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Spin Coated Al Doped ZnO Thin Film for Optical Application; Morphology and Optical Studies

Dr. S. Ashok Raj¹, Dr. P. Prabu², B. Dhivakar³

¹Assistant Professor, PG and Research department of physics, Government Arts College (Autonomous) Kumbakonam, Tamil Nadu

²Principal, Ponnaiyah Ramajayam Polytechnic College, Prist Deemed to be University, Thanjavur, Tamil Nadu

³M.Phil Scholar, Department of Physics, Prist Deemed to be University, Thanjavur, Tamil Nadu

Abstract: The different molar concentration (1-4Mole) of Aluminium Chloride Anhydrite was doped with Zinc acetate dehydrate (ZnO) thin film on glass substrate by spin coating process. The morphological and an optical property of AZO thin films were investigated. The X-Ray diffractometer results show that nature and the successful changes of Al at ZnO site in ZnO thin film. Further with Al doping, the crystalline size, and film thickness were found. Also, SEM results shows that spherical grains sizes of the films. Room temperature photoluminescence measurements were carried out using a spectrofluorometer using an excitation wavelength of 250 nm. PL spectra shows the Al doped ZnO thin films the electrons of Al³⁺ ion will be released when Zn²⁺ is replaced by Al³⁺, so the increase of carrier concentration can improve the conductivity of the thin film. The functional group was confirmed with FTIR spectrum. The optical transmittance measurement was carried out using UV-VIS spectrophotometer. The obtained results of all thin films are discussed in detail and are compared with other experimental results.

Keywords: ZnO-Zinc acetate dehydrate, Al-Aluminium Chloride Anhydrite, FTIR- Fourier Transform Infrared Spectroscopy, UV-VI-Ultraviolet-Visible-near-IR Spectroscopy, PL-photoluminescence.

I. INTRODUCTION

Over the past few decades, Zinc acetate dehydrate (ZnO) is one of the generally considered material among II-VI semiconductors because of its wide band gap (3.2ev) and huge exciton restricting energy of (60 meV), which is twice bigger than that of Gallium Nitride (GaN) (28meV)[1]. Because of peculiar properties, ZnO finds many technological applications in the field of optoelectronic [1], gas sensors [2] and solar cells [3], etc. In the current innovation, indium tin oxide (ITO) and GaN are discovered to be the promising materials for TCO and optoelectronic gadget applications, respectively. However, in last few years, group III components, specifically Al, doped ZnO thin film considered the alternative material of ITO, due to low cost, it also inform that, AZO thin film exhibit the good chemical, mechanical and thermal stability. ZnO is the alternative material for optoelectronic applications when doped with Al[3]. It is realized that, in pure ZnO thin film the observed photoluminescence is attributed to the presence of native defects in the material [4]. It is interesting to research the impact of Al doping and its concentration on the structure of the thin films, which affects the optical and photoluminescence properties. Till now, thin film is prepared using various methods such as spray pyrolysis, sputtering, sol-gel spin coating, pulsed laser deposition (PLD), chemical vapour deposition (CVD) [10-16]. In spite of few studies regarding to the sol-gel method, the sol-gel method has some advantage, such as the easy control of chemical components, and manufacture of thin film at a low cost and its simplicity. In recent time reported that the films with increased optical properties with high sol concentration of 1 mol/ml [5]. Further, it is also reported that, improvement in the defect related photoluminescence with the increase of sol concentration [6]. The obtained results of all thin films are discussed in detail and are compared with other experimental results.

II. EXPERIMENTAL METHODS

The sol-gel spin coating method was used to prepare the ZnO thin film deposited on the glass substrates. Zine Acetate Dehydrate ($ZnCH_3COO_2$) is a Starting material, 2-Methoxy Ethanol(2-MEA) is Solvent, Aluminium Chloride Anhydrite are Dopant, and Diethanolamine (DEA) was used as a stabilizer. The Zine acetate dehydrate were dissolved in 2-Methoxy ethanol (2-MEA) at room temperature to obtain origin solution (A), the mixture was stirred at 60°C and the stabilizer Diethanolamine (DEA) was added in drop wise until the clear solution was obtained. The Aluminium chloride Anhydrite were dissolved in 2-Methoxy ethanol (2-MEA) at room temperature to obtain the dopant solution (B), the mixture was stirred at 60°C and achieved the clear solution. Then solution (A) is added drop wise to the solution (B) in order to obtain the stoichiometry solution of pure (1-4 mol%) Al doped ZnO. The solution were stirred at 60°C for 2 hrs to obtain homogeneous mixture and then aged at room temperature for 48 hrs.

The concentration of the solution was 1 mol/ml and molar ratio of ZnO to DEA was maintained at 1:1 before to the deposition. Glass plate was used as a substrate and it was cleaned with soap solution, Chromic acid at 50°C the glass substrate was cleaned using by soap solution, chromic acid, Distilled water, Acetone. Fresh (1-4 mol%) dopant solution was deposited by spin coating method the sol at a rotation speed of 1000 rpm for 1 minutes and film were heated at 300°C for 10 mint and cooled down to room temperature. The process of coating is repeated 15 times in order to get the desired thickness of the thin film. Finally the film was heated in muffle furnace at 300°C for 2 hrs and cooled down room temperature.

The structural properties of the ZnO thin films were characterized by an X-Ray diffractometer (Cu K α radiation) [7]. The optical transmittance measurement was carried out using UV-VIS spectrophotometer [7]. FTIR measurements were performed in the spectral region 350-1600 cm $^{-1}$ [8]. Room temperature photoluminescence measurements were carried out using a spectrofluorometer using an excitation wavelength of 250 nm [9]. The surface morphology of the films was observed by using scanning electron microscopy [9].

III. RESULT AND ANALYSIS

A. Ftir Analysis

A predominant ester C=O stretching vibration is observed in the range 1879-1899 cm $^{-1}$ as a sharp peak in all four combination. It is quite understandable that there are no significant changes in the Zinc acetate molecule was found due to the moderate temperature value at the reaction condition. Though the molar concentration of Zinc acetate is constant and the concentration of Aluminium chloride Anhydrite are varied and studied. The comparative study of IR spectrum indicates that the first trial with the 1 mole addition of AlCl $_3$ nH $_2$ O in to the 1 mole of Zinc acetate didn't show any sharp or broad peaks in the range of 3000 and above whereas, due to the increasing the molar concentration of AlCl $_3$ nH $_2$ O there will be the appearance of some characteristic sharp peaks in the range of 3000 and above, These comparisons indicates that when increasing the molar concentration of AlCl $_3$ nH $_2$ O, the evaporation of water molecules are hindered during the reaction condition. They will stick with Zinc atom by the co-ordinate covalent bond and showing the significant vibration of O-H stretching on the IR spectrum. Besides, the common Al-Cl and Zn-Cl stretching are also observed in the range of 600-1000cm $^{-1}$. Usually, the co-ordinate covalent bonds are comparatively weaker than the co-valent bonds but the molecule formed during the reaction are kinetically and thermodynamically stable. [9, 10].

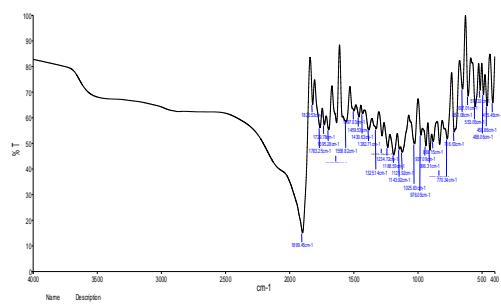


Fig (3.1.1) 1mole

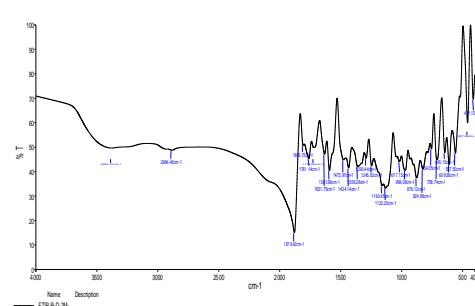


Fig (3.1.2) 2mole

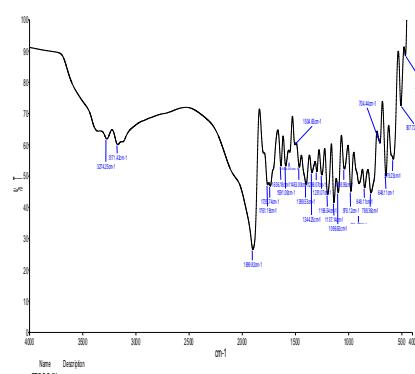


Fig (3.1.3) 3 mole

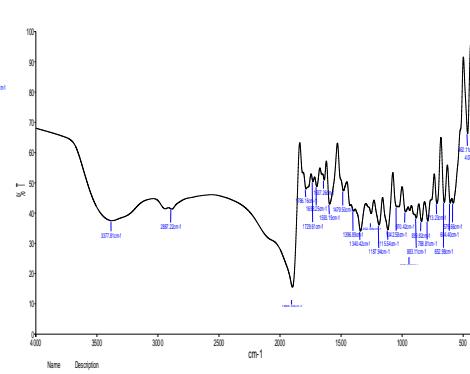


Fig (3.1.4) 4 mole

Fig No.3.1. FTIR for Aluminium Chloride Anhydrite (Al) doped Zinc acetate dehydrate (ZnO)

B. Optical Analysis

1) UV-VIS NIR Spectrum Analysis: UV-Visible Absorption spectroscopy involves measuring the absorbance of light by a compound as a function of wavelength in the UV-Visible range. When a molecule absorbs a photo of UV-VIS light, the molecule is excited from its ground state to an electronic excited state. In other words, an electron is promoted from the HOMO (Highest-energy Occupied Molecular Orbital) of the molecule to the LOMO (Lowest-energy Unoccupied Molecular Orbital) of the molecule. For most conjugated molecules, the photons with the correct amount of energy just happened to visible light. The wavelength which is most strongly observed by a compound is called λ_{\max} . Here Aluminium Chloride Anhydrite (Al) doped Zinc acetate dehydrate (ZnO) thin film shows λ_{\max} as 371.50 nm which invisible region (violet or blue). This is shown in UV absorption spectrum. Optical transmission spectra of an Aluminium chloride dehydrate doped in different concentration with ZnO thin films are shown in (3.2.1) here the wavelength is taken from 300 to 800 nm, this spectra reveals all films exhibited higher transmittance than 85% within the visible region which has sharp absorption edge when an Al concentration increase the absorption becomes broadening indicating the increasing the optical band gap that is the blue shift of the absorption edge of the Al doped ZnO thin films are associated with an increase of the carrier concentration blocking the lowest state in the conduction band it is known as Burstein-Moss effect. [11,12].

The refractive index and thickness of a thin film can be calculated from a simple transmittance spectrum using the Swanepoel method.

a) The Refractive Index

$$n = [N + (N^2 - S^2)^{1/2}]^{1/2}$$

$$\text{Where } N = 2S \frac{T_M - T_m}{T_M T_m} + \frac{S^2 + 1}{2}$$

S – Refractive index of the substrate (1.655)

T_M , T_m – Maximum and Minimum transmittance envelope functions

$T_M(\lambda)$, $T_m(\lambda)$

$N=1.86$

The refractive index of the Aluminium Chloride Anhydrite (Al) doped Zinc acetate dehydrate (ZnO) thin film is

$N=1.86$

b) Thickness of the Thin Film

$$d = M \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}$$

$M=1$ for two adjacent maxima or minima

$n_1=n(\lambda_1)$ and $n_2=n(\lambda_2)$

$$d = \frac{(400 \times 10^{-10})(450 \times 10^{-10})}{2[(1.238 \times 400 \times 10^{-10}) - (1.1238 \times 450 \times 10^{-10})]}$$

$$d = 8.3955 \times 10^{-8}$$

$$d = 0.839 \times 10^{-9} \text{ m}$$

Thickness of the thin film $d = 0.839 \times 10^{-9} \text{ m}$

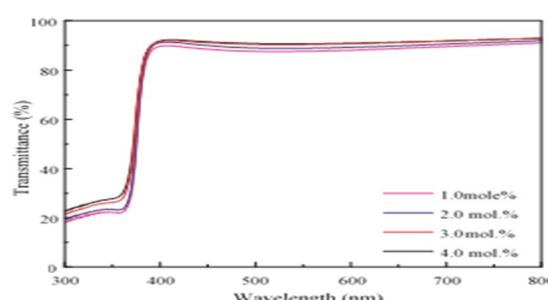


Fig No.3.2.1 UV for Aluminium Chloride Anhydrite (Al) doped Zinc acetate dehydrate (ZnO)

- 2) *Photoluminescence Analysis:* Photoluminescence analysis is a very conventional and an effective tool for characterizing and evaluating luminance material. The Photoluminescence spectra of AZO thin film for different doping concentration was recorded at room temperature which is shown in fig () from these we observed two distinct peaks for all doping concentration in near band age emission and deep level emission the near band age peeks are due to free exciton recombination and the deep level emission are related to oxygen defects [13, 15] when increasing the Al concentration the orange colour emission peaks are disappeared because of Al ions exist in Al^{3+} and Zn ions in Zn^{2+} , when Al is doped with ZnO Al ions can consume residual O ions and decrease the concentration of interspatial oxygen in the AZO thin films.

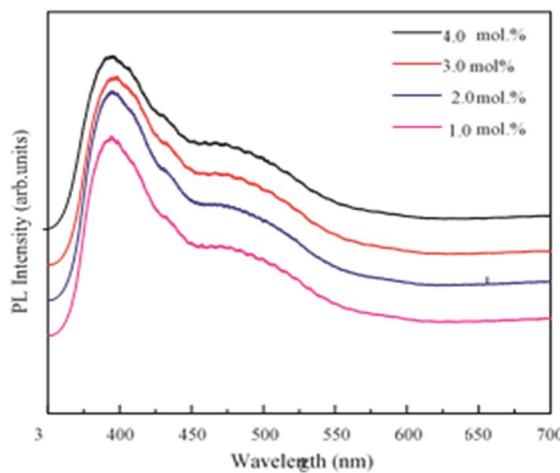


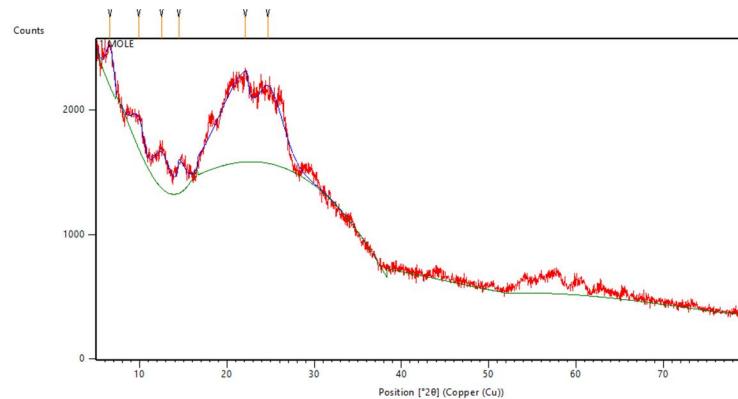
Fig No.3.2.2 PL for Aluminium Chloride Anhydrite (Al) doped Zinc acetate dehydrate (ZnO)

IV. MORPHOLOGICAL STUDIES

A. Structural Studies

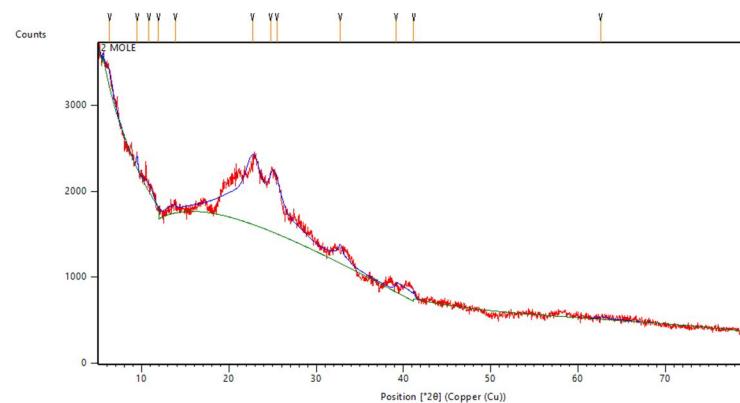
The crystal structure of the as deposited ZnO: Al films with Different molar concentration (1,2,3,4 mol%) were studied using X-ray diffraction technique. The XRD patterns obtained for the films deposited from the starting solutions having different solvent volumes are shown in the fig (4.1). The diffraction peaks appeared in the spectrum have been identified and indexed using the standard diffraction data (JCPDS card no: 36-1451). The interplanar spacing (d) confirms that the deposited films are of ZnO with hexagonal structure.

The X-ray diffraction profiles clearly showed that all the films have preferential orientation along the (002) plane with hexagonal wurtzite structure irrespective of the solvent volume. Even though there is no significant impact of solvent volume on the preferential orientation plane, the degree of preferential orientation growth varies with the change in the solvent volume. The preferential orientation is caused by the minimization of the internal stress and surface energy and it is well known that in a ZnO crystal the (002) orientation has the lowest surface energy density. [16,17].



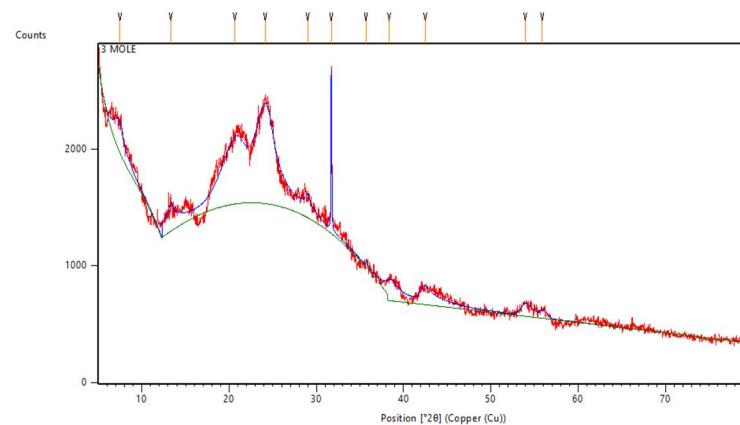
Pos. [$^{\circ}2\theta$]	Height [cts]	FWHM Left [$^{\circ}2\theta$]	d-spacing [Å]	Rel. Int. [%]
6.5724	210.93	1.0915	13.43780	46.39
9.8877	167.85	1.7643	8.93830	36.92
12.4947	201.27	2.0207	7.07857	44.27
14.4510	196.44	0.2515	6.12444	43.20
22.1137	454.67	7.1144	4.01651	100.00
24.6846	420.75	3.8725	3.60370	92.54

Fig 4.1 (a) XRD pattern of ZnO:Al films prepared from different molar dopant concentration(mol) 1 mol %



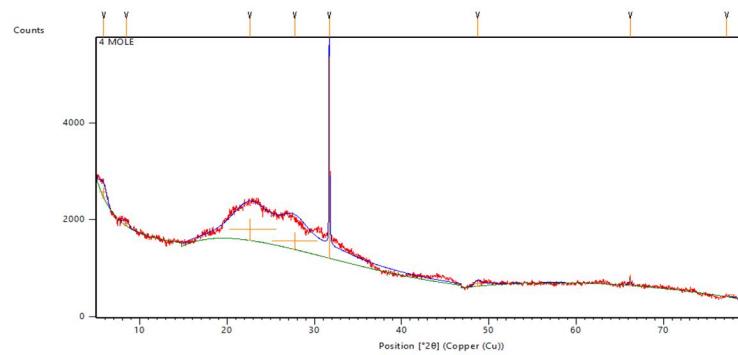
Pos. [$^{\circ}2\theta$]	Height [cts]	FWHM Left [$^{\circ}2\theta$]	d-spacing [Å]	Rel. Int. [%]
6.3119	129.58	0.7590	13.99173	7.32
9.4484	94.49	0.2007	9.35290	5.34
10.8090	61.71	1.0867	8.17842	3.48
11.9080	73.20	0.3740	7.42600	4.13
13.8345	109.54	2.9344	6.39593	6.19
22.6954	619.54	3.1154	3.91486	34.98
24.7751	511.90	2.4487	3.59075	28.91

Fig 4.1.2 (b) XRD pattern of ZnO:Al films prepared from different molar dopant concentration(mol) 2 mol %



Pos. [°2θ]	Height [cts]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]
7.4774	187.66	1.5923	11.81328	14.26
13.3067	145.96	1.4690	6.64839	11.09
20.6660	250.18	3.5252	4.29449	19.01
24.1408	594.93	3.5572	3.68364	45.21
28.9863	95.39	0.8024	3.07795	7.25
31.6885	1316.01	0.0520	2.82137	100.00
35.6939	68.94	0.1082	2.51341	5.24
38.3519	228.47	0.9845	2.34511	17.36
42.4906	130.99	1.2301	2.12578	9.95
53.9631	70.10	1.2814	1.69780	5.33
55.8862	45.46	0.8942	1.64385	3.45

Fig 4.1.3 (c) XRD pattern of ZnO:Al films prepared from different molar dopant concentration(mol) 3 mol %



Pos. [°2θ]	Height [cts]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]
5.8315	209.80	0.9967	15.14316	5.04
8.4143	74.04	0.8311	10.49985	1.78
22.5926	462.94	4.7577	3.93245	11.13
27.7198	354.33	5.3315	3.21563	8.52
31.6848	4159.46	0.0537	2.82169	100.00
48.6962	105.55	0.9943	1.86839	2.54
66.2140	223.65	0.1744	1.41028	5.38
77.2491	83.32	0.0842	1.23403	2.00

Fig 4.1.4 (d) XRD pattern of ZnO:Al films prepared from different molar dopant concentration(mol) 4 mol %

1) Structural Parameters

The following are the formula used for calculating structural parameters.

$$D = 0.94\lambda/\beta \cos\theta \text{ (Scherrer formula)}$$

D → The size of the crystallites.

λ → The X-ray wavelength.

θ → The maximum of Bragg diffraction peak (in radians).

β → Peak's full width at half maximum (FWHM).

$$D = \frac{0.94 \times 1.5418\text{\AA}}{31.6848 \times \cos(15.8)}$$

$$D = \frac{1.44}{0.9638}$$

$$D = 14.94\text{\AA}$$

Different molar concentration (mole)	D Nm	$\delta \times 10^{14}$ Lines/m ²
1	20.56 Å	0.706
2	46.96 Å	0.135
3	25.7 Å	3.6352
4	14.94 Å	3.35

B. Morphological Properties

Fig (4.2) shows SEM micrographs that were taken at resolution of (a) 5 μm(b) 10 μm(c) 100 μm(d) 100 μm for 1,2,3 and 4 molar dopant concentration, respectively. Fig (a) shows uniform plan fill with some grains from fig b, c and d shows when the doping concentration increase the density of the incorporate crystals were increased on the surface of the film and these grains are more or less cover the substrate uniformly. The SEM micrograph portraits that the agglomerated practical size decrease with increasing the Al concentration after the annealing treatment. The Al doped ZnO film having some fractures on the surfaces, this fracture properly results from the different in thermal expansion coefficient between film and substrate during cooling.[18].

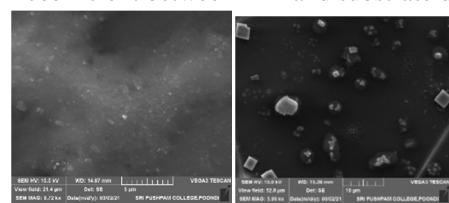


Fig (a) 1 mole

Fig (b) 2 mole

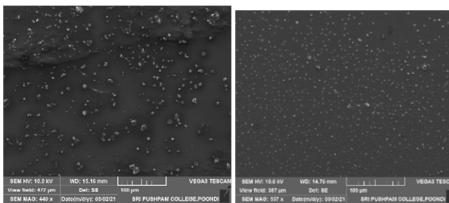


Fig (c) 3 mole

Fig (d) 4 mole

Fig. 4.2 Shows Morphological image (SEM)

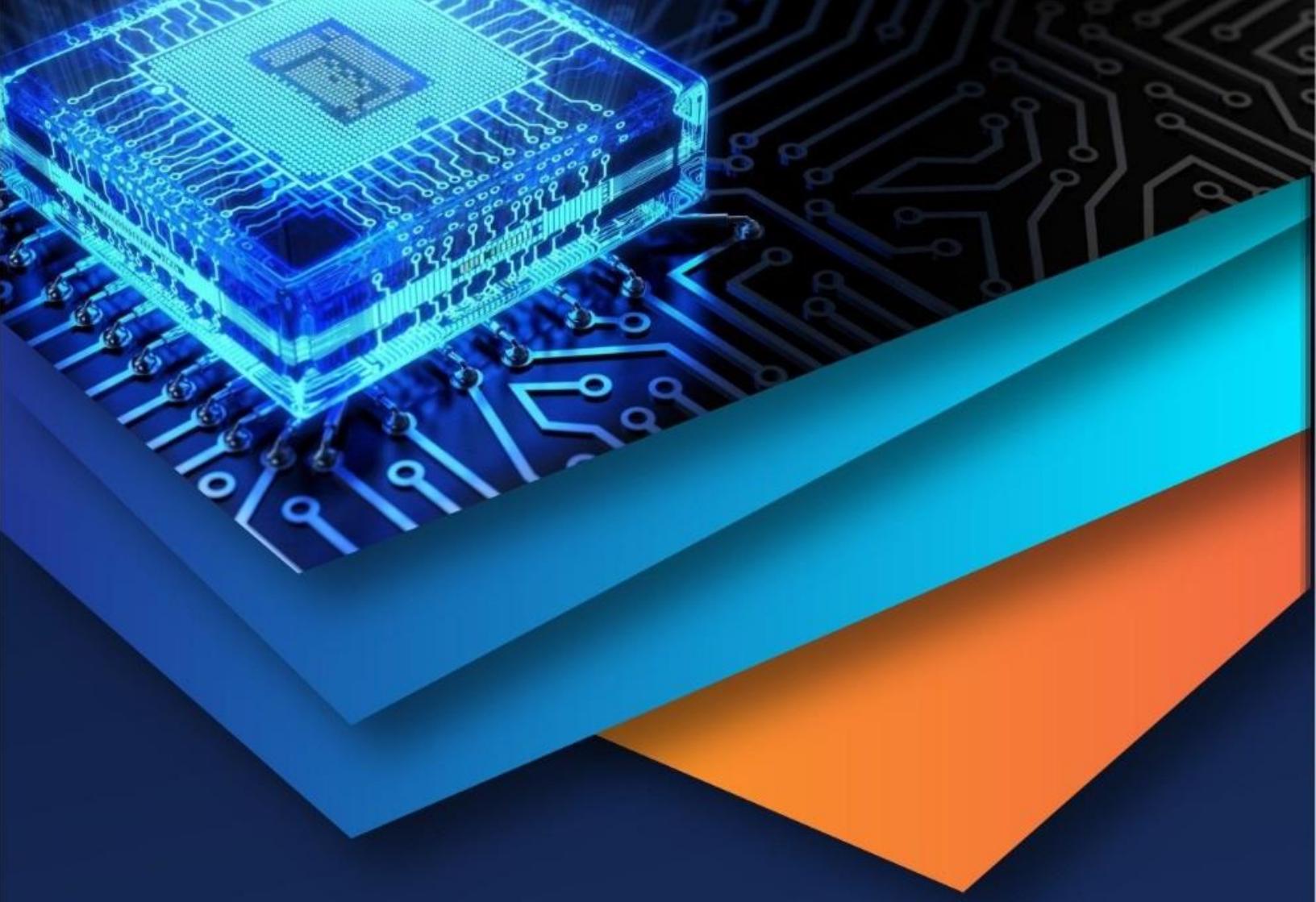
V. CONCLUSION

For the purpose of photonic applications AZO thin films was coated in glass substrate with different doping concentration by sol-gel spin coating method. An optical and Morphological studies were carried out for coated thin films. From FTIR analysis we confirmed the functional group of coated thin film and we observed Al atoms are sticks with Zinc by the covalent band and produced significant O-H stretching on the IR spectrum. The optical characteristic of the coated thin film were confirmed with UV-VIS NIR spectrum analysis, when the doping concentration the optical band gap of the AZO thin films become broader and the transmittance reaches 85% in these character s are very important for an opto electronic device like LED. From the morphological studies we confirmed the structure AZO film and an estimated the grain size of the coated films for different doping concentration. From SEM micrographs the agglomerated practical size were decreases with increasing the Al concentration after the annealing treatment.

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