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Influence of Oxygen Partial Pressure on Structural and Optical Properties of In_2O_3 Thin Films

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***Abstract*: In_2O_3 thin films were grown by PLD technique, under different oxygen partial pressures (0 mTorr to 1 mTorr). Structural, chemical and morphological characterization was performed using GIXRD, SEM, SAED, EDS, Raman spectrometer and Stylus profilometer. The GIXRD and SAED patterns have revealed polycrystalline with cubic bixbyite structure. Raman spectra of the deposited film have shown the peak of In_2O_3 at a wave number of 303 cm^{-1}. Photoluminescence spectra confirm the variation of defect states with the increase in oxygen partial pressures and these films show primary blue emission.**
***Keywords*: Metal oxide thin films; Pulsed laser deposition; Photoluminescence etc.**

I. INTRODUCTION

Identifying this Volatile Organic Compounds (VOC), Nanostructured semiconductors are promising materials for gas sensing applications, Because of their portability and surface to Volume ratio is comparably very large than bulk materials, and one can easily tune their conductivity by varying deposition parameters. Chemical gas sensor is a device/material that reacts with a gas and changes the electrical (generally) or another property of the material. The change is mostly proportional to the concentration of the gas in the ambient environment of testing. Metal oxides as chemical sensors have been in research and commercial application since long due to their chemical reactions with the redox gases and changing the electrical parameters of the sensing material. Nanomaterials with varied properties due to their size have shown tremendous improvements in chemical sensing features of metal oxides.

In_2O_3 being a transparent conducting metal oxide, it has been in the study for many technical applications like electro-optic modulators, in the electronic field as window heater, solar cells, electrochromic mirrors and flat-panel displays. In addition, nanostructures based on indium oxide are promising device materials for chemical sensors. This metal oxide, when heated to higher temperatures, is expected to absorb oxygen from the environment. This oxygen takes away the conduction band electrons of the metal oxide making it less conducting. When this metal is introduced into a reducing environment of the testing gas, the oxygen ions are removed from the surface and lead to an increase in the conductivity of the film surface. Thus oxygen plays an important role in the sensing mechanism of the metal oxide.

The Indium oxide thin films are prepared by different synthesis techniques such as spray pyrolysis, Thermal evaporation, Rf sputtering, electron beam and pulsed laser deposition [1-7].

In this investigation, we deposited In_2O_3 thin films by Pulsed Laser Deposition (PLD) technique under different oxygen partial pressures (0 mTorr to 1 mTorr). Structural, chemical and morphological characterization was performed using Glancing Incidence x-ray diffraction (GIXRD), Scanning Electron Microscope (SEM), Selected Area Electron Diffraction (SAED), and Energy-dispersive X-ray Spectroscopy (EDS), Ramana spectroscopy and Stylus profilometer. The studies show good phase formation, the nanometric grain structure of deposited films. And we studied oxygen partial pressure effect on the optical, electrical and the gas sensing properties of deposited films.

II. EXPERIMENTAL

A. Materials and Method to prepare In_2O_3 thin films:

In the deposition of In_2O_3 thin films, to achieve desirable film growth the first priority goes to the cleaning of the substrate. The Silica (100) substrates are cleaned by immersing in double distilled water [8]. 3 parts of concentrated sulfuric acid and 1 part of 30% hydrogen peroxide solution is used to clean organic residues of substrates. The substrates are soaked in chromic acid and are then cleaned in a detergent solution with an ultrasonicator for 20 mts. After thoroughly washing with double distilled water again, these substrates are rinsed with acetone and dried in nitrogen gas atmosphere in the tube furnace to get moisture free substrates.

In_2O_3 thin films are grown on Silica (100) substrates by PLD technique. The vacuum chamber is evacuated by the Turbomolecular pump. The source material In_2O_3 of 99.999% purity is pelletized by taking the fine powder from Sigma-Aldrich Chemicals. The well-grounded powder is heated in air at 800 ^oC for 10 h and the prepared powder is cold pressed at 10 ton load and made the pellet

of 2 cm diameter and 2 mm thickness. This pellet was sintered at 800 ^{o}C for 12 hours [9].

The In_2O_3 thin films were deposited on Silica (100) substrates by PLD, with a miniature heater to maintain substrate temperature at 673 K. A KrF (248 nm) excimer laser (Lambda Physik COMPex) operating at a pulse repetition rate of 10 Hz and a 220 mJ of energy is used for deposition. The energy density of the laser beam is kept at 2 J/cm^2. Initially, 2x10^{-6} Torr base pressure is maintained in the vacuum chamber. To maintain an oxygen atmosphere in the chamber, a needle valve is used to admit oxygen into the chamber. The final pressure is maintained at oxygen ambient pressure of 0.0 mTorr to 1 m Torr) maintained inside the vacuum chamber.

B. Characterization Techniques.

All deposited films are characterized structurally using GIXRD (Bruker D8 Advance, USA). GIXRD is carried out using nickel-filtered Cu-Kα radiation (λ= 0.15418 nm) under 40 kV voltage and a current of 30 mA. For all the measurements, Diffraction space is spanned over a 2θ range of 15–80^{o}, to investigate the structural and crystallographic phases present in the films. We estimated crystalline parameters by using Debye Sherrer formula. Employed the Stylus profilometer to estimate thickness of deposited thin films.

The film morphology is examined using SEM (Carl ZEISS EVO 18, Germany). The elemental composition is recorded with Energy-dispersive X-ray spectroscopy (EDS) attached with SEM. The SAED pattern was collected from TEM apparatus which was carried out using double-tilt liquid-nitrogen-based low –temperature holder (GATAN-636MA) in a Tecnai G2-20 TEM operator at 200 kV monochromatized photon source Al Kα hυ =1486.6 eV. Raman spectroscopy carried was out on (Renishaw, UK) in the wavenumber range 100 –700 cm^{-1} . The phonon lifetime (τ) can be derived from Raman spectra via the energy-time uncertainty relation.

Optical studies were done by Uv-Vis spectrophotometer (UV-Vis 3000, Lab India Analytical Instruments, India). Photoluminescence (PL) measurements were performed on Jobin Yvon Fluorolog-3 Spectrofluorimeter.

III. RESULTS AND DISCUSSIONS

A. Structural Characterization

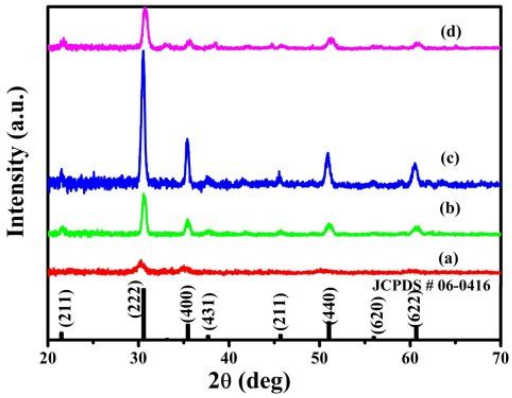

Figure 1 GIXRD of In2O3 thin films under different Oxygen partial pressures (a) 0.00 mTorr, (b) 0.03 mTorr, (c) 0.3 mTorr, (d) 1 mTorr.

Table 1 Crystallite parameters of In_2O_3 thin films deposited under different Oxygen partial pressures.

Oxygen pressure (mTorr)	Lattice constant (a) (A^{o})	Crystallite size(D) (nm)	Strain (ε)	Dislocation density (δ)	Thickness (nm)	Number of particles (N) x 10^{18}
0	10.11	31	0.0045	0.00104	217	0.00728
0.03	10.11	27	0.0051	0.00137	221	0.01123
0.3	10.12	22	0.0063	0.00207	215	0.02019
1	10.13	20	0.0068	0.0025	221	0.02763

Figure 1 (a, b, c and d) shows the GIXRD pattern for the In_2O_3 films deposited at different oxygen partial pressures. It is observed from the figure that the crystallinity of the films is increasing with increasing oxygen partial pressure until the oxygen partial pressure 0.3 mTorr and then decreases. GIXRD patrons of In_2O_3 thin films deposited under different Oxygen partial pressures are well matched with JCPDS Cord No.06-0416 and find the cubic bixbyite phase of deposited thin films. No additional diffraction peaks are observed, Planes (211), (222), (400), (411), (431), (440), (611), and (622) with their corresponding diffraction angles 21.49, 30.57, 35.46, 37.68, 45.68, 51.03, 55.98 and 60.67 respectively. Estimated crystallite size by Debye Sherrer equation and found monotonous decrease of crystallite size with oxygen partial pressure asserts a close relation between the oxygen partial pressure and the crystal growth. Increasing oxygen environment of the crystal growth may be reducing the cohesive forces and resulting in smaller crystallites. The structural parameters like lattice constant, crystallite sizes and the dislocation density, lattice strain and Number of particles for the unit cell was calculated by using Bragg's law and Debye Sherrer equation and tabulated in Table 1. We estimated the thin films thickness by Stylus profilometer and tabulated in Table 1 it shows there is no much variation in thickness because deposition time and distance were fixed.

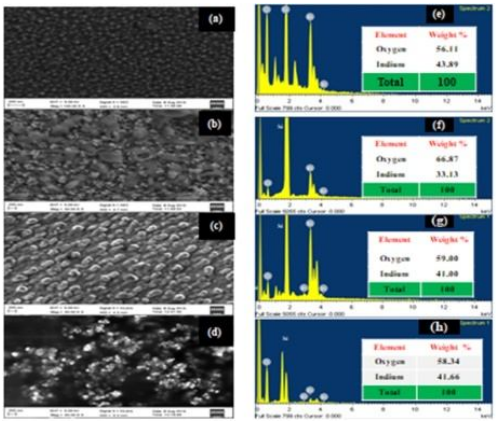

Figure 2 SEM micrographs and corresponding EDS In_2O_3 thin films deposited under different Oxygen partial pressures (a) 0.00 mTorr, (b) 0.03 mTorr, (c) 0.3 mTorr, (d) 1 mTorr corresponding EDS spectra shown in (e) 0.00 mTorr, (f) 0.03 mTorr, (g) 0.3 mTorr, (h) 1 mTorr.

Figure 2 (a, b, c and d) are shown the SEM pictures of the films deposited at various oxygen partial pressures of 0.00, 0.03, 0.3 and 1 mTorr respectively. Changing oxygen partial pressure shows a clear effect on the morphology of the film surfaces. The homogeneous spherical headed tubular, scarcely packed particles for 0.0 mTorr oxygen partial pressure seem to change in shape and size with changing oxygen partial pressure. The films deposited at 0.03 mTorr partial pressure of oxygen show large agglomerations with fine particle agglomerations dispersed between them. Again in case of film deposited at 0.3 mTorr pressure, the film shows a well-defined mushroom-like growth on the substrate surface. These epitaxial growths show a well-ordered distribution of size and space on the surface. They show nanorod-like structures of the height of about 200 nm, the width of 50 nm and separated by 300 nm on all sides. The film grown at 1.0 mTorr shows the low order in their special distribution and has large porous regions. EDS data Figure 2 (e, f, g and h) acquired for the film shows good stoichiometry and confirm the presence of oxygen and indium in the required proportion.

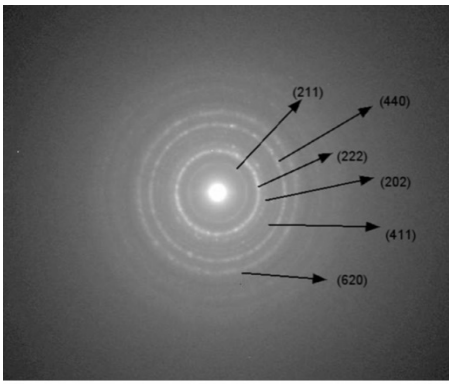

Figure 3 SAED patron of In_2O_3 thin film deposited at a 0.3 mTorr Oxygen partial pressure.

The Selected Area Electron Diffraction (SAED) picture, in Figure 3, taken from the film deposited under 0.3 mTorr oxygen partial pressure shows well-defined concentric circles suggesting high crystalline nature of the deposited film. The picture shows that (222) planes give high-intensity reflections and (211) planes give least intensity reflections as observed from the GIXRD peak distribution.

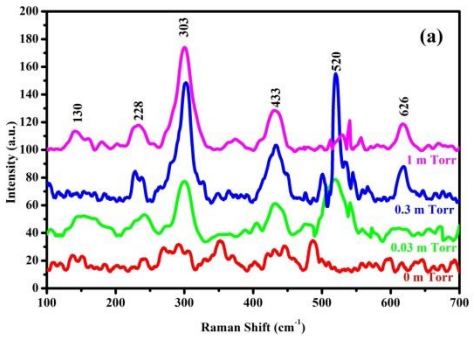

Figure 4 (a) Raman spectroscopic images of In2O3 thin films deposited under different Oxygen partial pressures (0.00, 0.03, 0.3 and 1 mTorr).

The defect states of In_2O_3 thin films for various Oxygen pressures are analyzed using room temperature Raman scattering. Figure 4 (a) shows Raman shift data from 100 -700 cm^{-1}. Raman investigations by Fetely et al [12] for In_2O_3 thin films suggests body-centred cubic bixbyite structure with a space group I_{a3} (Inversion). According to crystal group theory analysis for the factor group T_h (Translation), yields 117 optical modes at K=0 and the canter of the Brillouin Zone and optical modes are distributed as

$$\Gamma_{opt} = 4A_g(\text{Raman}) + 4E_g(\text{Raman}) + 14F_g(\text{Raman}) + 5A_u + 5E_u + 16F_u \quad \text{-----(3)}$$

Where the A_g, E_g and F_g modes are Raman active, Fu modes are infrared active, The A_u and E_u modes are inactive. The Raman spectra of In_2O_3 thin films for different Oxygen partial pressures has shown in Figure 4(a)The plots presents two sharp bands one at 300 cm^{-1} and the other at 520 cm^{-1} along with several another medium intense and weak intense bands. In comparison to the bulk material, thin films show weak Raman scattering. Raman peak shifts and broadening are explained by the quasi-momentum conservation rules for vibrational mode relaxation that may arise due to decreasing of the crystalline correlation length in nanometric structures. MR Lopez suggested that relaxation depends on the particle size while studying InP thin films. The high-intensity band at ~303 cm^{-1}can be attributed to the bending vibrations of InO_6 at the Octahedron site and the band at ~620 cm^{-1} can be attributed to the stretching vibrations of InO_6. The band at 520 cm^{-1} may be the spectral contribution from substrate material [13-17].

B. Optical Characterization

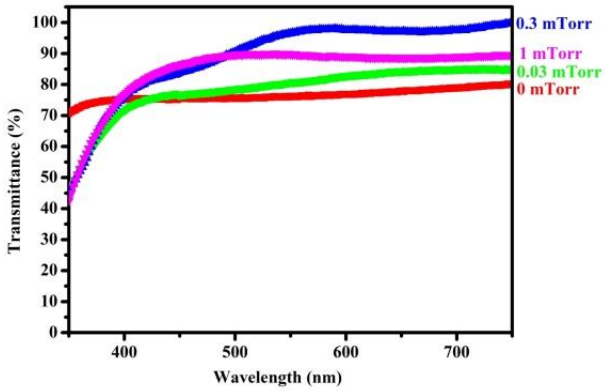

Figure 5 UV-vis spectra of In2O3 thin films deposited under different Oxygen partial pressures (0.00, 0.03, 0.3 and 1 mTorr).

Thin films show high optical transmittance and this property of the films make them versatile in their applications. The transmittance studies on the films are performed in the wavelength range 350 nm to 750 nm. The transmittance graphs are shown in Figure 5, and from these graphs we observe that the films show good transmittance in the visible region for all the films and show a

decreasing transmittance for lower wavelength radiations. The film deposited under 0.3 mTorr oxygen partial pressure shows the highest transmittance for the most part of the radiation spectrum. This film is also observed to have high crystallinity as seen from the SAED picture and a very highly ordered distribution of mushroom-like grown rods as seen from the SEM picture graphs.

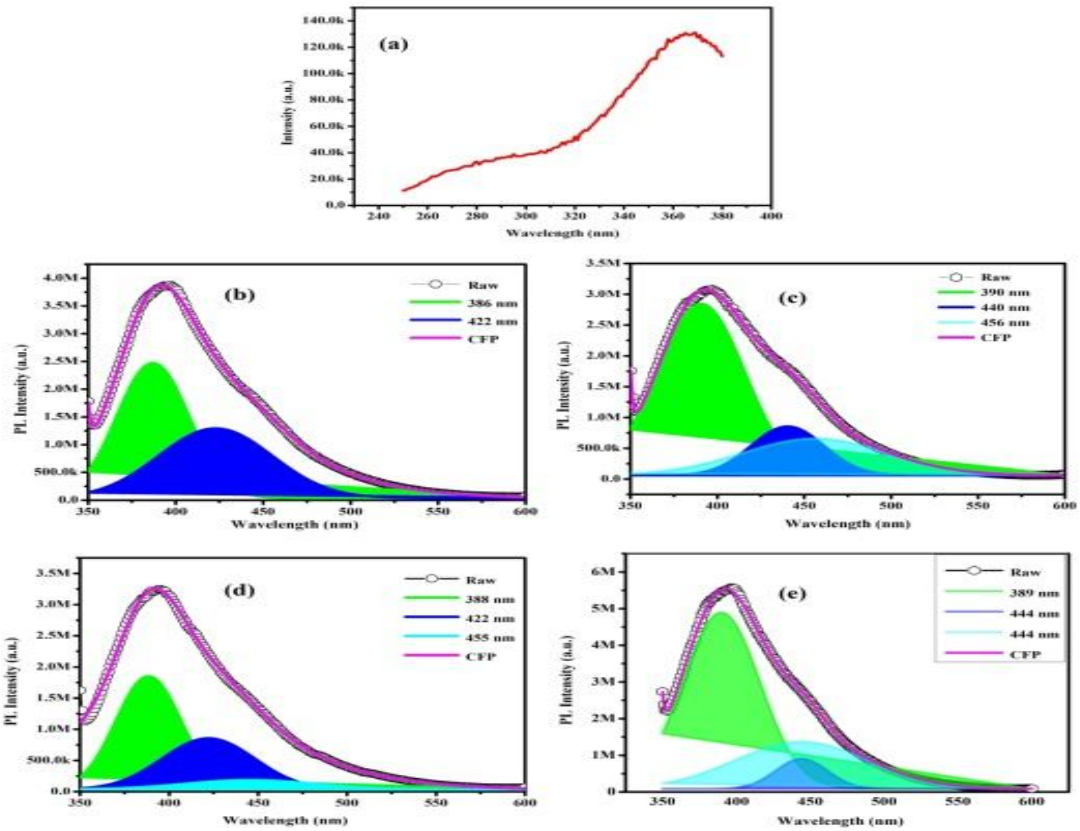

Figure 6 (a) Excitation spectra of In2O3 thin films, (b) PL Spectra of In2O3 thin films deposited under 1.00 mTorr Oxygen partial pressure, (c) 0.3 mTorr Oxygen partial pressure, (d) 0.03 mTorr Oxygen partial pressure and (e) 0.00 mTorr Oxygen partial pressure.

Photoluminescence (PL) of indium oxide nanoparticles and compared them with that of the bulk value as well as the band gap energies obtained from the UV-Vis spectroscopic data. [18]. The plot of the variation of luminescence intensity of In_2O_3 thin films for different oxygen partial preasures. The thin films were excited with an excitation wavelength of 367 nm is shown in Figure 6(a). All the films show photoluminescence emissions with wavelengths around 390 nm and 422 nm. The 455 nm emission shows great variation with the oxygen partial pressure change. This is the film that shows high crystallinity as discussed from GIXRD, SAED and Raman studies. This film as seen from UV Vis- studies also show high transmittance.

for the 0.3 mTorr deposited film. The major emission wavelength of 390 nm also shows changes in its peak position with changing oxygen partial pressure of the deposited films. This change may be more associated with decreased oxygen deficiency defect of the films and may not be associated to the quantum confinement effect. This is because the crystallite or particle sizes that are determined from the GIXRD are much larger than the literature suggested Bhor diameter of 2.6 nm for Indium oxide [19].

IV. CONCLUSIONS

The In_2O_3 thin films under different oxygen partial pressure (0 mTorr to 1 mTorr) were deposited using PLD. The films have shown structural, chemical, morphological consistency as verified from GIXRD, SEM with EDS and SAED studies. Patterns have revealed polycrystalline nature with cubic bixbyite structure. From Raman, the films are in phase by showing a peak of In_2O_3 at 303 cm^{-1}. Photoluminescence confirms the variation of defect states with the increase in oxygen partial pressures and these films shown primary blue emission.

V. ACKNOWLEDGMENT

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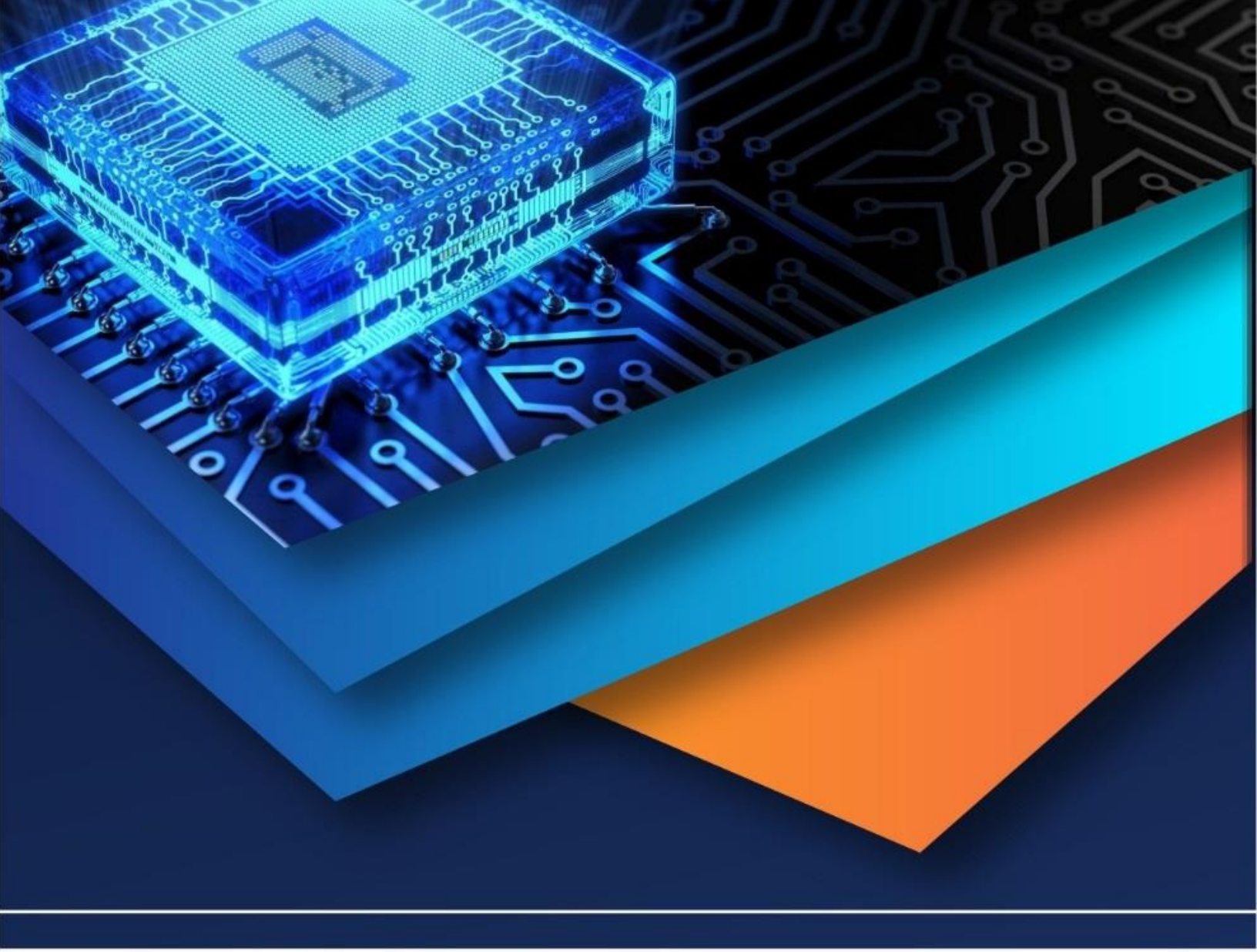

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