Effect of Al-Doping on the Structure and Optical Properties of ZnO Thin Films by Sol-Gel Spin Coating

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***Abstract*: Zinc oxide (ZnO) and Aluminium-doped zinc oxide (AZO) thin films were successfully synthesized using the sol-gel spin coating technique. The synthesis of pure phase of ZnO thin films with Polycrystalline-hexagonal wurtzite structure and characterized by lattice parameters (a=3.194Ao and c=5.194Ao) using XRD analysis. There is No significant changes in phase structure were observed upon aluminium doping. The crystallite size, lattice constants, and strain remained nearly unchanged with increasing Al concentration, suggesting that Al ions substitute interstitially at Zn sites in the ZnO lattice an inference supported by EDX analysis. surface morphology Al doping levels up to 3 wt% to 5 wt% films exhibited a nanowire-like structure and reduction in grain size that indicates aluminium incorporation influences the film's growth and surface characteristics. UV-Vis Spectroscopy results indicate that the optical band gap of ZnO thin films decreases from 3.288 eV in the undoped state to 3.178 eV with increasing Al doping concentration.**

***Keywords*: Zinc oxide (ZnO), Aluminium doped Zinc oxide (AZO), Thin films, Sol-gel.**

1. Introduction

Metal oxides are inorganic crystalline solid structure this material contains a metal cation and oxide anion (O^{2-}). When synthesized as nanoparticles the behaviour is altered by their increased surface area, high reactivity and quantum confinement effect. The metal oxides exhibit both acidic and basic properties. Because of their wide-ranging chemical and physical properties, many metal oxides like ZnO, TiO_2, SnO_2, and ZrO_2 are widely used in developing bio polymers, sensors and biosensors [1]. The presence of cation (metal) and oxygen vacancies in deposited metal oxide thin films is beneficial for various transparent conducting applications [2]. In recent years, material science research has heavily focused on wide band gap semiconductors, with Zinc Oxide (ZnO) emerging as a prominent n-type material. Because ZnO films are n-type semiconductors with optical transparency in the visible range, they've become a prime target for developing various electronic and optoelectronic devices. This includes applications such as transparent conductors, solar cell windows, gas sensors, and surface acoustic wave devices [3]. Aluminium doped zinc oxide (AZO) thin films are n-type semiconductors with a wide band gap of 3.3 eV. While pure ZnO films exhibit high transmittance in the visible and near-ultraviolet spectra, low thermal stability in air due to thermal edging. AZO, however, is a highly insoluble and thermally stable. Aluminium source, making it suitable for applications involving glass and ceramics [4]. The aluminium doped zinc oxide can exist in both crystalline and amorphous forms, depending on the deposition condition and post deposition treatments with molecular formula Zn_l-XAl_xO. The aluminium doped zinc oxide insoluble in water, molecular mass 95.87g/mol, density is 5.8- 6.0g/cm, melting and boiling point (1800^0 C to 2200^OC), odourless substance. The band gap ranging from 3.2 to 3.8eV, Refractive index is 1.9 to 2.1, lattice constant (a=3.2568A^0 and c=5.2l08A^0). Finally, the exciton binding energy of aluminium doped zinc oxide is 50-70MeV [5]. Aluminium-doped zinc oxide (AZO) is hexagonal wurtzite crystal structure form under stable ambient conditions, both zinc (Zn) and aluminium (Al) atoms are tetrahedrally bonded to four oxygen atoms. The material's lattice symmetry, characterized by its 6mm point group, gives rise to both piezoelectricity and pyroelectricity in hexagonal AZO. While AZO exhibits relatively weak piezoelectricity, its ionic nature allows its planes to carry electric charges [6]. The multi-layered AZO thin films can increase the electrical properties of films optimised multi layered AZO films can be designed to achieve low resistivity and high transparency making it suitable for application in solar cells and light emitting diodes. the sol-gel process is one of the attractive techniques for film deposition. The thin films by sol-gel technique have good homogeneity, excellent composition control with good electrical and optical properties [7].

2. Materials and Methods

A. Materials

Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), Aluminium nitrate ($Al(NO_3)_3{\cdot}9H_2O$), 2-Methoxy ethanol ($CH_3OCH_2CH_2OH$), Mono-ethanol amine ($HOCH_2CH_2NH_2$) were obtained from SRL Pvt. Ltd. Ethanol (EtOH) was received from Merck. The above chemicals were used in Aluminium doped zinc oxide thin film synthesis. Aluminium-doped zinc

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oxide (AZO) nano thin films are widely researched due to their excellent electrical, optical, and structural properties. Aluminium-doped zinc oxide (AZO) is a transparent conducting oxide (TCO) where a small percentage of Zn^{2+} ions are replaced by Al^{3+}. This improves the conductivity and sometimes the transparency of the ZnO film. They're used in various applications such as Solar cells (as TCO layer), Gas sensors, Photodetectors, LEDs and display technologies, UV-blocking coatings.

B. Experimental Details

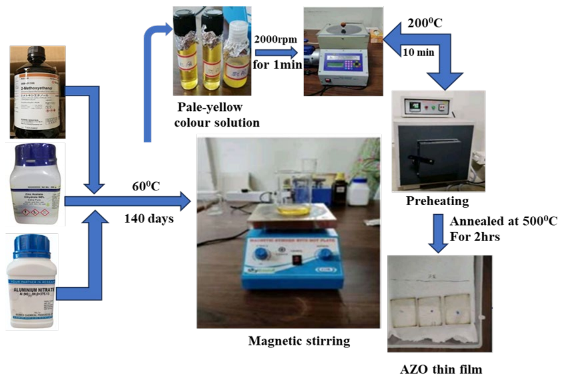

Fig. 1. Step-by-step schematic of nanocrystalline aluminium doped zinc oxide thin films

The multi-step sol-gel spin coating process for synthesizing nanocrystalline Aluminium doped Zinc Oxide (AZO) thin films. This cost-effective method begins with solution preparation, where Zinc Acetate Dihydrate is used as the Zinc precursor and Aluminium Nitrate as the dopant. Varying the amount of Aluminium Nitrate allows for precise control of doping concentrations at 1%, 2%, and 3%. These precursors are dissolved in 2-methoxyethanol, with Monoethanolamine (MEA) acting as a stabilizer to prevent premature precipitation. After stirring at 800 RPM for 30 minutes, the solution is aged to increase its viscosity. The deposition process involves dispensing the sol onto a pre cleaned glass substrate, which is then spun at 2000 RPM for 60 seconds to form a thin, uniform film. The entire deposition to drying process is repeated 10 times to achieve the desired thickness. The films are then pre annealed at 200^0C for 10 minutes and finally subjected to a higher temperature annealing step at 500^0C for 2 hours to fully crystallize the film into a wurtzite structure and optimize its electrical and optical properties [8], [9].

C. Instrumentation

As-synthesized nanocrystalline Aluminium doped Zinc Oxide thin films were characterized for their structural and optical properties. Structural analysis was carried out using X-ray diffraction with a Malvern PANalytical X'Pert PRO MPD system. The SEM analysis was carried out using a JEOL JSM-IT200 equipped with SE and BSE detectors at an accelerating voltage of 15 kV and a working distance of 10 mm under high-vacuum conditions. Non-conductive samples were carbon-coated and elemental composition was determined using an EDS detector (SDD, 30 mm^2). Optical absorbance and transmittance spectra were measured using a UV-Visible-NIR spectrometer (USB4000-XR, Ocean Optics) in the wavelength range 200–1000 nm with a step size of 0.25 nm.

3. Results and Discussion

A. XRD Analysis

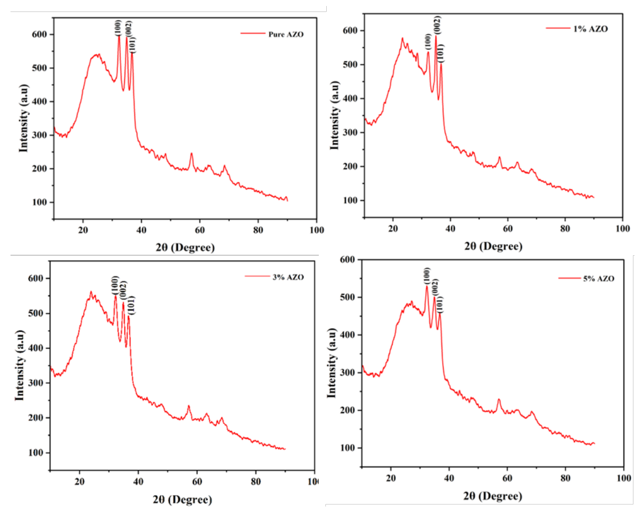

Fig. 2. X-ray diffraction analysis of pure and aluminium-doped zinc oxide thin films

The XRD patterns confirm a polycrystalline hexagonal wurtzite crystal structure, with primary peaks at the (100), (002), and (101) planes. This is consistent with JCPDS card 36-1451. The analysis of the Full Width at Half Maximum and peak intensity reveals a direct correlation with precursor concentration and an inverse relationship with doping concentration. For pure ZnO, an increase in sol concentration leads to a decrease in FWHM and a corresponding increase in peak intensity, indicating improved crystallinity. Conversely, for Al-doped ZnO (AZO) films, an increase in doping concentration causes a decrease in peak intensity, as shown by the drop from above 600 nm for pure ZnO to below 550 nm for the 5% AZO film [10].

B. SEM Analysis

Scanning Electron Microscopy (SEM) analysis of pure and Aluminium doped Zinc Oxide (AZO) thin films on glass substrates reveals a significant evolution in their surface morphology. Initially, pure ZnO films exhibit and will defined surface morphography. However, with the incorporation of aluminium dopants, the films become more crystalline and their

Table 1
Structural parameters of pure and Al doped ZnO thin film

Sample	Crystaline size (D) (nm)	Dislocation density $(1/D)^2 10^{15}$ line/m²	Micro strain10^{-3}	Lattice parameter (A^0) a=b	c	Cell volume $(A)^3$
Pure (0.5M) ZnO	16.96	2.68	0.685	3.19	5.555	49.70
1%ZnO	13.39	5.071	0.8115	3.192	5.184	46.480
3%ZnO	19.08	6.859	0.814	3.192	5.18	46.44
5%ZnO	23.65	4.931	0.814	3.194	5.194	46.62

structure transforms into visible nanowires. As the aluminium concentration continues to increase, the average diameter of these nanowires decreases, directly illustrating the morphological changes induced by the dopant [11].

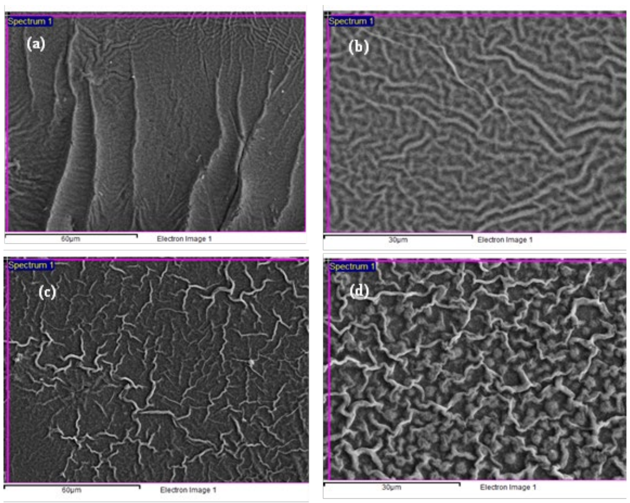

Fig. 3. SEM images of pure and Al doped ZnO thin film

1) EDX Analysis

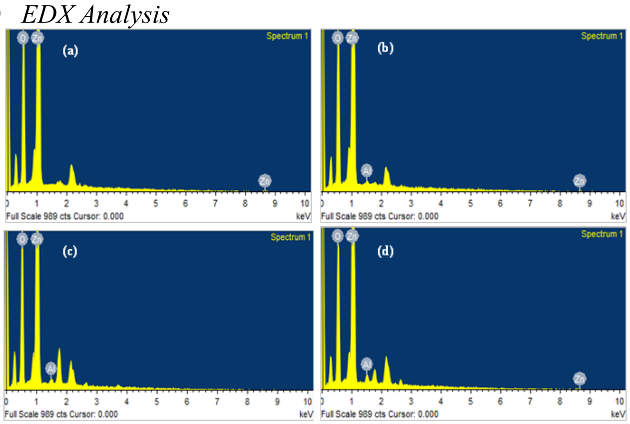

Fig. 4. EDX images of pure and Al doped ZnO thin film

Table. 2
Elemental composition of AZO thin films

Doping Concentration	Element	Weight (%)	Atomic (%)
0% (Pure 0.5 M)	Zinc	76.76	44.71
	Oxygen	23.24	55.29
	Aluminium	-	-
1% AZO	Zinc	75.83	43.64
	Oxygen	23.67	55.67
	Aluminium	0.49	0.69
3% AZO	Zinc	71.97	38.87
	Oxygen	27.22	60.07
	Aluminium	0.81	1.06
5% AZO	Zinc	74.03	41.64
	Oxygen	24.55	56.42
	Aluminium	1.42	1.94

The elemental analysis of the film exposed a composition of 1.94% Aluminium, 41.64% Zinc, and 56.42% Oxygen. As the doping concentration increased, a higher oxygen content was observed. This increase can be attributed to several factors, including the replacement of Zn^{2+} ions by Al^{3+} ions, a reduction in oxygen vacancies, increased oxygen adsorption, and the formation of Al-O bonds. These changes have significant consequences for the film's properties. The increased oxygen content enhances the film's transparency, reduces oxygen vacancies to improve electrical conductivity, and alters the band structure, which affects both its optical and electrical characteristics. Furthermore, the enhanced oxygen content can improve the film's reactivity [12].

C. UV–Visible Absorption Measurements

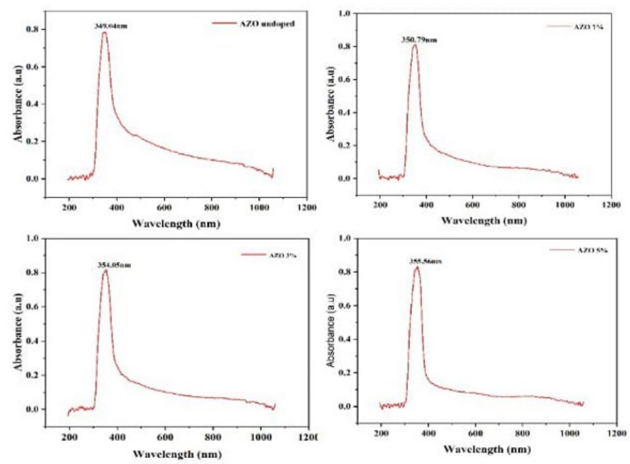

Fig. 5. UV–Visible absorbance spectra of pure and Al doped ZnO thin film

The UV-Vis absorption spectra of pure and aluminium doped zinc oxide (ZnO) thin films in the wavelength range of 300–800 nm demonstrate a clear increase in absorption wavelength (redshift) with rising Al doping concentrations. In the undoped ZnO thin films, the absorption edge occurs at a shorter wavelength, indicating a wider optical band gap. However, as the concentration of Al dopant increases, the absorption edge progressively shifts toward longer wavelengths. This shift signifies a narrowing of the optical band gap, primarily due to the incorporation of Al^{3+} ions into the ZnO lattice. The substitution of Zn^{2+} with smaller Al^{3+} ions introduce additional free carriers and structural defects such as oxygen vacancies, which in turn create localized states near the band edges. These defect states facilitate band tailing and reduce the effective band gap energy, resulting in enhanced absorption at longer wavelengths. This trend confirms the successful tuning of ZnO's optical properties through Al doping, making the material more responsive to visible light and suitable for applications in transparent electronics and optoelectronic devices [13].

1) UV-Vis Transmittance Spectral Studies

UV-Vis transmittance spectra of pure and Al-doped ZnO thin

Table 3
Direct and indirect energy band gap values of pure and Al-doped ZnO thin films

Optical parameters	Wavelength (nm)	Direct band gap (eV)	Indirect band gap (eV)
Pure ZnO	352.95	3.288	3.19
1% ZnO	353.07	3.28	3.183
3% ZnO	354.70	3.26	3.137
5% ZnO	355.33	3.178	3.067

films (300–800 nm) show a gradual decrease in transmittance with increasing Al concentration. Undoped ZnO films exhibit high transparency (>80%) in the visible range, while Al doping results in the generation of free carriers and defect states (e.g., oxygen vacancies), leading to enhanced absorption and scattering. This causes reduced transmittance, indicating that higher Al doping affects the optical clarity of ZnO films, which is critical for transparent optoelectronic application [14], [15].

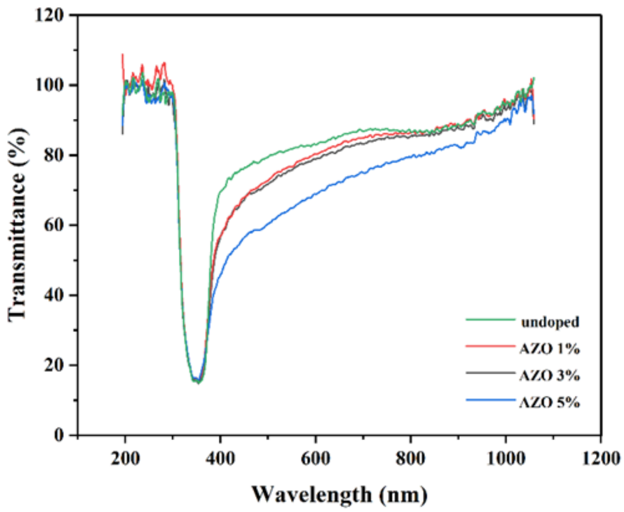

Fig. 6. UV-Vis transmittance spectra of pure and Al-doped ZnO

2) Optical Band Gap

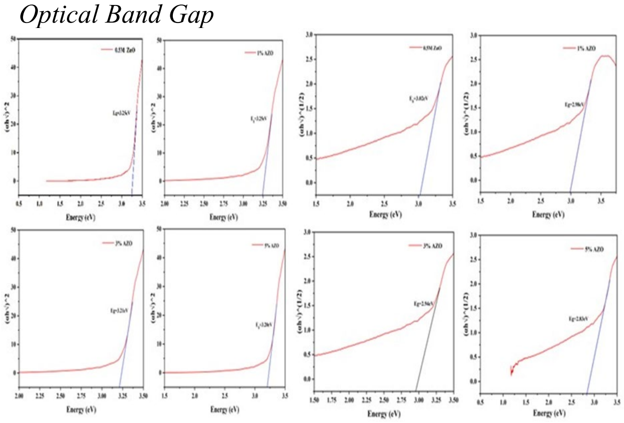

Fig. 7. Tauc Plots for Optical Band Gap Determination of pure and Al-doped ZnO

The optical band gap of pure and Al-doped ZnO thin films was determined using Tauc's relation from the UV-Vis absorption spectra. Both direct and indirect band gaps were evaluated by plotting $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ as a function of photon energy (hν), respectively [16], [17].

The analysis indicates that the band gap decreases with increasing Al doping concentration. Specifically, the direct band gap decreases from 3.25 eV (undoped) to 3.20 eV (highest doping level), while the indirect band gap declines more significantly from 3.02 eV to 2.83 eV. This reduction in band gap is mainly due to the rise in carrier concentration and defect states caused by Al incorporation, which modify the band structure and cause a shift in the absorption edge. These results indicate that Al doping effectively adjusts the electronic properties of ZnO [18]-[20].

4. Conclusion

Aluminium doped ZnO thin films were fabricated by the sol-gel spin coating method. AZO thin films of different doping concentration and aging were obtained by 10 cycle spin coating of Zinc acetate films followed by annealing at a temperature of 500^0C.The obtained values of XRD shows the crystalline size goes on decreases on increase in doping concentration. The same micro strain value and lattice parameter is a 3.19 A^0 and c is 5.19 A^0. Cell volume will be $(46\ A^0)^3$, intensity value decreases as well as increase in the doping concentration. The SEM image revealed that the structure of ZnO become in nano behaviour with Al-doping up to 5%wt, which indicated that the optimum condition makes these materials promising to use in many optoelectronic applications. EDAX results tells the purity of the materials. U-V results shows that the wavelength increases with increase in the doping concentration. Both direct and indirect bond gap values decrease with increase in doing concentration, and it can be absorbed various applications in photovoltaics, window materials, solar cells etc. optical transmittance of pure ZnO thin films is grater than 80% in the visible region and it's decreased with decreasing of Al-doping. The optical direct band gap energy of ZnO thin film decreased from 3.28 eV to 3.178eV with increase in Al doping. Also, optical indirect band gap energy of ZnO thin films decreased from 3.183eV with increase in Al doping. Optical indirect band gap energy of ZnO thin films decreased from 3.183 eV to 3.067 eV with increase in Al doping.

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