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Structural, Morphological and Optical Properties of Pure and Mg Doped ZnO Thin Films Using SILAR Method

S. Dineshraj[1], M. Karunakaran[2], K. Kasirajan[3], V.Annalakshmi[4], S. Maheswari[5]
[1, 2, 3, 4] Department of Physics, Alagappa Government Arts College, Karaikudi – 630 003, India.
[5]Department of Physics, Caussanel College of Arts and Science, Muthupettai – 623 523, India.

***Abstract:** In the present study, undoped and Mg doped ZnO thin films were prepared by modified SILAR method. The coated films were annealed at 350^{0}C. The structural, surface morphological and optical properties were studied by X-ray diffraction, scanning electron microscopy, and UV– vis spectroscopy, respectively. The hexagonal wurtzite structure formation with preferential orientation along the (002) plane was confirmed from structural analysis. The surface morphology of the undoped and Mg doped ZnO thin films have the some nanorods and flower like shapes. The sizes of the grains are found to be in the range between 400 and 450 nm. The optical properties of the thin films were estimated using the transmission spectrum in the range of 200–1100 nm. The optical band gap energy of undoped and Mg doped ZnO thin films was found to be 3.2 and 3.4 eV.*

***Keywords:** Zinc Oxide, Thin Films, Structural Studies, Morphological Studies, Optical Properties, Optical band gap.*

I. INTRODUCTION

Diluted magnetic semiconductors (DMS) have attracted much interest due to their potential application in Spintronics devices, such as spin-valve transistors, spin light-emitting diodes, non- volatile memory, logic devices, optical isolators and ultrafast optical switches [1]. In DMSs, transition metal doped II–VI and III–V semiconductors have been studied extensively [1]. One of the materials at the focus of much attention is the wide band gap wurtzite phase zinc oxide, a II–VI semiconductor, a well-known piezoelectric and electro-optic material with wide direct band gap (~3.37eV) and large exciton binding energy (60 meV) in which some of the zinc can be substituted by the manganese ions responsible for the ferromagnetic coupling [2,3].ZnO doped with Mn has also been considered as an ideal material for short wavelength magneto-optical applications due to its wide band gap and the thermal solubility of Mn in ZnO [4].Since the ionic radius of Mg2^{+} (0.57 Å) is similar to that of Zn2^{+}(0.60 Å), the latter can be substituted by the Mg2^{+} ion resulting in a wide range of solid solution [5]. However, the thermo dynamic solubility limit of MgO in ZnO is only about 4% as suggested by the phase diagram of MgO–ZnO binary system [6]. There are a number of reports on the growth of MgxZn1xO thin films using various techniques such as pulsed laser deposition (PLD) [7,8], laser ablation-molecular beam epitaxy (LA-MBE) [9], and radio frequency(rf) magnetron sputtering [10-11]. The substitution limit was found to be different for different techniques which are about33% for PLD [12], 49% for molecular beam epitaxy (MBE) [13], and metal organic vapor phase epitaxy (MOVPE) [14]. Ohtomo et al. [15] have found that the thermodynamically MgO is soluble in MgxZn1xO up to a value of x = 0.15, while recently Ryoken et al. [16] reported the value to be in the composition range 0.12 < x < 0.18. There are very few studies on the sol–gel MgxZn1xO thin films where substitution up to 20%, 33%, and 36% were reported [17–19]. Most of the reported work mainly correlates with the ferromagnetic properties of Mn-doped ZnO nanostructures and its origin. Thus, much work is needed to address the structural and optical properties of Zn1-xMnxO owing to a growing interest of the magneto-optical effect. Pradhan et al. showed that Zn1−xMnxO films grown at a substrate temperature of 500 °C exhibited room temperature ferromagnetism and beyond 500 °C the crystalline quality of the film increased at the expense of a decrease in the magnetization due to the formation of Mn related clusters [20]. Heo et al. studied the effect of post deposition annealing on the ferromagnetic properties of Mn implanted ZnO film deposited on sapphire substrate at 400 °C [21]. A significant enhancement in the magnetization of Zn1−xMnxO film with an increase in annealing temperature (<600 °C) was observed and attributed to the improvement in crystalline quality [21].

II. EXPERIMENTAL PROCEDURE

Experimental details MZO thin films were grown on glass substrates employing SILAR method. Thin films of different thicknesses were deposited onto glass substrate. These substrates were precleaned well with distilled water, Iso-propyol alcohol and acetone before undertaking deposition. The deposition bath comprises of Zinc sulphate (ZnSO4) 1.5 M is dissolved in 20 ml of water and varied percent of (1.5 M) magnesium sulfate (MgSO4) and 3 M sodium hydroxide (NaOH). The pH was adjusted by using NaOH or ammonium hydroxide. The substrates were immersed in the experimental bath for less than 15 s. Initially, sodium zincate formed in the bath is adsorbed onto the substrate. Subsequently, it is converted to ZnO in the second immersion in hot water kept at 95 ^{0}C. The time of immersion in first and second dipping are maintained as 10 s. The intervals between the dips are also kept as 10 s. The films were annealed at 350 ^{0}C for 5 hours uniformly before characterization.

The reaction mechanism for the formation of Mg doped ZnO Thin films is given below

$Mg\ (So_4.H_2O) \rightarrow Mn^{2+} + So_4^{2-}$
$Zn\ (So_4.7H_2O) \rightarrow Zn^{2+} + So_4^{2-}$
$Na\ OH \rightarrow Na^{+} + OH^{-}$

The formation of Mg doped ZnO thin films process could be expressed as

$Mg\ (So_4.H_2O) + Zn\ (So_4.7H_2O) + Na\ OH \rightarrow Mg\ ZnO + 2NaSo_4 + H_2O$

Characterizations of the samples were performed at room temperature. X-ray diffractometer (XRD 6000, Shimadzu japan) with CuKa line wavelength 1.5406 A ° was used to analyze the structure. Surface morphological study was carried out using a scanning electron microscopy (Philips Model XL 30, USA). For optical characterization, the transmission spectra of Mg doped ZnO thin films annealed at different temperatures were recorded using a UV-Vis spectrophotometer (Varian Cary 500 Scan).

III. RESULT AND DISCUSSION

A. *Structural Studies*

Figure1 (a).shows the typical X-ray diffraction pattern obtained for the unoped ZnO. The XRD profiles, showing hexagonal wurtzite structure, were matched well with the values taken from JCPDS diffraction file (No. 89-0511). The doping molar concentration of the films produces a considerable improvement in crystallinity, showing more intense and sharper XRD peaks. The predominant peak at 35.76^0 indicates that ZnO is preferentially oriented along (002) plane. The sharpened X-ray line profile and higher intensity of (101) plane is observed at undoped ZnO. The structural parameters such as of Crystalline size (D), Dislocation density (δ) and Micro strain (ε) were calculate from the XRD Pattern [22].

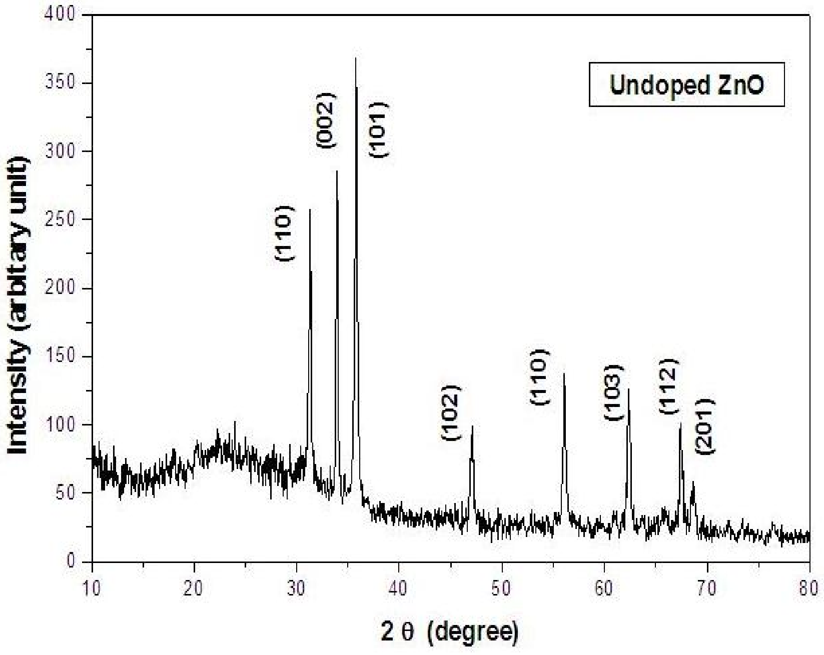

Figure 1 (a). XRD pattern of pure ZnO

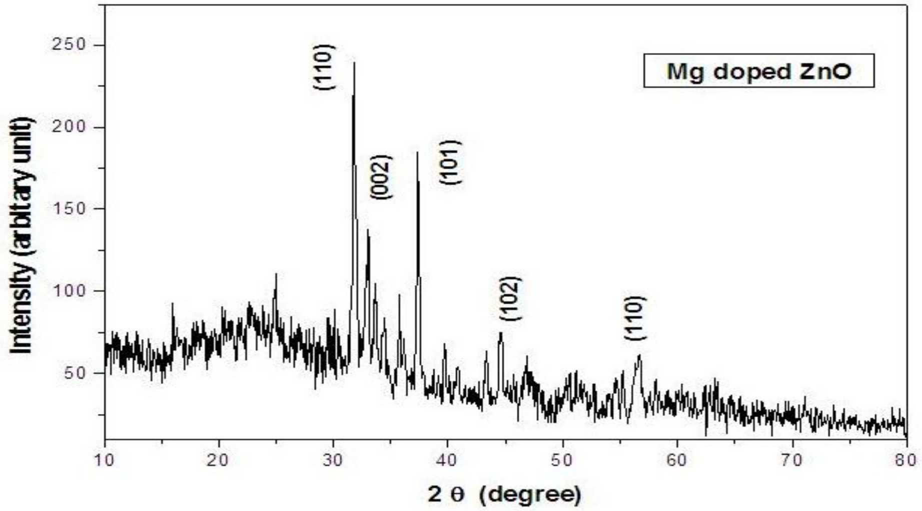

Figure 1 (b). XRD pattern of Mg doped ZnO

Figure.1.(b) shows the XRD pattern of Mg doped ZnO Thin films. The diffraction patterns reveal good crystalline quality without any appreciable changes from pure ZnO films and are genuinely polycrystalline with a hexagonal wurtzite structure. These results imply that there are no secondary phases such as a magnesium cluster or oxides. It also shows that the high intense peak is oriented along the c-direction and the corresponding peak is (*110*). Hence, this crystal ZnO film with stronger (*002*) preferred orientation will increase the Hall mobility [23]. Also Crystallized ZnO seed layers have a hexagonal crystal structure which was confirmed by the main diffracted peaks for the (*002*) (*1 0 1*) and *(1 0 2*) planes [24]. The observed‘d’ spacing values are in good agreement with the standard values of ZnO. Hence the overall structure of the doped films remains unchanged with the introduction of Mg. Also, no additional peaks of Mg or its phases are observed in the XRD spectrum and it suggests that the doped Mg atoms are incorporated into the ZnO thin film. The calculated values of crystallite size, Dislocation density and Micro structures are given in table1.

Material	2θ	Crystallite Size D (10^{-9}m)	Dislocation density(δ) 10^{14} lines/m	Micro Strain ε x 10^{-3} Lines^{-2}m^{-4}
ZnO	34.76	32.923	8.584	1.338
Mg doped ZnO	30.26	22.982	16.386	2.467

Table 1: Structural parameters of pure and Mg doped ZnO thin films

B.Morphological studies

The SEM photographs provide the nature of the surface (i.e) uniformity, smoothness and cracks, the nature of the grains (i.e) shape of particle and grain size. In these studies the surface morphology of prepared samples like undoped and Mg doped ZnO were carried out using SEM and are discussed. Figure 2(a) and (b) shows the SEM micrographs of undoped and Mg doped ZnO with the same magnification of (1µm). SEM image of pure ZnO shows the spherical particles with the collection of nano rods. Figure 2 (b) shows some nano rods and flower like shapes. This kind of micro structure is desirable for sensor applications.

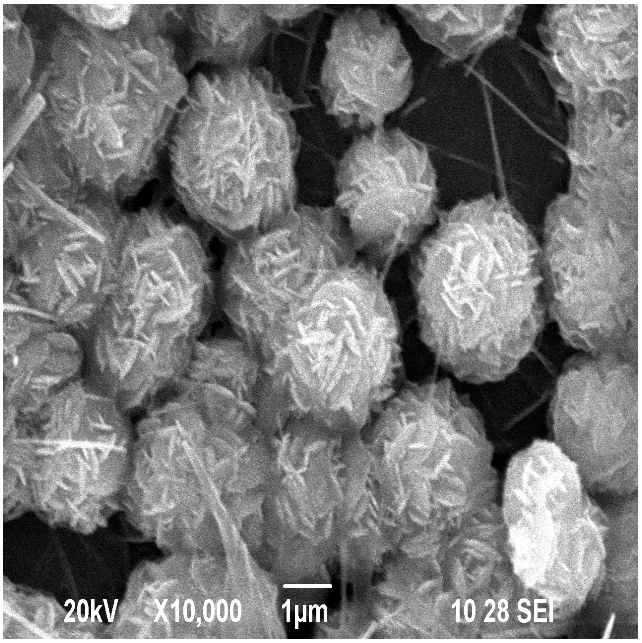

Figure 2 (a). SEM image of pure doped ZnO

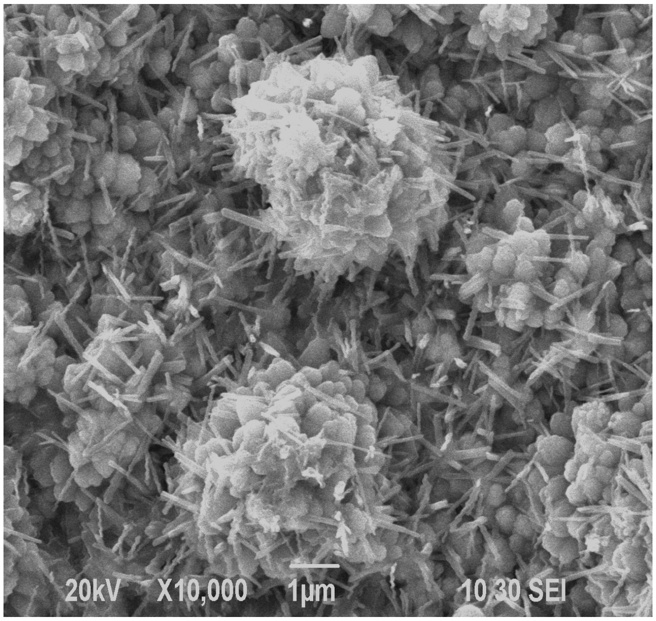

Figure 2 (b). SEM image of Mg doped ZnO

C. Optical studies UV-Visible Spectroscopy

The transmittance spectra depict a high refractive index in the range of low absorption with a sharp fall of transmittance at the band edge implying the good crystal quality of the undoped and metals doped ZnO nano structured films. High transmission >90% transmittance is achieved at the far infrared region whereas the transmittance is found to decrease when ZnO films are doped with ‘Mg’ content and the transmittance still decreases for all the cases. The undoped ZnO films show 70 to 80% optical transmission in the visible range. As it is clearly seen, the transparency of is decreases when the dopants are added. The result is in good agreement with previously reported data. The undoped ZnO has a transmittance 89% in the blue region of the visible spectrum and the transmittance is found to have red shift. The transmittance value of Mg doped ZnO thin film is observed at 68 % in visible region as shown in fig.3. It is also confirmed the Mg ions incorporated with ZnO matrix. The Mg atoms slights decrease the optical properties of Mg doped ZnO thin films.

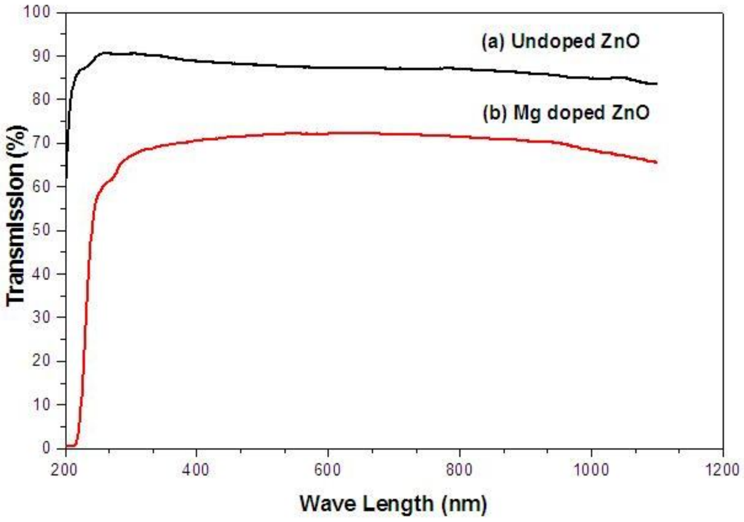

Figure 3. Transmission spectra of pure and Mg doped ZnO thin films

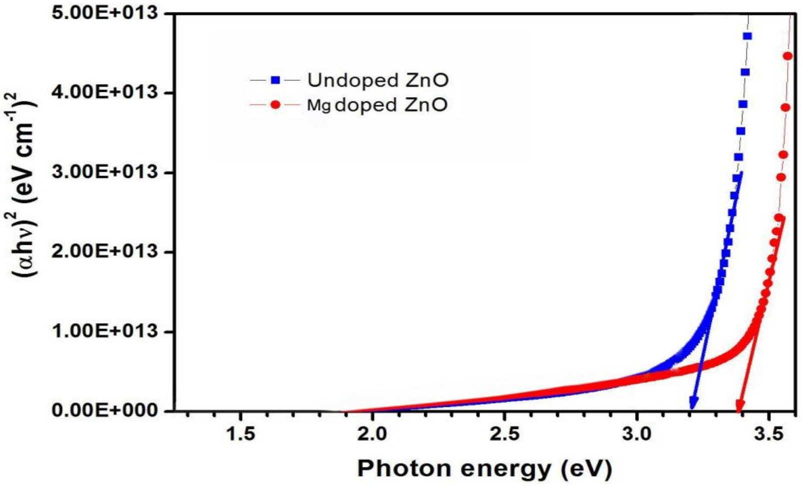

Figure 3. Taugh plot of pure and Mg doped ZnO thin films

Fig. 4 shows the variation of $(\alpha h\nu)^2$ with the photon energy for undoped and metals doped ZnO thin films deposited on glass substrate. The absorption coefficient (α) and incident photon energy (hν) can be related as [25]

$$\alpha = \frac{A(h\nu - E_g)^m}{h\nu}$$

Where A is a constant and E_g is the band gap of the material. From the above equation, it is clear that the plot of $(\alpha h\nu)^2$ versus hν . The band gaps are found to be 3.2 eV for ZnO thin films and it is decreased with doping metals in ZnO films. The optical band gap value increased to 3.4 eV as Mg atoms are incorporated in ZnO matrix. The Mg doped ZnO thin film band gap is about 3.4 the band gap increase may be due to increase of metal ion concentration in doped ZnO thin films.

Materials	Direct Energy Band Gap (eV)
Undoped ZnO	3.2
Mg doped ZnO	3.4

IV. CONCLUSION

Mg doped ZnO thin films were prepared by employing SILAR technique. The films are annealed in air to improve the crystallinity and grain sizes. The observed structural, optical, electrical, morphological and compositional properties were plausibly explained in this work. The presence of the XRD pattern represents that the deposited films were found that polycrystalline in nature with hexagonal wurtzite structure. Also the micro structural parameters such as crystallite size, strain, dislocation density, were estimated. The SEM results represented that the film annealed at 5 h, have homogeneous surface with nanorods and flower like shaped grains. The optical band gap energy of undoped and doped ZnO thin films was found to be in the range between 3.2- 3.4 eV. This kind of micro structure is desirable for sensor applications.

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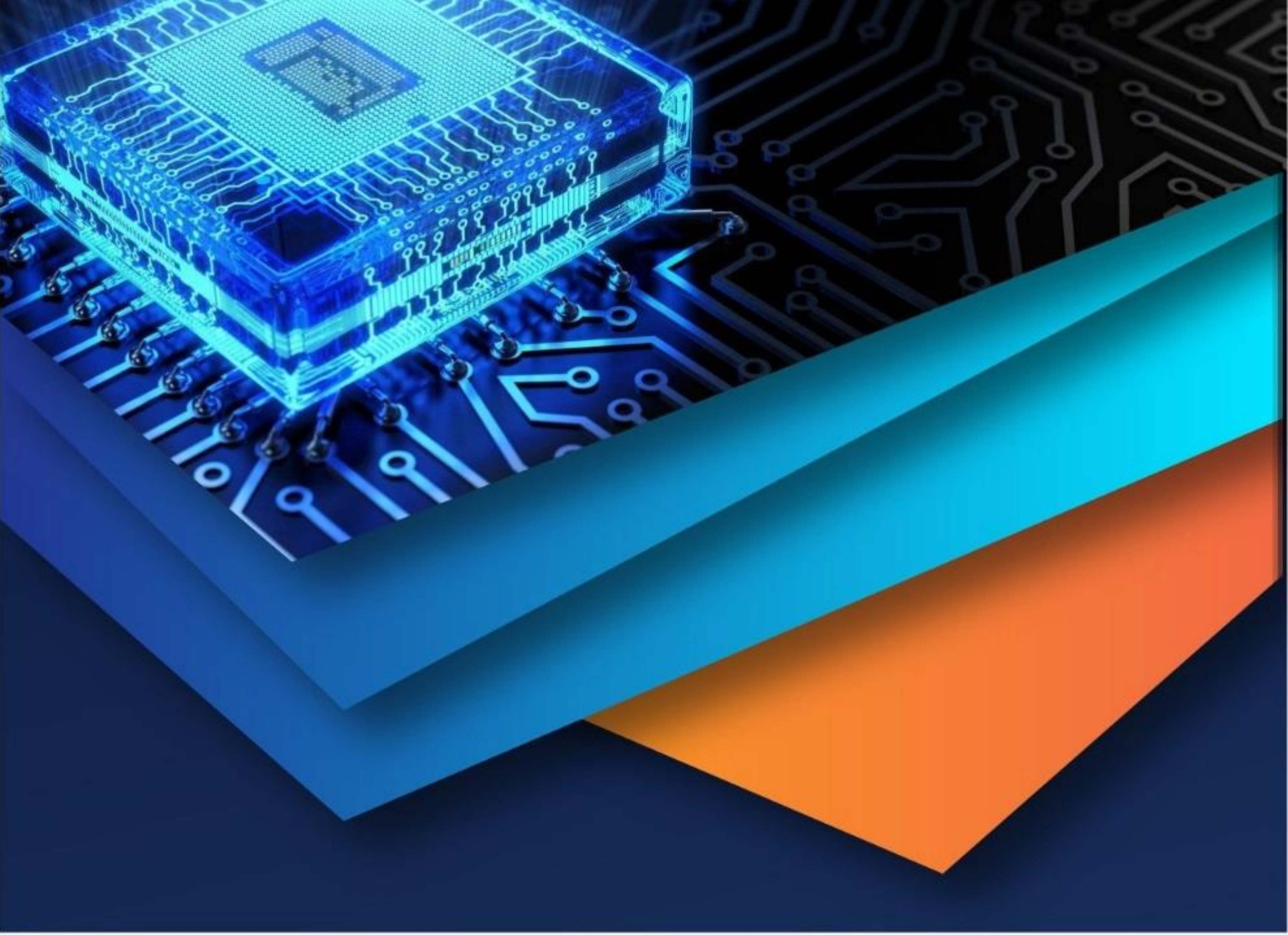

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