Synthesis and Characterization of Ag doped ZnO Thin Films

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Abstract - *Pure Zno,2% and 4% Ag doped ZnO (SZO) thin films synthesized on silicon substrate by varying parameters like doping concentration, number of layers , spinning speed and annealing temperature using low cost sol-gel method. The effect of silver doping on structural, morphological, and electrical properties of SZO films were investigated. The X-Ray Diffraction (XRD) indicated the poly crystalline nature having hexagonal wurtzite crystal structure. Scanning Electron Microscopy (SEM) shows uniform distribution of spherical grains and increasing annealing temperature increases the c-axis orientation and crystal size of the film. The morphologies, surface roughness and film thickness were observed by Atomic Force Microscopy (AFM). Analysis of variance showed, Silver doping concentration was influenced by 80.71 % for roughness, 85.56 % for thickness and 90.84 % for conductivity. Regression model* R^2 *value indicated 87.92 % for roughness, 89.27 % for thickness and 98.04 % for conductivity. Comparison of initial process parameter with Grey theory prediction showed that roughness increased from 14.20 nm to 21.34 nm, thickness decreased from 226.21 nm to 198.33 nm, and conductivity increased from 136.24 nA to 328.61 nA.*

Keywords: - *ZnO Thin Films, SZO, Sol-gel Spin coating, Structural properties.*

1. INTRODUCTION

ZnO is one of the most important promising materials that are applied to many fields such as transparent conductive contacts solar cells [1], laser diodes, ultraviolet lasers, thin film transistors, optoelectronic and piezoelectric applications and gas sensors [2, 3]. Many different methods such as RF/DC sputtering [4], sol-gel method [5-10], spray pyrolysis [11], metal organic chemical vapor deposition and pulsed laser deposition [12] have been used for the preparation of ZnO thin films. Among these techniques, sol-gel method is widely used and sol-gel method attracts much attention due to some unique advantage including low cost, simple deposition equipment, easy adjusting composition and dopants and fabricating large area film [13]. The structural[6,10,11], optical and electrical[13-15] properties of ZnO films were governed by deposition parameters like number of layers, spinning speed [16], post-annealing [7,9] and doped material such as Al, Ga, Y, Mn, Cu, Ag, etc. Among them, Ag-doped ZnO was considered for the study of electrical and optical properties of the film. A small amount of Ag can indeed lower the processing temperature but results in good structural and electrical properties [11, 13-15]. Although many researchers have been reported, but very scarce work has been done by doping with Ag and parametric study for thickness, roughness and conductivity using design of experiment. Investigated the structural, morphological, electrical properties of Ag doped ZnO (SZO) thin films using AFM, XRD, SEM, resistivity meter. The work examines the effect of deposition parameters such as Doping concentration, Number of layers, Spinning speed and Annealing temperature on the properties of SZO thin films. Also investigated the effects of the factors on performance as well as to study the influence of individual factors to determine which factor has more influencing. Signal to noise ratio analysis was done to analyze and rank the parameters, Analysis of variance was carried out to find the influencing parameter, Response surface methodology was done to quantify relation between input parameter and obtained response where as Grey relation analysis was done to find highest grading.

2. EXPERIMENTAL PROCEDURE

ZnO solution was prepared with the mixture of zinc acetate dehydrate (5.5 gm) as precursor solution, isopropanol (IPA) as solvent and diethanolamine (DEA) as stabilizer. The precursor concentration was maintained at 0.5 mol and the molar ratio of DEA: zinc acetate dihydrate was maintained 1:1. Meanwhile, SZO solution was prepared separately by adding silver nitrate as a doping in to the ZnO solution. While varying doping concentration 0 %, 2 %, 4 % solution was stirred at 60 ºC for 2 hr using a magnetic stirrer. It was kept in a room temperature for aging process for another 24 hr. The solution coated on Silicon substrates by spin coating at 1000, 2000, 3000 rpm for 30 sec. After spin coating, the substrates were preheated at 400°C for 10 min. Finally the substrates were annealed using high temperature furnace. In order to study the effect of annealing treatment the samples were annealed at temperatures of 600°C, 700°C and 800°C for 1 hr.

The surface morphology were examined by Scanning Electron Microscopy (SEM), the crystal structure of the sample were seen by X-Ray Diffraction (XRD). The coating thickness and surface roughness were measured by Atomic Force Microscopy (AFM).

3. RESULTS AND DISCUSSION

3.1 Experimental Results

Table - 1 Experimental Result

Expt. No	Roughness (nm)	Thickness (nm)	Conductivity (nA)
1	6.20	580.12	37.44
2	8.80	482.2	23.68
3	6.30	512.3	14.67
4	12.43	328.21	62.80
5	9.24	346.35	82.87
6	11.38	392.48	46.40
7	14.20	334.23	136.24
8	13.40	314.90	105.59
9	11.60	226.21	120.91

3.2 S/N Ratio

3.2.1 Probability plot for roughness, thickness and conductivity of SZO

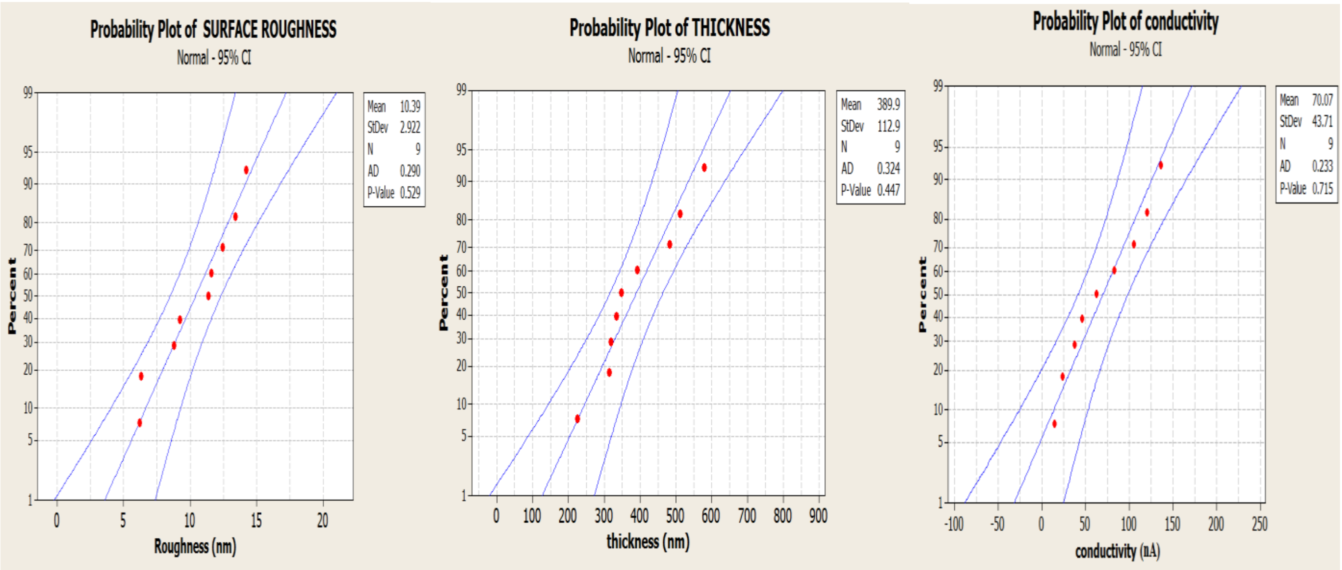

Fig - 1 S/N ratio plot for roughness, thickness and conductivity

Normal probability plots for S/N ratios of roughness, thickness and conductivity are shown in Fig.1 from experimental response result were found to be equally distributed along the trend line of a normal probability plot. Hence the process is said to be stable.

3.3. GRA of Surface Roughness, thickness and Conductivity Results

3.3.1 Data normalization

In grey relational analysis data processing is first performed in order to normalize the raw data for analysis. In this work, linear normalization of experimental results is performed in the range between zero and unity. Usually, there are three categories of performance.

Characteristics in the analysis of normalized value, i.e. the 'Lower the better', 'Higher the better' and the 'Nominal the better'. 'Lower the better' and 'Higher the better' were considered for the percentage parameter response. Then, the normalized results can be expressed as

$$X_i^*(k) = \frac{\max x_i^* - x_i^{(0)}(k)}{\max x_i^* - \min x_i^{(0)}(k)}$$

$$X_i^*(k) = 1 - \frac{x_i^{(0)}(k) - OV}{max\left\{\max x_i^{(0)} - OV, OV - \min x_i^{(0)}(k)\right\}}$$

$$X_i^*(k) = \frac{x_i^{(0)}(k) - min\, x_i^*(k)}{\max x_i^* - \min x_i^{(0)}(k)}$$

Where, $X_i^*(k)$ is the value after the grey relational generation, min $X_i^{(0)}$ (k) is the smallest value of $X_i^{(0)}(k)$ for the k^{th} response, and the max $X_i^{(0)}(k)$ is the largest value of the $X_i^{(0)}(k)$ for the k^{th} response. An ideal sequence is $X_i^*(k)$ (k=1, 2….9). The values of the all factors are set to be the reference sequence, $X_0^{(0)}$ (k), k =1. Moreover, the results of nine experiments were the comparability sequences $X_i^{(0)}(k)$, i=1, 2... 9, k =1.

Also, the deviation Δ_{0i}, Δ_{max} and Δ_{min} (k) for i =1–9, k =1 can be calculated. The deviation sequences Δ_{01} (1) can be calculated as follows:

$\Delta_{01}(1) = | X0^*(1) - X1^*(k)|$

3.3.2 Computation of grey relational coefficients

The grey relational coefficients are calculated to express the relationship between the ideal (best) and actual experimental results. The grey relational coefficient $\xi_i(k)$ can be expressed as

$$\xi_i(k) = \frac{\Delta_{\min} + \xi\Delta_{\max}}{\Delta_{0i}(k) + \xi\Delta_{\max}}$$

Where,

$\Delta_{0i} = || X_0^*(k) - X_i^*(k) ||$ is the difference of the absolute value between $X_0^*(k)$ and $X_i^*(k)$, ξ = distinguishing coefficient between zero and one.

In this study ξ value is taken as 0.5

Δmin = smallest value of Δ_{oi}

Δmax = largest value of Δ_{oi}

Table - 2 Grey Relational Coefficient, Grey Relational Grade and their order

Expt. No.	Grey relation coefficients			Grade	Order
	Roughness	Thickness	Conductivity		
1	0.333	0.333	0.381	0.349	9
2	0.425	0.408	0.351	0.394	7
3	0.336	0.382	0.333	0.350	8
4	0.692	0.634	0.452	0.592	4
5	0.446	0.595	0.532	0.524	5
6	0.586	0.515	0.403	0.501	6
7	1	0.620	1	0.873	1
8	0.833	0.666	0.669	0.722	3
9	0.606	1	0.797	0.801	2

$A_3B_1C_3D_2$ has the highest Grey relation grade as in experiment 7; it has the best multiple performance characteristic among all experiments. The mean value of the Grey relation grade for each coating parameter level is summarized in Table - 3.

Table - 3 Grey Relational Grade and their order for each deposition level

Level	Grey Relation grade	Order
A1	0.364	3
A2	0.539	2
A3	0.798	1
B1	0.604	1
B2	0.546	3
B3	0.550	2
C1	0.524	3
C2	0.595	1
C3	0.582	2
D1	0.558	2
D2	0.589	1
D3	0.554	3

From the Table - 3 the optimized levels of the parameters for ZnO and SZO thin films by Grey relation analysis of different levels ($A_3B_1C_2D_2$). The obtained GRA levels are in compliance with the RSM levels.

3.4 Confirmation Tests

Table - 4 Results of confirmation test for SZO thin films.

Responses	Initial process parameters $A_3B_1C_3D_2$	Grey theory prediction design $A_3B_1C_2D_2$
Surface Roughness (nm)	14.20	21.34
Thickness (nm)	226.21	198.33
Electrical Conductivity (nA)	136.24	328.61

Table - 4 shows the coating experimental result for multiple performance characteristic of SZO thin films. A comparison of the grey theory prediction design ($A_3B_1C_2D_2$) with the initial process parameters ($A_3B_1C_3D_2$) shows surface roughness increases from 14.2 nm to 21.34 nm, thickness decreases from 226.21 nm to 198.33 nm and electrical conductivity increases from 136.24 nA to 328.61 nA.

3.5 Characterization Techniques

3.5.1 X – RAY DIFFRACTION (XRD)

Figure 2 shows the XRD pattern Ag-doped ZnO thin films. The diffraction peaks at 2θ =34.45° correspond to hexagonal wurtzite phase for SZO films and diffraction peaks at 2θ =38.17° correspond to FCC metallic Ag phase.

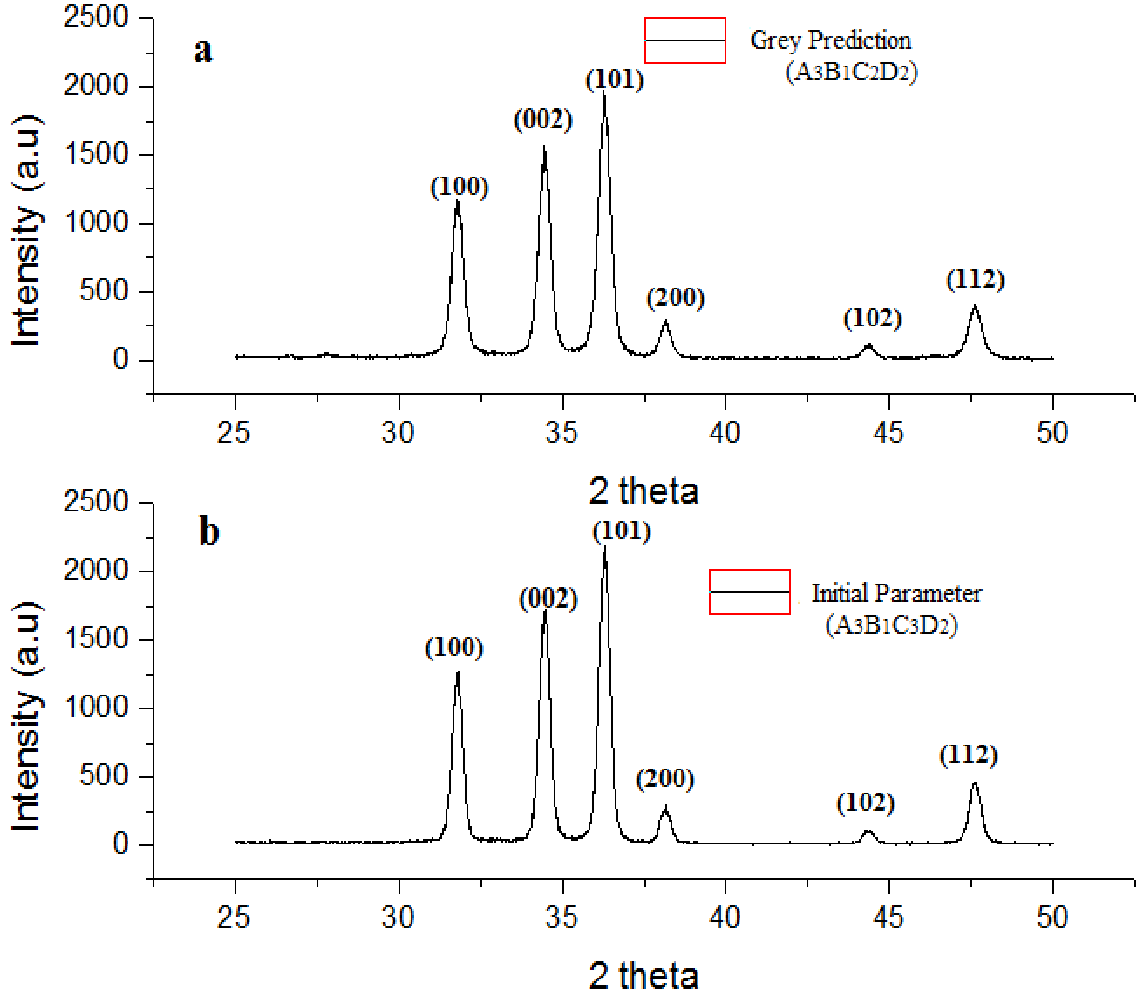

Fig - 2 XRD patterns of SZO Thin Films

In Figure 2 (a) Ag peak (200) was slowly improved with Ag doping which indicates formation of Ag – ZnO. The peak position of the (002) plane was shifted to lower 2θ values with increasing amount of Ag content and also increasing Ag content the intensity of 002 peak decreased from 1710-1573 (a.u). The reason is that the crystallinity decreased with increasing Ag dopant in SZO films [11].

3.5.2 Scanning Electron Microscope (SEM)

The surface morphological study of ZnO and SZO films are carried out by scanning electron microscopy. In Figures 3(a), and 3(b) shows the images of $A_3B_1C_2D_2$ and $A_3B_1C_3D_2$ levels of experiment respectivly.

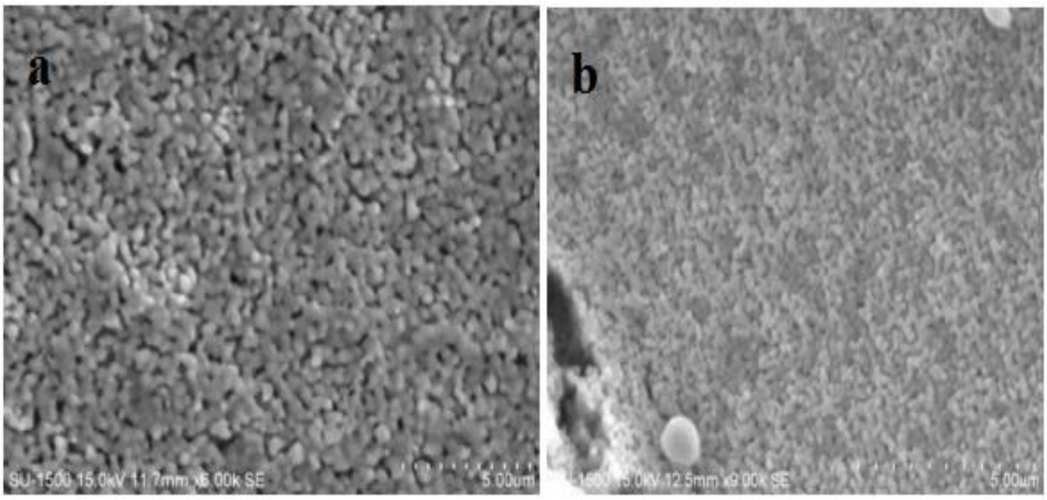

Fig - 3 SEM images SZO Thin Films.

For $A_3B_1C_3D_2$levels of samples surface had nonuniform distribution and high grain growth observed. $A_3B_1C_2D_2$levels of samples relativly more compact and uniform distribution of grains observed. In this increasing the annealing temperature and doping concentration(4%) increases grain growth.

3.5.3 Atomic Force Microscopy (AFM)

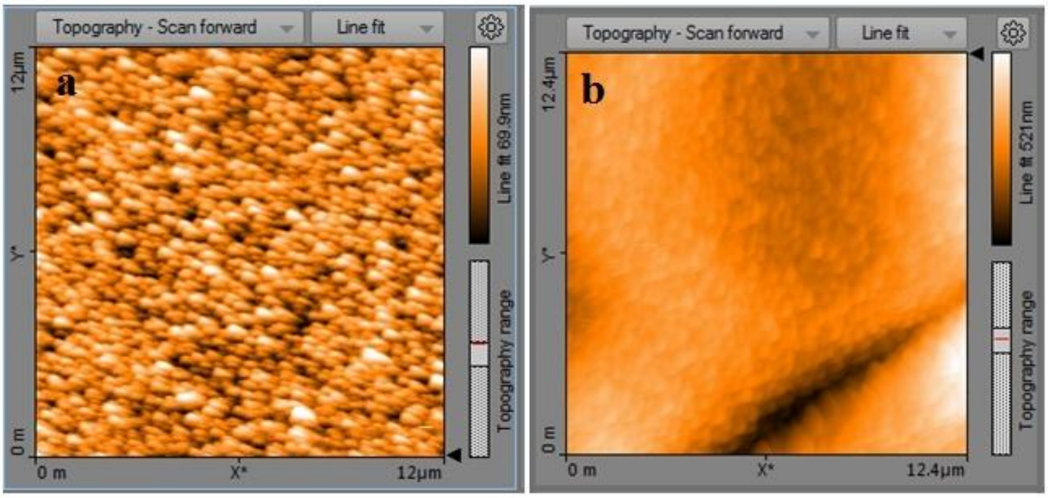

Fig - 4 AFM images of SZO Thin Films.

Surface roughness and coating thickness measured by AFM are shown in 2-Dimensional Figures 4(a) and 4(b) for $A_3B_1C_2D_2$ and $A_3B_1C_3D_2$ levels of experiment respectively. The scanning area was 12μm×12μm shows sample surface roughness and uniformly distributed nanometer sized grains. Grain size increases with increasing temperature. For the different factor level combinations ($A_3B_1C_3D_2$) 4% Ag doping, 8 layers, 3000rpm and 700 °C annealing temperature the maximum surface roughness and minimum coating thickness values obtained 14.20 nm and 226.21nm respectively. For 4% Ag doping, 8layers, 2000rpm and 700 °C annealing temperature ($A_3B_1C_2D_2$) the maximum surface roughness and minimum coating thickness values obtained 21.34 nm and 198.33nm respectively.

3.5.4 Resistivity meter

Electrical conductivity measured by resistivity meter, in this process conductive electrodes are placed by depositing silver paste on the surface of the film and we connected the electrodes other end to resistivity meter, varied voltage from 0 mv to 5 mv. The graph shown in Figure.5.16 for conductivity plot for SZO thin films, from this clearly observed that when voltage is varying the current is also linearly increasing also confirmed that conductivity range is 136.24 nA for 3 millivolt in film coated by 4% Ag doped, 8 layers, 3000 rpm and 700 °C annealing temperature ($A_3B_1C_3D_2$) and 328.61 nA for 3 millivolt in film coated by 4% Ag doped, 8 layers, 2000 rpm and 700 °C annealing temperature ($A_3B_1C_2D_2$).

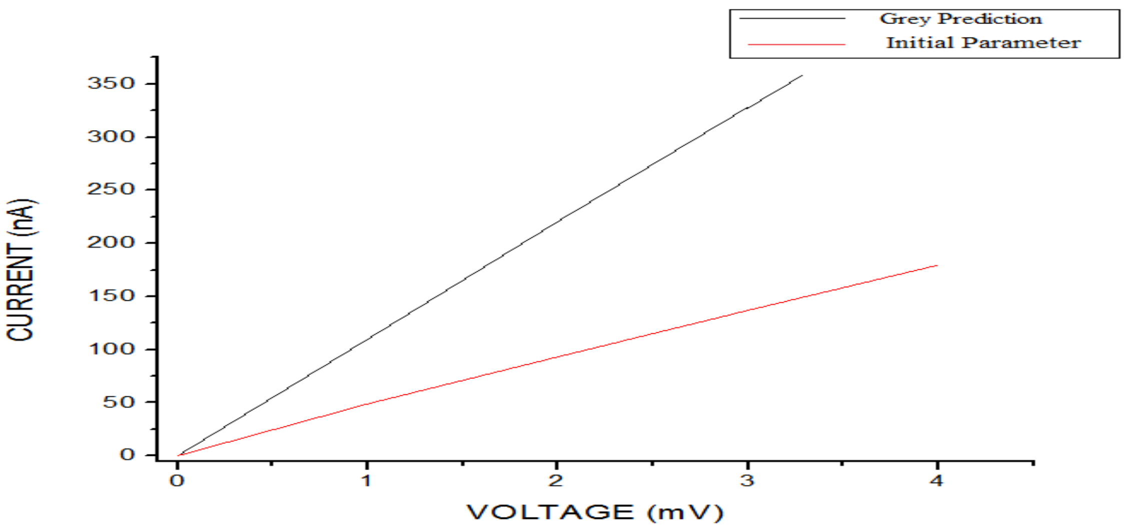

Fig - 5 Conductivity for SZO films

So, the optimal process parameters in SZO thin films deposited on silicon substrates can be effectively improved using Grey-Taguchi method.

4. CONCLUSIONS

Experimental studies of surface roughness, thickness and electrical conductivity were conducted for SZO thin films. L_9Experimental was designed considering doping concentration, number of layers, spinning speed and annealing temperature.

Based on the experimental results the following conclusions were arrived at:

- The range of factors such as doping concentration (0-4%), number of layers (8-12), spinning speed (1000-3000 rpm) and annealing temperature (600-800 ºC) was explored by all factor at a time approach.
- XRD pattern of undoped and Ag-doped ZnO thin films. The diffraction peaks at 2θ =34.45° correspond to hexagonal wurtzite phase for ZnO films and diffraction peaks at 2θ =38.17º correspond to FCC metallic Ag phase; the Ag peak was improved with Ag doping which indicates formation of Ag – ZnO films.
- ANOVA results showed that silver doping concentration was the most influencing factor with 80.71 % for roughness, 85.56 % for thickness and 90.84 % for resistivity.

- The optimal value by RSM for maximum roughness 87.92%, minimum thickness 89.27% and maximum conductivity 98.04% was found to be 4% Ag doping, 8 layers, 2000 rpm and 700 °C annealing temperature. The GRA values obtained are in agreement with the RSM values.
- The GRA obtained Initial process parameter was found to be 14.20 nm for roughness, 226.21 nm for thickness, 136.24 nA for conductivity of SZO thin films.
- The grey prediction obtained was 21.34 nm for roughness, 198.33 nm for thickness and 328.61 nA for conductivity of SZO thin films.

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