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# Study of the Surface Texture of Magnetron Sputtered Transparent Conducting ZnO:Al films by Atomic Force Microscopy

Rajesh Das
School of Applied Science and Humanities, Haldia Institute of Technology (Autonomy), Haldia-721657, Purba Medinipur, West Bengal, India

***Abstract: Transparent conducting ZnO: Al films with proper surface texture have been developed on glass substrate at $350^0$C by rf-magnetron sputtering under Ar and Ar+$O_2$ gas ambients. ZnO:Al films exhibit low resistivity (~ $8.9x10^{-4}$ Ω-cm), and high optical transmittance (T~ 85% to 90%) in visible region.***

***Study of surface texture ZnO:Al films by dry (hydrogen plasma) etching and wet chemical etching in diluted 0.5% HCl acid solution have been reported in this paper.***

***Due to hydrogen plasma etching surface topography as well as morphology of ZnO:Al films is modified into suitable texture for light scattering. But surface texture is deteriorated drastically for wet chemical etched films. Electrical properties have been improved slightly and optical transmittance remains undeviated due to H-plasma etching but significant changes in electrical and optical properties have been observed in wet chemical etching.***

***Keywords: ZnO:Al films, Surface Texture, Wet Chemical etching, Atomic Force Micrograph, Thin film solar cell.***

## I. INTRODUCTION

Transparent conducting oxide (TCO) plays an important role in various optoelectronic devices such as display, thin film solar cell, thin film LED due to its low sheet resistance and high transparency. Moreover the antireflection property of TCO greatly increases light diffusion inside the solar cell.

Light scattering from the TCO layer mainly depends on the surface roughness of the layer [3,4]. Optimization of the surface texture of TCO films has the key role for the improvement of solar cell performance. Optimized surface texture of TCO thin film reduces optical reflection at the TCO/silicon interface that ultimately leads to the enhancement in optical absorption of weakly absorbed light in the active layer of thin film solar cells.

Conventionally transparent conducting indium tin oxide (ITO), tin oxide ($SnO_2$) thin films are widely used as a front electrode due to its good conductivity as well as good light trapping properties. But, recently textured ZnO thin film has got the attention as a very promising material for the application as front contact in hydrogenated amorphous silicon (a-Si:H) and microcrystalline silicon (□c-Si:H) based thin film solar cells [1,2] for its suitable optoelectronic properties as well as its high stability in hydrogen plasma [5]. Though texture in ZnO films have been fabricated by different deposition techniques [6,7] such as Spray Pyrolysis, MOCVD or by reactive sputtering in Ar/$H_2O$ gas mixtures [6-8] but uniform ion damage free ZnO films with precise control of thickness, high deposition rate rf-magnetron sputtering is most suitable.

Textured TCO consists of microcrystallites whose size is comparable to visible light wavelengths. Because of the broad distribution of grain size and shape, the interaction between the incident light and the multilayered structure is complex. Surface texture and columnar or granular character of ZnO:Al films depends on several parameters.

In this paper details study on the effect of dry (hydrogen plasma) and wet chemical etching on electrical, optical and surface roughness properties of magnetron sputtered ZnO:Al thin films have been discussed.

## II. EXPERIMENTAL DETAILS

Aluminium doped ZnO films have been deposited on glass substrate by RF-magnetron sputtering. Both reactive and non-reactive sputtering have been done using Ar and Ar+$O_2$ gases in the deposition chamber. Optimum deposition conditions in terms of chamber pressure, rf-power, substrate temperature and gas flow rates for ZnO films deposition are listed in Table-1

 

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Table-1: Experimental set up and range of typical deposition parameters

| | |
|---|---|
| Sputtering mode | RF |
| Sputtering configuration | Sputtering up |
| Target Composition | $ZnO:Al_2O_3$ (2wt%) |
| Target Size | 4 inch diameter |
| Target-substrate distance | 70 mm |
| Substrate potential | Grounded |
| Base vacuum | $10^{-6}$ Torr |
| Power ($P_w$) | 120 watt |
| Chamber pressure (Pr) | 4 mTorr |
| Sputtering gases and flow rates | Ar (50 sccm); $O_2$ (1-3 sccm); $H_2$ (5 sccm) |
| Substrate temperature ($T_s$) | $350^0$C |

Dry chemical etching is done in hydrogen plasma atmosphere. Hydrogen plasma is produced by capacitively coupled RF-power supply and plasma etching is done by fixing the substrate potential at 5watt and 10watt respectively. Wet chemical etching of ZnO:Al films was performed by dipping those films in diluted (0.5%) HCl acid solution (for different durations). The electrical sheet resistance and optical transmission of the as deposited and chemically etched ZnO films were measured by 4-probe Vander Pauw method and UV-VIS-NIR spectrophotometer respectively before and after etching. Thicknesses of ZnO:Al films have been measured by stylus type thickness measuring equipment. A multi-mode scanning probe technique was utilized in analyzing topographical and grain size distribution with the help of contact mode Atomic Force Microscopy (AFM).

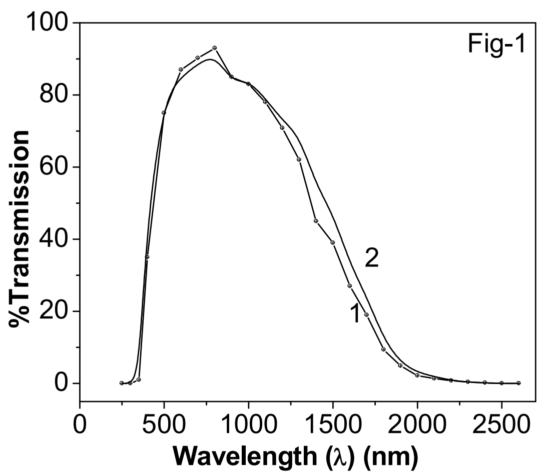
## III. RESULTS AND DISCUSSIONS

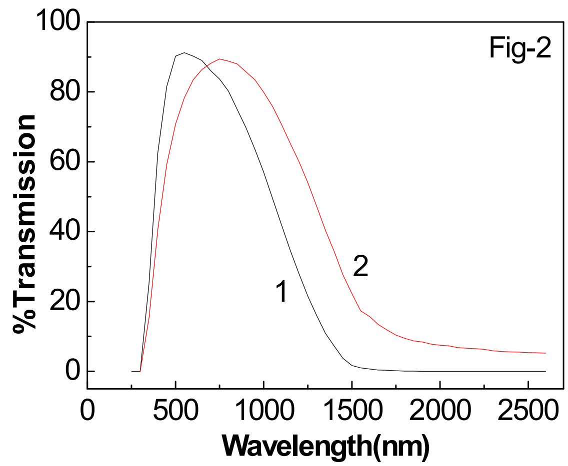
Dry etching and wet chemical etching has great impact on the materials properties of ZnO:Al films such as in etching rate, electrical properties, optical transmittance, and surface roughness. The above mentioned properties are highly co-related with each other. Rates of etching are different for the different sets of films, shown in the Table-1. Due to hydrogen plasma etching electrical sheet resistance is improved for Ar and Ar+$O_2$ deposited ZnO:Al films but becomes more than double in both cases for wet chemically etched ZnO:Al films. For the Ar deposited ZnO:Al films, the rate of etching is 10.4nm/sec under 0.5% HCL solution whereas the etching rate of Ar+$O_2$ deposited ZnO:Al films is very low and it becomes 4.4nm as compared to Ar deposited ZnO films shown in Table-2.

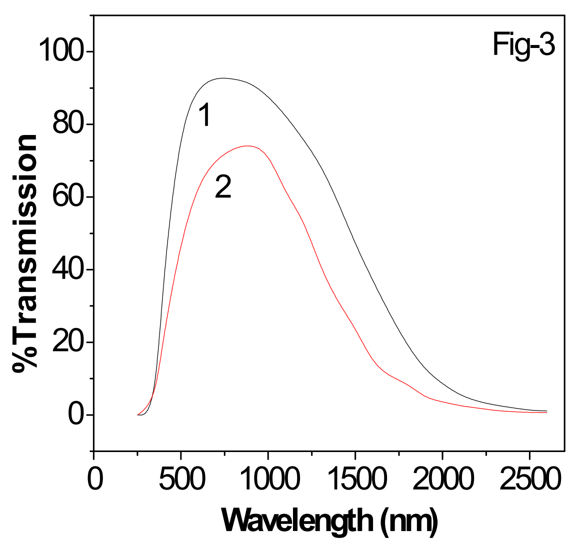
Table-2: Variation of Surface Roughness, Sheet Resistance and Optical transmission of ZnO thin films

| No. of Observation | ZnO:Al films deposited under ambient | | Surface Roughness (nm) | | | Rate of Etching under 0.5% HCl solution (nm) |
|---|---|---|---|---|---|---|
| | | | As deposited | Hydrogen plasma etched | Wet chemical etched | |
| 1. | Ar | | 6.134 | 8.355 | 28.714 | 10.4 |
| 2. | Ar+$O_2$ | $C_O = 2\%$ | 9.276 | 9.962 | 60.584 | 4.4 |
| 3. | | $C_O = 4\%$ | 13.206 | 26.216 | | 3.2 |
| | | | Sheet Resistance (ohm/square) | | | |
| | | | As deposited | Hydrogen plasma etched | Wet chemical etched | |
| 1 | Ar | | 5 | 4 | 12 | |
| 2. | Ar+$O_2$ | $C_O = 2\%$ | 8 | 6 | 15 | |
| 3. | | $C_O = 4\%$ | 1000 | - | - | |
| | | | Average Visible Transmission (%T) | | | |
| 1. | Ar | | 92% | Remains unchanged | Transmission peak shifted | |
| 2. | Ar+$O_2$ | $C_O = 2\%$ | 94% | >90% | ~70% | |

The variation of etching rates for different films can be explained on the basis of different binding energy of different ZnO films. During the reactive sputtering under $Ar+O_2$ ambient molecular oxygen is employed for conventional ZnO crystal growth. Oxygen molecular bond (binding energy 5.17eV) breaks into atomic or ionic oxygen and the oxygen atoms migrate into the matrix of growing ZnO film and create the donor defects $Zn_I$ and $O_i$. The relative formation enthalpies of donors increase approximately the twice the shift of oxygen reservoir chemical potential due to dislocating molecular oxygen [9]. More stoichiometric ZnO thin films are formed and the binding energy of $Ar+O_2$ deposited ZnO this films becomes high. On the other hand, during sputtering with Ar deposited ZnO:Al films are more non-stoichiometric. ZnO:Al films deposited under $Ar+O_2$ ambient have more compact structure as compared with the Ar deposited ZnO:Al films. Denser ZnO film might have less internal voids in the bulk. So, binding energy should be high. This void free closed packed structure prohibits the penetration of fluid etchant. Only the highly oriented ZnO clusters will come into contact with the etchant from its crystallite site. This explains the slower rate of etching.




Optical transmittance of Rf-Sputtered ZnO:Al film
Fig-1-As deposited under $Ar+O_2$ plasma (1) and after hydrogen plasma etched ($Ar+O_2$ deposited) (2); Fig 2-As deposited under Ar plasma (1) and for same film after 15sec wet chemical etched in 0.5% HCl solution (2) and Fig 3 - As deposited under $Ar+O_2$ Plasma (1) and for same film after 15sec wet chemical etching in 0.5% HCl solution (2)

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Fig.1, and 2,3 show the optical transmittance of as deposited and chemical etched (plasma etched and wet chemically etched) ZnO films deposited under Ar and Ar+$O_2$ ambients. Fig.1 shows the optical transmittance of as deposited and hydrogen plasma etched Ar+$O_2$ deposited ZnO:Al films where the visible transmittance remains unchanged. Fig.2 shows the optical transmittance of as deposited and wet chemically etched Ar deposited ZnO:Al films where the visible transmittance remains unchanged but the peak position of transmittance intensity is shifted towards the IR side. But, after wet chemical etching the films becomes hazy and the transparency falls rapidly shown in Fig.3. The nature of both the transmittance spectra is similar but in Fig.3 the transmittance intensity decreases due to wet chemical etching.

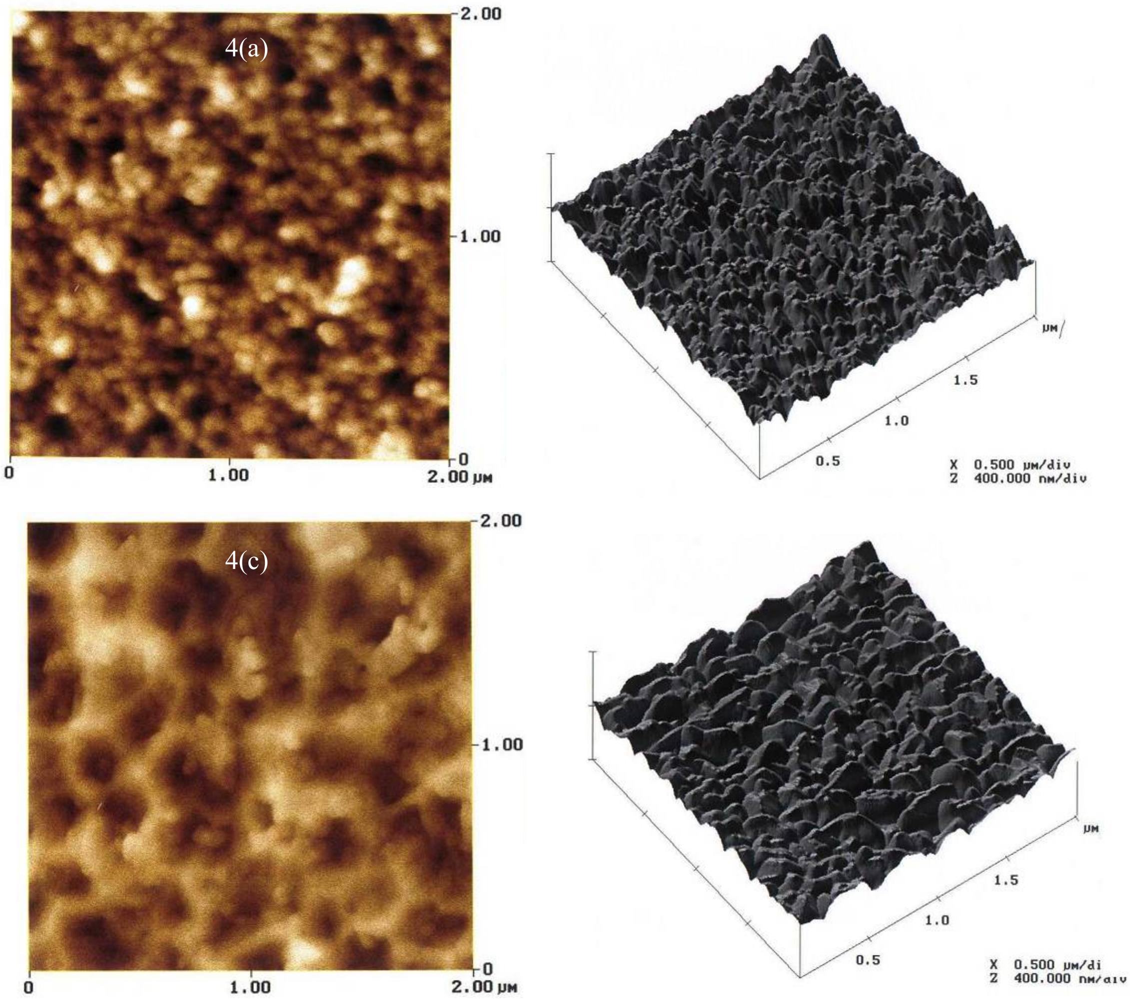


Fig 4: AFM image (2D and 3D topography) of wet chemically etched ZnO:Al films deposited under 4(a,b) Ar ambient and 4(c,d) Ar+$O_2$ ambients ($C_O$ = 1.8%)

Fig 4 (a,b,c and d) show the comparative study on 2-D topography studied by Atomic Force Micrograph (AFM) of as deposited, hydrogen plasma etched and wet chemically etched ZnO:Al films that clearly shows the grain size distribution and surface roughness analysis of the said films. The rms roughness describes the fluctuations of surface heights around an average surface height. From the micrographs shown in Fig. 4(a) shows the surface of Ar deposited ZnO:Al film consists very small grains with average size 30 -50nm whereas the average grain size becomes 100nm granular round shape structure for hydrogen plasma etched Ar deposited ZnO:Al film. The grains usually consist of cluster of crystallites. The root mean square value ($\delta_{rms}$) of roughness of Ar deposited ZnO:Al film is 6.134 nm (shown in Fig.4(a)) whereas ($\delta_{rms}$) values for hydrogen plasma etched ZnO:Al films deposited under Ar ambient becomes 8.355nm (shown in Fig.4(b)). The grains are not properly round shape, rather elongated in nature and grain size is bigger compared to that of former one. Fig. 4 shows the 2-D surface topography of wet chemically etched by 0.5% HCL for 15 sec of ZnO:Al film deposited under Ar ambient.

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Here, the surface roughness increases from 6.1nm to 28.7nm. Fig. 4(c), and (d) show the 2-D surface topography of $Ar+O_2$ deposited [$C_o= O_2/(Ar+O_2)\times100\% =2\%$], hydrogen plasma etched and wet chemically etched of same ZnO:Al films. As deposited $Ar+O_2$ ZnO:Al film consists very small grains with average size 30nm, surface roughness value 9.276nm. But, hydrogen plasma etched $Ar+O_2$ deposited ZnO:Al film becomes slightly more rough (see Table -2) compared to the as deposited ZnO:Al film and grain size becomes 150 -200nm (Fig. 4d). The grains become properly round shaped, and grain size is bigger compared to that of former one. The approximate value of grain size of hydrogen plasma etched ZnO:Al films is about 200 nm and surface roughness becomes 9.692nm which is clearly shown in Fig.4(d). As the etch rate was very slow, so we exposed $Ar+O_2$ deposited ZnO:Al film in 0.5% HCl solution more time to get etched surface, but it was not controlled and the surface becomes more rough, transparency as well as film resistivity completely deteriorated (values are listed in Table-2).

Experimental observations show the granular features of ZnO:Al film surface with surface roughness 13.2nm. The as deposited film was slightly resistive and highly transparent. But, after hydrogen plasma exposure the film became more conducting but transparency was un-deviated. During hydrogen plasma etching, initially molecular hydrogen decomposes into atomic and ionic species and these reactive hydrogen species could remove oxygen or interstitial metal atoms from ZnO:Al film. More oxygen vacancies are created in the ZnO film matrix and it becomes non-stoichiometric. In this way, hydrogen plasma etching control the ZnO:Al film resistivity. But the Zn-O bond is very stronger for $Ar+O_2$ deposited ZnO:Al film, so the etching rate may be assumed to be low. Therefore hydrogen plasma etching can do fine control of surface texture as well as surface roughness. The surface roughness increases from 13.2nm to 26.2nm after hydrogen plasma etching for the ZnO:Al film deposited under $Ar+O_2$ with $C_o=$ 4%. Here the variation of surface roughness can be explained as follows. The decrease of grain size corresponds to an increase in film smoothness, which agrees with the result obtained by AFM. That is why the surface roughness of as deposited ZnO films deposited under $Ar+O_2$ ambient is higher than the other as deposited films.

Here, the surface roughness, sheet resistance and optical transmittance of as deposited, plasma etched and post-deposited wet chemically etched ZnO:Al films, estimated by atomic force microscopy (AFM) has been shown given in Table-2. Here etching causes the reduction in correlation length, and increases the root means square roughness, $\delta_{rms}$. Consequently, the ratio $\delta_{rms}/ a_{corr}$ increases, which improves light coupling [9]. Kluth et al [8] reported that the ZnO films were textured by diluted HCl acid and were used as substrate for microcrystalline silicon (μc-Si) thin film solar cell. Significant improvement in the performance of solar cells has been observed when they used post-deposited chemically textured ZnO instead of Asahi-$SnO_2$ substrate. But, there is a critical value of roughness of the substrate surface for getting good performance of thin film solar cells. Matsui et al [10-13] suggested that the optimum value of $\delta_{rms}$ of the substrate surface is 38nm, otherwise $\delta_{rms}>$ 38nm the solar cell performance deteriorates. The field-dependent carrier collection behaviors reveal that the carrier diffusion length in the poly-Si layer on textured substrates with $\delta_{rms} >$ 38nm decreases due to the change in poly-Si microstructure.

## IV. CONCLUSIONS

Natively textured ZnO:Al films with moderate surface roughness have been developed by rf-magnetron sputtering under Ar and $Ar+O_2$ ambients at high substrate temperature. The surface texture of the growing film can be controlled by fine control of oxygen partial pressure during film deposition. Surface roughness as well as the surface texture is controlled with hydrogen plasma etching. The electrical sheet resistance is decreased significantly for the ZnO:Al films deposited under $Ar+O_2$ ambient due to hydrogen plasma exposure but the optical transmittance of ZnO:Al film prepared under same conditions remains unchanged due to its stronger Zn-O bond formation. On the other hand, the wet chemical etching has negative effect on its optical transmittance, sheet resistance and the surface texture of ZnO:Al films. The etching rate is low in case of $Ar+O_2$ deposited ZnO:Al films as compared with the same film deposited under Ar ambient. The fine tuning to control the surface texture in terms of surface roughness, 3-D features along with its optical as well as electrical properties is very tough with wet chemical etching. Hydrogen plays crucial role for fine tuning the surface texture as well as the electrical properties of ZnO:Al thin films so that it can be optimized to achieve the U-type surface feature of transparent conducting ZnO:Al films for substrate applications in thin film solar cell as well as in different opto-electronic devices.

## IV. ACKNOWLEDGEMENT

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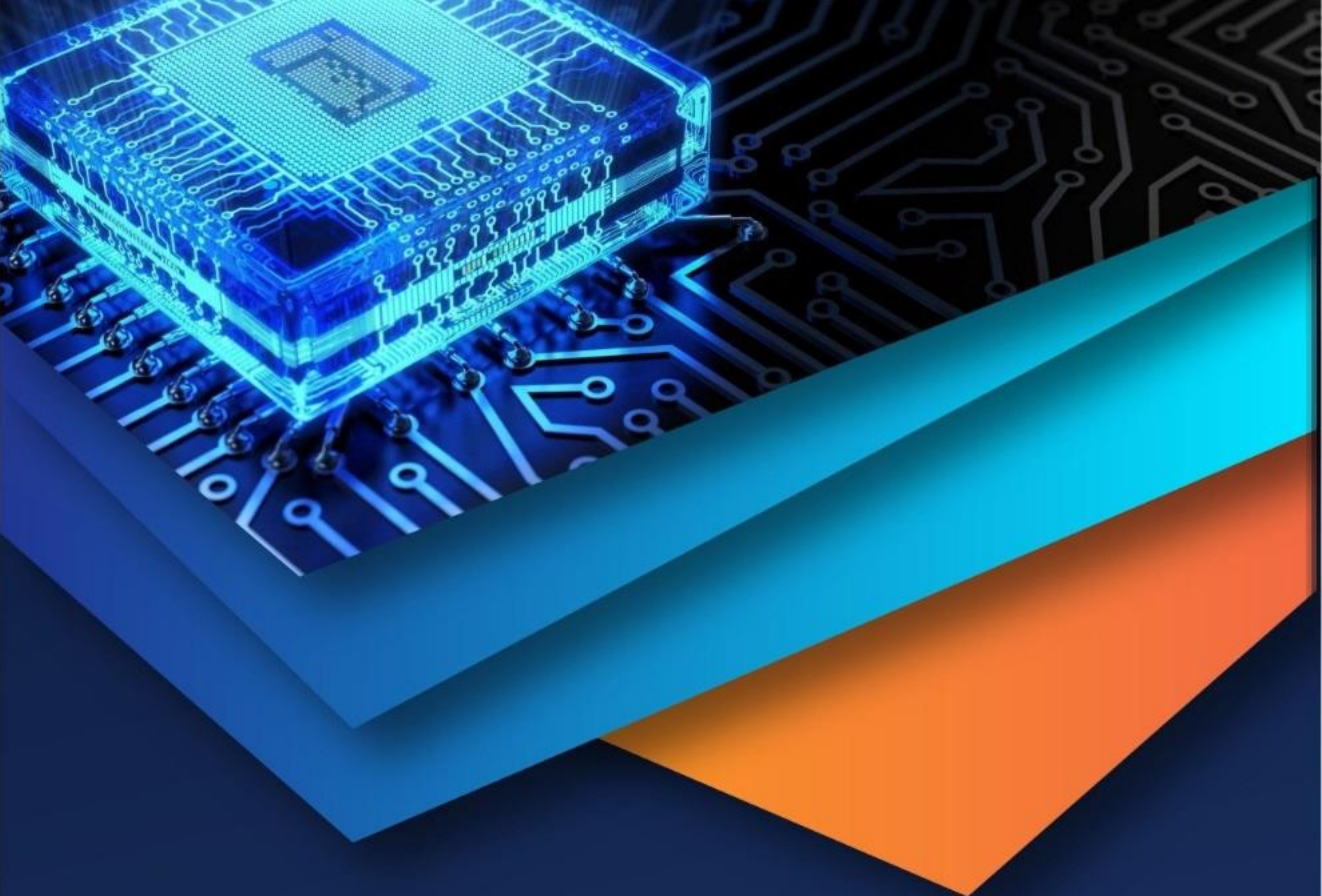


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