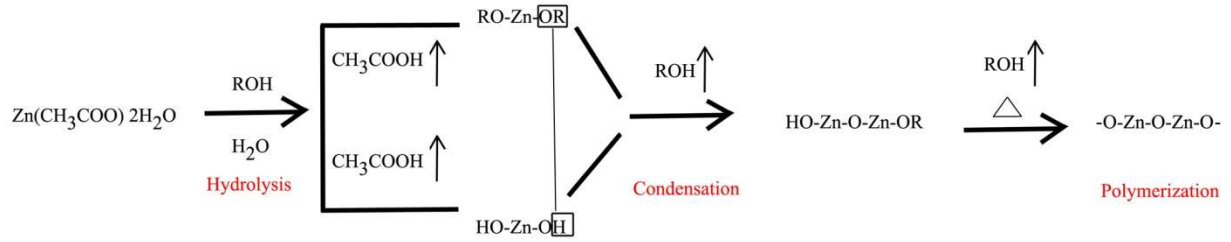

Fig.-1: A simplified Diagram of the Sol-Gel Synthesis for ZnO Nano Thin Film Coating

Instrumentation Used for Thin Film Characterization

The X-ray diffraction pattern was obtained using a Rigaku (Smart lab). FESEM (TESCAN and Bruker-MIRA 3 model) and AFM (Agilent technologies – Model: 5000) were used to investigate the surface morphology of the films. The Raman analysis was performed using Horiba Scientific-XploraPlus V1.2. Finally, optical characteristics were investigated by examining transmission spectra collected using a UV-VIS spectrophotometer (Intech made – India).

RESULTS AND DISCUSSION

Structural Analysis

The XRD spectrum of sol-gel synthesized ZnO nano-thin films is shown in Fig.-2. The observations show that all the samples' distinctive peaks of the obtained XRD spectrum match the standard database (JCPDS 36-1451). The presence of multiple peaks in the diffraction pattern suggests the formation of a polycrystalline wurtzite crystal structure of the ZnO in the prepared ZnO nano-thin film material. The diffraction pattern reveals valuable information about the preferred orientation of crystal growth. Films deposited by methanol solvent and blending methanol and ethanol have the most intense peak along the (100) direction. In comparison, films deposited by blending 2-Methoxyethanol/ methanoland 2-Methoxyethanol/ ethanol have the most intense peak along the (101) direction. It was observed that the intensities of peaks of deposited films using solvent blendings were enhanced when compared with the diffraction pattern of the film deposited using methanol. This indicates that the blending of solvents is improving ZnO crystalline quality. The structural parameters of the ZnO phase were carried out using the relations.[7]These obtained structural parameters are included in Table-1.

$$\text{Grain size } L = \frac{k\lambda}{\beta Cos\theta} nm \quad (1)$$

$$\text{Lattice dislocation density } \delta = \frac{1}{L^2} lines m^{-2} \quad (2)$$

$$\text{Microstrain} \varepsilon = \frac{\beta}{4\,Tan\theta} lines^{-2} m^{-4} \quad (3)$$

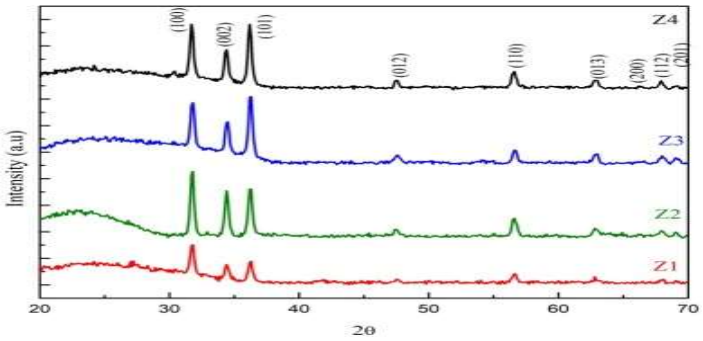

Fig.-2: X-Ray Diffraction Spectra of Deposited ZnO Nano Thin Films

Surface Morphology

The electronic microscopic images of the deposited thin film surface and the corresponding particle cluster size hysterograms are shown in Fig.-3. From all the images, all the samples clearly show nanoparticle cluster formation regardless of the blending solvents used in fabricating the samples.

Therefore, the cluster formation can be explained based on particle aggregation.[8] As a result of blends of solvents, the smaller nanoparticles formed within one solvent can interact with the larger nanoparticles formed within another solvent leading to the formation of particle clusters. These particle clusters are a foundation for the upcoming deposited particles, allowing a denser cluster to develop.

Table-1: Structural Parameters of Deposited ZnO Nano Thin Films

Sample	Solvent blending	Intense Peak (hkl)	2θ	Planar spacing d(Å)	FWHM	Grain size D(nm)	Dislocation density δ ($\times 10^{15}$)	Micro strain ε ($\times 10^{-3}$)	Lattice parameters (Å)
Z1	Methanol	(100)	31.75^0	2.8160	0.5355	16.12	3.8483	8.2	3.24968 5.21528
Z2	Methanol+Ethanol	(100)	31.75^0	2.8160	0.4729	20.17	2.4580	6.6	3.25803 5.20460
Z3	Methanol+2Methoxyethanol	(101)	36.25^0	2.4761	0.3932	22.21	2.0272	5.2	3.24948 5.20424
Z4	Ethanol+2Methoxyethanol	(101)	36.20^0	2.4794	0.3729	23.42	1.8231	5.0	3.25247 5.20714

The cluster sizes that were measured using the hysterogram are summarized in Table-2, and it is abundantly evident that the mixture of ethanol and 2-Methoxyethanol solvents has the largest cluster size compared to the other mixtures of solvents. In addition, prior studies have shown that the solvent's boiling point influences particle size.[9] In the case of blending two different solvents, the particle size of the particles grown in the two different solvents will not necessarily be the same. As a result, the properties of the particles, such as their size, shape and orientation, may differ significantly. As a result of solvent blending, the smaller nanoparticles formed within one solvent can interact with the larger nanoparticles formed within another solvent leading to the formation of particle clusters.

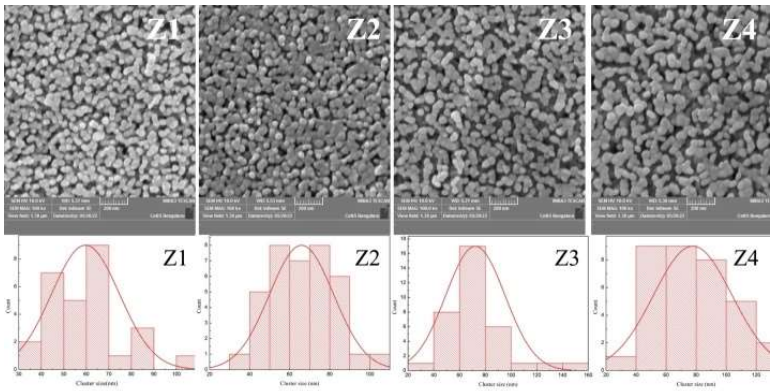

Fig.-3: SEM Images of Deposited ZnO Nano Thin Films and Their Cluster Size Histogram Profile

Table-2: Particle Cluster Size and Surface Roughness Values Determined using SEM and AFM Images

Sample	Solvent	Particle cluster size (measured from SEM images) nm	Surface roughness $R_{rms}(nm)$
Z1	Methanol	59.62	23.61
Z2	Methanol+Ethanol	65.92	27.44
Z3	Methanol+2-Methoxyethanol	72.31	25.44
Z4	Ethanol+2-Methoxyethanol	77.76	30.98

Surface Roughness Analysis

Figure-4 illustrates the synthesized films' 3D-AFM images and the corresponding roughness profiles. Table-3lists the measured RMS roughness of ZnO thin films synthesized using different solvent mixtures. The RMS roughness values of thin films made by blending solvents show that as the cluster size increases, so does the surface roughness of the film.[10]This demonstrates a correlation between a film's surface roughness and nanoclusters' size, where the cluster size varies as solvent blending.

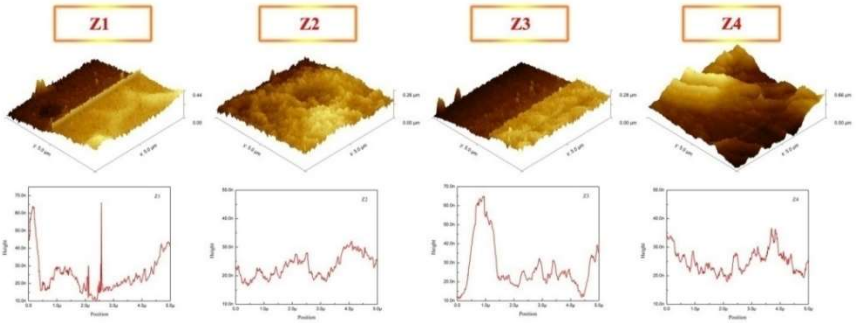

Fig.-4: AFM 3D Images of the Surface of Deposited ZnO Nano Thin Films and the Corresponding RMS Roughness Profile

Table-3: Optical Parameters of Deposited ZnO Nano Thin Films

Sample (Solvent blending)	Film thickness t (nm)	Optical transparaancy (T%)	Optical bandgap Eg (eV)	Refractive Index (n)
Z1 (Methanol)	250	89	3.282	2.325
Z2 (Methanol+Ethanol)	310	85	3.267	2.329
Z3 (Methanol+2Methoxyethanol)	360	83	3.258	2.331
Z4 (Ethanol+2Methoxyethanol)	450	75	3.241	2.335

Elemental analysis

Compositional analysis of zinc oxide was performed by analyzing the EDS spectra of the deposited thin films; the corresponding image is shown in Fig.-5. The presence of characteristic peaks of elements Zn and O in EDS spectra confirms the existence of these elements in the deposited nano-thin films.

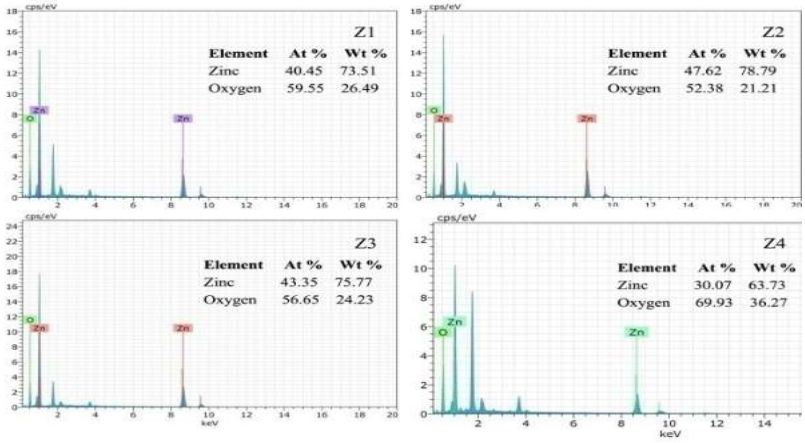

Fig.-5: EDS Spectrum of Deposited ZnO Nano Thin Films

Raman vibrational spectroscopy analysis

The Raman spectrum of the deposited nano-thin films in the spectral region of 200/ Cm to 800/ Cm is shown in Fig.-6. It can be seen that all samples exhibit Raman peaks at 331Cm^{-1}, 380Cm^{-1}, and 437Cm^{-1}. A strong peak at 437/ Cm is related to the high-frequency optical phonon E_2^{High}. This peak signifies the formation of the ZnO phase's wurtzite hexagonal crystal structure, which also supports the XRD data.[11] The other peaks found around 331cm^{-1} and 380cm^{-1} are due to $E_2^{(High)}$-$E_2^{(Low)}$ and A_1(TO) vibrating modes, respectively.[12]

Analysis ofOptical Characteristics

The optical parameters such as transmittance(T%), energy band gap (E_g), and thin film refractive index in the optical band of ZnO nano thin films coated with various solvent mixes were studied in the 300 Cm^{-1} to 800 Cm^{-1} wavelength range. Figure-7(a) demonstrates the optical transmittance in the visible band and the Tauc plot used to calculate the band gap. All nano-thin films have a transmittance of above 75%. The

film deposited using methanol solvent has the highest optical transparency than others. The decrease in transparency may be due to the rise in thin film thickness and ZnO film surface roughness.[13,14] The optical bandgap was evaluated using the Tauc plot, as shown in Fig.-7(b), and it should be noted that the obtained bandgap values are independent of the solvent blend used.

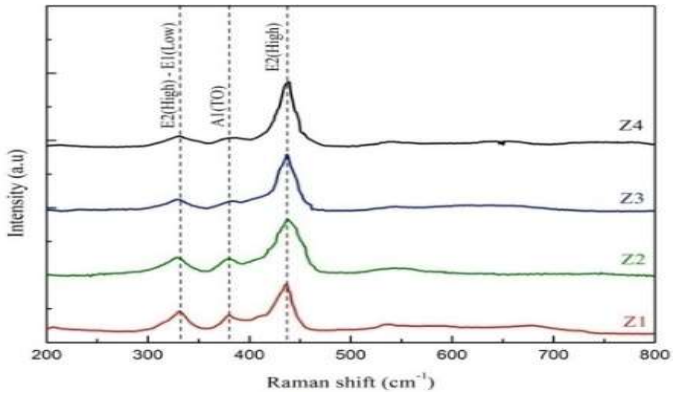

Fig.-6: Raman Spectrum of Deposited ZnONano Thin Films

The refractive index(n) of Sol-Gel synthesized ZnO nano thin films was estimated using the relation.[15] $\frac{(n^2-1)}{(n^2+2)} = 1 - \sqrt{\frac{E_g}{20}}$ (4)

Table-3summarizes the evaluated optical parameters.

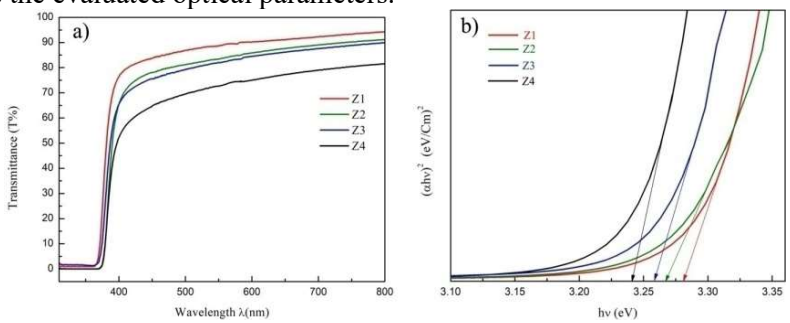

Fig.-7: UV-VIS Spectrum of Deposited ZnO Nano Thin Films a) Transmission Spectra b) Tauc Plot

CONCLUSION

Zinc oxide nano-thin films were fabricated by mixing different organic solvents with the Sol-Gel dip coating routine. The structural analysis of the films demonstrated the ZnO phase hexagonal crystal structure. Moreover, the structural studies also indicated that the preferential crystal growth direction strongly depends on the blending of solvents. ZnO thin film deposited with solvent blending with a high melting point of 2-methoxyethanol has preferential crystal growth along a (101) direction. In comparison, low solvent blending with a low melting point resulted in ZnO crystal growth along a (100) crystal growth direction. Hence it can be concluded that solvent blending significantly affects crystal growth.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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