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Investigation of Influence of Spin Coating Parameters on the Morphology of ZnO Thin Films by Taguchi Method

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Abstract: The objective of this research was to investigate the influence of spin coating process parameters on the thickness and surface roughness of Zinc oxide (ZnO) thin films using L9 Orthogonal Array. ZnO thin film was deposited on glass substrate at room temperature by sol-gel spin coating method. Spinning speed, spinning duration, volume of the solution and molar concentration of the precursor were studied as experimental factors. Molar concentration of the precursor significantly influenced both coating thickness and surface roughness. Combination of least coating thickness of 492 nm and best surface roughness of 3.27 nm was achieved at 5000 rpm spinning speed, 0.75 ml volume of the solution and 0.4 M Molar concentration of the precursor. But, the spinning duration was 30 seconds for the coating thickness of 492 nm and 60 seconds for surface roughness of 3.27 nm. Atomic Force Microscopy, X-ray diffraction and Scanning Electron Microscopy were used to analyze the surface morphology of the ZnO thin films.

Keywords: Zinc Oxide thin film, Spin Coating, Design of Experiments.

1. Introduction

ZnO thin films have been studied extensively due to their various applications, such as piezoelectric transducers, conductive gas sensors, display devices, transparent conductive electrodes, and solar cells [1–3]. There are various techniques used for preparation of ZnO thin films such as RF magnetron sputtering [4], Physical vapor deposition (PVD) [5],Chemical vapor deposition (CVD) [6], spray pyrolysis [7] and sol–gel technique [8,9]. Among them sol–gel technique especially spin coating has been receiving high attention because of simple deposition procedure, easy control of chemical components and low-cost preparation to obtain high quality thin films. However, the sol-gel method involves many process parameters such as molar concentration of precursor, chuck rotation speeds, pre and post heat treatment, aging time and drying time, which directly or indirectly influence the quality of thin films. Hence, it requires a greater understanding of the relation amongst the process parameters in order to optimize the quality of thin films. The properties of thin films deposited by spin coating technique are influenced by three major parameters such as pre-coating parameters, coating parameters and post coating parameter. Kashyout et al. [10] reported that 0.4 M of Triethanolamine yields maximum of 94 % of ZnO among the 0.1 to 0.5 M of precursors. Sorar and Tepehan [11] studied the effect of solution concentration between 0.2 and 0.4 M and reported that surface roughness increased with solution concentration. The surface roughness values of the films were 3.9 nm and 6.3 nm for 0.2M and 0.4M respectively. Grains were tightly packed and the average grain diameter was about 40 nm for 0.2M and 60 nm for 0.4M. Sharul Ashikin Kamaruddin et al.[12] investigated the influence of precursor concentration 0.3 M, 0.4 M, 0.5 M and 0.6 M on the structural properties of the ZnO films, and reported that higher precursor concentration

results in bigger grains and the surface roughness area increases with the increasing precursor concentration. Ilican et al. [13] studied the effect of chuck speed between 3000 and 5000 rpm for the preparation of thin films, which was concluded that greater the chuck speed lower was the grain size of the crystallite. The texture coefficient decreased with increase in chuck rotation. Maryanne et al. [14] studied the effects of drying time between 3 and 48 hours, on the thin films and reported that for optimal performance of the films, it should be dried under a lower relative humidity environment for at least 12 hours. The effect of heat treatment temperature considering 300°C, 400°C and 500°C on the physical properties thin films was studied. The authors reported that increase in the annealing temperature increased the average grain size. The average grain size was estimated as 14 nm for 300°C, 19 nm for 400°C, and 28 nm for 500°C [15]. The surface roughness gradually decreased and ZnO grains became more and more uniform, as the solution aged for 24 hours was very stable, homogenous and possessed good surface characteristics [16, 17]. Major research was focused on coating parameters to optimize the morphology of thin films by spin and dip coating by sol gel technique [18, 19].Experimentation as per Taguchi method was applied for important coating parameters and the method has been applied to various thin film coatings, such as copper deposition on PCB [20], to evaluate the effect of process parameters on size distribution, absorbance and coating thickness tin oxide thin film nanocrystalline [21], and tungsten coatings deposited by plasma spraying [22]. Review of literature [1-22] indicated that precoating, coating and post coating parameters have been individually studied and parametric study of spin coating parameters for ZnO thin films is not reported. The main objective of this research was to experimentally investigate the spin coating parameters such as spinning speed, spinning duration, volume of solution and molar concentration of precursor on the coating thickness and surface roughness of ZnO thin films based on Orthogonal Array Experimentation technique.

2. Experimental

2.1 Preparation of ZnO Solution

Solution preparation, coating and drying are the three stages of thin film coating process. ZnO solution was prepared by dissolving Zinc acetate dehydrate [$C_4H_{10}O_6Zn$] (10g) in a mixture of isopropyl alcohol [C_3H_8O] and diethanolamine [$C_4H_{11}NO_2$] at room temperature. The concentration of Zinc acetate dehydrates was varied from 0.4 M to 0.6 M. The molar ratio of diethanolamine to Zinc acetate dehydrate was maintained at 1: 1. The solution was stirred using magnetic stirrer for 30 minutes. The solution was kept in an air tight beaker for 2 hours for complete hydrolysis to obtain a homogenous and transparent clear solution. The ZnO solution prepared by the sol gel spin coating was deposited on a clean glass substrate, dried at 85 °C for 30 minutes and aged at room temperature for 24 hours and annealed for 400 ˚ C.

2.2 Spin coating for synthesis ZnO thin films

Spin coater with speed range 100-10,000 rpm and spinning duration up to 120 seconds was used in this research. Table.1 shows the design of experiments for coating thickness and surface roughness were measured in each of the experiments.

Table 1: Design of experiments for Spin Coating parameters (L_i refers to the level of the factor at which experiment was performed).

Expt. No.	Spinning speed (A)	Spinning duration (B)	Volume of solution (C)	Precursor conc. (D)
01	3000 (L_1)	30(L_1)	0.25(L_1)	0.4(L_1)
02	3000(L_1)	60(L_2)	0.50(L_2)	0.5(L_2)
03	3000(L_1)	90(L_3)	0.75(L_3)	0.6(L_3)
04	4000(L_2)	30(L_1)	0.75(L_3)	0.5(L_2)
05	4000(L_2)	60(L_2)	0.25(L_1)	0.6(L_3)
06	4000(L_2)	90(L_3)	0.50(L_2)	0.4(L_1)
07	5000(L_3)	30(L_1)	0.50(L_2)	0.6(L_3)
08	5000(L_3)	60(L_2)	0.75(L_3)	0.4(L_1)
09	5000(L_3)	90(L_3)	0.25(L_1)	0.5(L_2)

2.3 Characterization of ZnO thin films

The coating thickness and surface roughness of ZnO thin films were measured using surface profilometer and Atomic Force Microscope, (AFM, Nanosurf Easy Scan 2). The structural property of thin films was studied using a high resolution X-ray Diffractometer (XRD Maxima-7000 (Shimandzu) at a scanning rate of 2° min-1 using Cu-Kα radiation (λ = 1.54 A^0) from scanning range of 200 to 80° operating at 40 kV and 30 mA. XRD was performed for phase identification of ZnO films. Scanning Electron Microscopy (SU-1500, HITACHI) was used for studying the morphology of thin films. Accelerating potential of 15 kV and the beam current of 20 mA were adopted for the SEM studies. The thin films were dried at room temperature before applying the gold coating.

2.4 Experimental Results

The results of the experiments conducted using L_9 Orthogonal Array are presented in Table 2. Three replicates were used along with the mean and standard deviation of the samples for obtaining the S/N Ratio for each experimental run.

Table 2: Experimental results.

Expt. No.	Coating thickness (nanometer)						Surface roughness(RMS value, nanometer)					
	R1	R2	R3	Mean	Std. Deviation	S/N ratio	R1	R2	R3	Mean	Std Deviation	S/N ratio
01	1016	537	555	702	271	-8.26	5.55	3.29	4.53	4.45	1.13	-11.88
02	838	406	439	561	240	-7.36	4.40	3.78	5.08	4.42	0.65	-16.60
03	787	1782	1736	1435	561	-8.15	17.36	16.44	16.72	16.84	0.48	-30.97
04	1016	2170	1168	1451	627	-7.29	11.69	11.34	11.49	11.51	0.17	-36.41
05	584	837	677	699	127	-14.75	7.68	6.78	7.54	7.33	0.48	-23.60
06	1600	1607	783	1330	473	-8.97	11.48	11.44	11.36	11.43	0.06	-45.47
07	838	754	567	719	138	-14.30	5.67	5.02	5.98	5.56	0.49	-21.15
08	508	1346	1297	1050	470	-6.98	12.97	10.66	11.09	11.57	1.23	-19.47
09	508	1092	697	765	297	-8.20	6.98	5.13	5.63	5.91	0.96	-15.83

3. Results and Discussion

3.1 Optimization based on coating thickness of film

Highest S/N ratio of 14.75 for coating thickness corresponded to the factors and levels of Experiment No.5, i.e. spinning speed 4000 rpm, spinning duration 60 seconds, volume of solution 0.25ml and precursor concentration 0.5M. Figure 1 shows the effect of the factors on the coating thickness. Precursor concentration most significantly influenced the coating thickness, followed by spinning duration, spinning speed and volume of the solution. Coating thickness with quality characteristic ‘smaller the better’ was considered for computing the S/N ratio.

Fig 1 (a) shows that the coating thickness increased with increase in spinning speed from 3000 to 4000 rpm. But, it decreased for further increase in speed from 4000 to 5000 rpm. This shows a non-linear relationship between spinning speed and coating thickness. This is in conformance with that of Yonkoski. R.K and Soane D. S [23] who proposed three stages of spin coating as deposition and spin up, spin off and film drying. During the first stage, the solution is allowed to fall on a rotating substrate from a micro syringe and the substrate is accelerated to the desired speed. Spreading of the solution takes place due to centrifugal force and height is reduced to the critical height. During the second stage (spin off), subsequent reduction in film height is dominated by the evaporation of the solvent. During the final stage

centrifugal outflow stops and further shrinkage is due to solvent loss. This results in the formation of thin film on the substrate. In actual practice, these three stages overlap with each other.

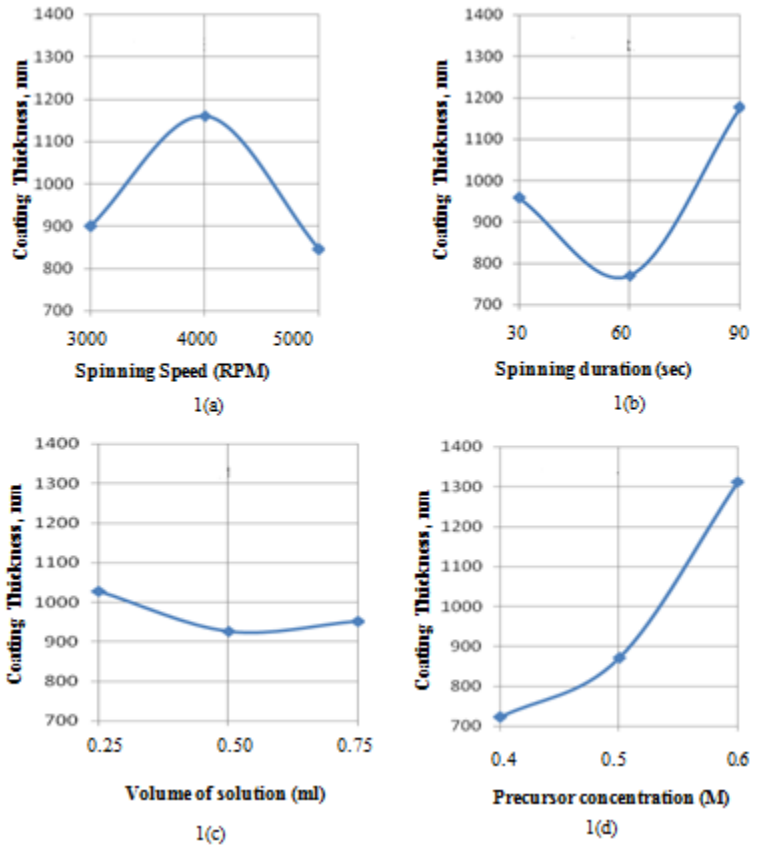


Figure 1: Effect of spin coating parameters on coating thickness of thin film a) Spinning speed, b) Spinning duration, c) Volume of solution and d) Precursor concentration

Fig 1 (b) shows that the coating thickness decreased with increase in spinning duration from 30 to 60 sec. But, it increased for further increase in spinning duration from 60 to 90 sec, exhibiting a non-linear relationship between spinning duration and coating thickness. This is in agreement with the reports of Carcano, G et al. [24] who proposed that coating thickness is dependent on the spinning duration. The range of spinning duration selected for the experiments of the present research includes durations when the coating is not stable so that the coating thickness decreases quickly in the first 30 seconds of spinning when centrifugal forces are driving the thinning process. The thinning rate decreases significantly once evaporation dominates i.e. during 60 seconds implying that coating thickness is less sensitive to spinning duration during the evaporation stage. During the final stage i.e. during 60 - 90 seconds, the coating thickness increases due to the loss of solvent. Since the design space selected in this set of experiments includes times shorter than that required for the onset of evaporation, the thinning rate is not stable and highly sensitive to spinning duration.

Fig 1 (c) shows that the coating thickness decreased with increase in volume of solution from 0.25 to 0.50 ml. However, it increased for further increase in volume from 0.50 to 0.75 ml. This shows a non-linear relationship between volume of solution and coating thickness. This is in agreement with the reports of Niranjan sahu et al. [25] who proposed that there are three stages of deposition. During the first stage, only a portion of substrate to be coated is covered and is not spread uniformly. Hence, coating thickness is high in this stage. It starts reducing in the second stage because the solution starts spreading over the substrate. In the third stage the solution deposits radically due to the outward flow of the solution over the entire substrate and excessive volumetric deposition is limited. Thus, the stage ends when delivery ceases so that thickness is increased.

Fig 1(d) shows that coating thickness increased with molar concentration of precursor from 0.4 to 0.6 M, which indicates a linear relationship between coating thickness and molar concentration of the precursor. This is in agreement with the reports of W.W Flack et al. [26] who proposed that increase in precursor concentration results in thicker film. During the first stage, increase in precursor concentration of 0.4 M results in thicker film because of increase in fluid viscosity and during second stage i.e. from 0.5 M the film thickness is controlled by convective radial flow of the solution so that the coating thickness increases during third stage i.e. for 0.6 M the film thickness increased due to the evaporation of the solvent.

3.2 Optimization based on surface roughness of film

Highest S/N ratio 45.47 corresponds to the factors and levels of experiment No.6, i.e. spinning speed 4000 rpm, spinning duration90 seconds, volume of solution 0.50 ml and precursor concentration of 0.4M. Figure 2 shows the effect of the factors on the surface roughness. Precursor concentration most significantly influenced the surface roughness, followed by spinning duration, volume of the solution and spinning speed. Surface roughness with quality characteristic ‘smaller is better’ was selected for S/N ratio computation.

Fig 2(a) shows the effects of spinning speed on the roughness of the films. The RMS values of surface roughness were 8.65, 10.11 and 7.75nm for thin films obtained at 3000, 4000 and 5000 rpm, respectively. This shows that the RMS increased as the spinning speed increased during the first stage. However, it decreased for further increase in speed from 4000 to 5000 rpm. This shows a non-linear relationship between spinning speed and RMS roughness. This is in conformance with that of R. Dewi et al. [27] and Shim et al.[28] who reported that highest spinning speed produced the roughest surface, while the lowest spinning speed produced the smoothest surface. Thus, the thin film processed in the present research is very smooth and uniform.

The RMS value increased linearly with spinning duration as shown in Fig. 2 (b) due to solvent evaporation, adhesive forces and centrifugal reaction of the solvent. The solvent evaporated more at the extreme end of the substrate due to higher velocity of air and disc contact ($v = \omega r$) than middle of the disc. In other words, although adhesive force is same throughout the disc the centrifugal force of the film is increased with distance ($m\omega^2 r$) and to overcome the adhesive force efficiently. Because of these two reasons, the thickness reduced along the distance of the disc almost in a tapered way. A. R. Fazeli & Majid Ghoreishi [29] showed that in higher rotation rate of spin coating, the movement of the film produces local deformation throughout the surface of the disc which reduces the wall thickness of the film

from the initial point to the extreme point, due to centrifugal reaction of films [30,31]. High percentage thickness reduction and low disc rotation speed minimize the surface roughness [29].

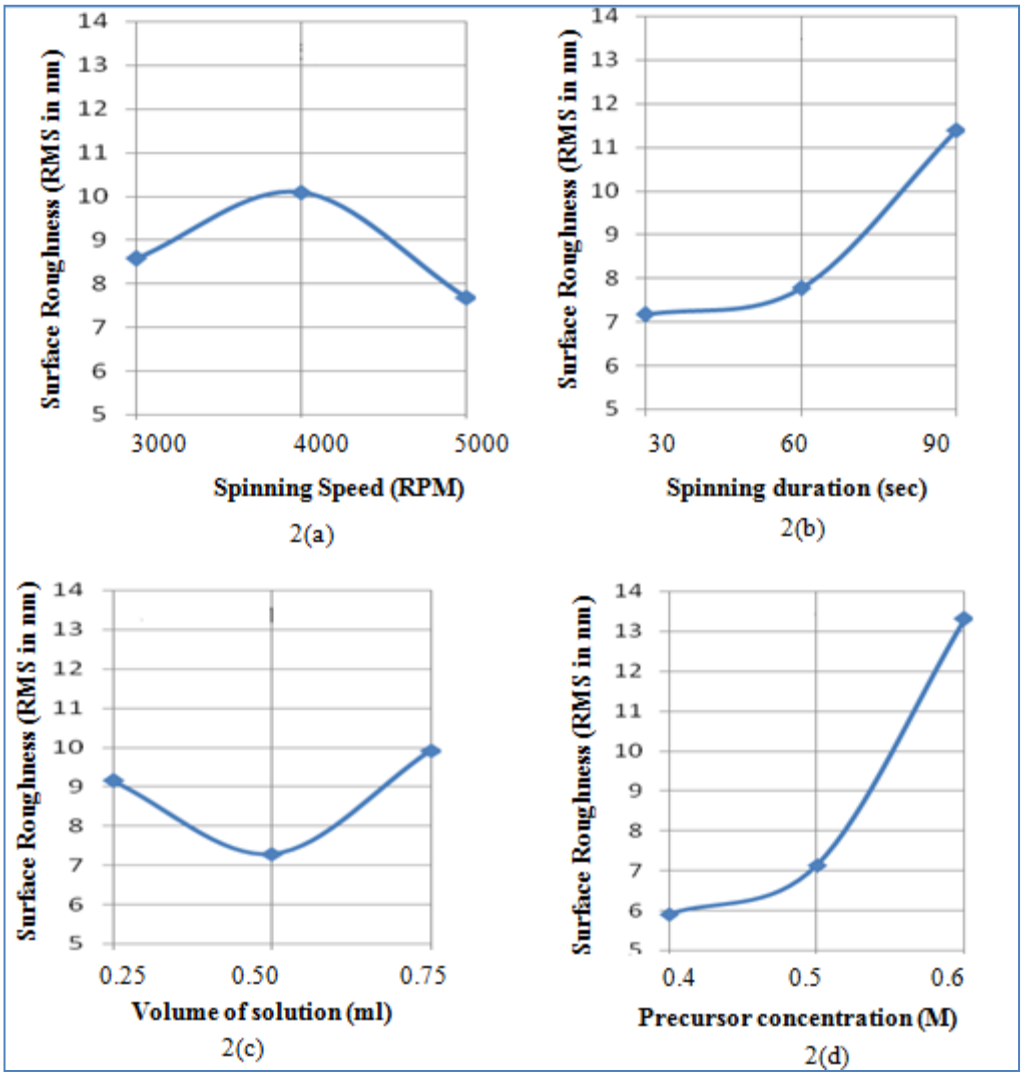


Figure 2: Effect of spin coating parameters on surface roughness of thin film a) Spinning speed, b) Spinning duration, c) Volume of solution and d) Precursor concentration

Fig 2 (c) shows that RMS value decreased with increase in the volume of the solution i.e. from 0.25 to 0.50 ml. But, it increased for further increase volume from 0.50 to 0.75ml. This is in agreement with that of Wenzel R. N [32] who reported that initially high RMS value is high due to small portion of substrate getting wetted as quantity of solution is less and during second stage as the volume of solution increased the RMS value decreases because of decrease in contact angle between substrate and the solution and further as the contact angle. During the third stage as the volume of solution is increased the RMS value increases this is in agreement with the Shuttleworth and Bailey [33] who stated the as the rough surfaces contact line start distort locally which give rise to a spectrum of micro contact angles near the substrate surface which results in increase in RMS value.

Fig 2 (d) shows that RMS value increases with increase in precursor concentration from 0.4 to 0.6 M which is agreement with X.Zhao et al. [34]. The authors suggested that increase in RMS during the first stage is due to the crystal growth, which is relatively fast at liquid solid interface. During the second stage, increase in the precursor concentration increases the colloidal particles. Hence, the reaction will be faster so that roughness increases. During the third stage as the amount of solute increases in sol the electrostatic interaction between the solute particles becomes larger, thus increasing the probability of more solute to be gathered forming a grain so that roughness increases. Therefore, with increase in precursor concentration the roughness also increases.

3.3 ANOVA

3.3.1 Influence of parameters on coating thickness

Table 3 shows ANOVA results for the coating thickness of ZnO film to study the contribution ratio of spin coating process parameters. It can be observed that the molarity of precursor concentration (P = 56.47 %) and spinning duration (P = 24.85 %) showed significant influence on the coating thickness of film and the best combination for the least coating thickness is $A_3B_2C_2D_1$ and hence separate spinning experiments were conducted to find the coating thickness and the results are shown in Table 5.

Table 3: ANOVA for coating thickness.

Factors	Levels			DOF	SS	MS	F_{cal}	F_{tab}	P (%)	Optimum Level
	1	2	3							
A	899.56	1160.22	845.22	2	170120	85060	1.82	3	17.01	A3
B	957.89	770.22	1176.89	2	248562	124280	2.65	3	24.85	B2
C	1027.67	926	951.33	2	16805	8402	0.17	3	1.68	C2
D	722.56	870.22	1312.22	2	564869	282434	6.04	3	56.47	D1

DOF: Degree of Freedom, SS: Sum of squares, MS: Mean squares, F: F- Test, F0.05 : 95 % confidence band, P : Percentage of Contribution.

3.3.2 Influence of parameters on Surface roughness

ANOVA results for the surface roughness are presented in Table 4. The molarity of precursor concentration (P = 64.87%) and spinning duration (P = 21.47%) had significant influence on the surface roughness of the film and the minimum surface roughness corresponded to the factor level combination of $A_3B_2C_2D_1$. Spinning experiments were conducted for this combination and the results are shown in Table 5.

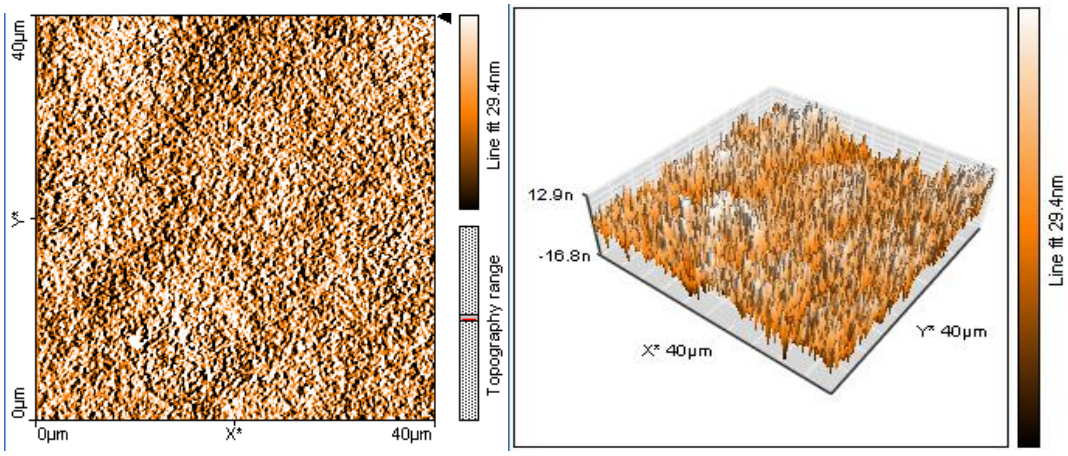
Table 4: ANOVA for surface roughness.

Factors	Levels			DOF	SS	MS	F_{cal}	F_{tab}	P (%)	Optimum Level
	1	2	3							
A	8.57	10.09	7.68	2	8.91	4.45	0.89	3	6.12	A3
B	7.17	7.77	11.39	2	31.27	15.62	3.14	3	21.47	B1
C	9.15	7.28	9.91	2	10.99	5.49	1.10	3	7.54	C2
D	5.90	7.14	13.31	2	94.51	47.22	9.49	3	64.87	D1

3.4 AFM, XRD and SEM Characterization of thin films

3.4.1 Atomic Force Microscopy (AFM)

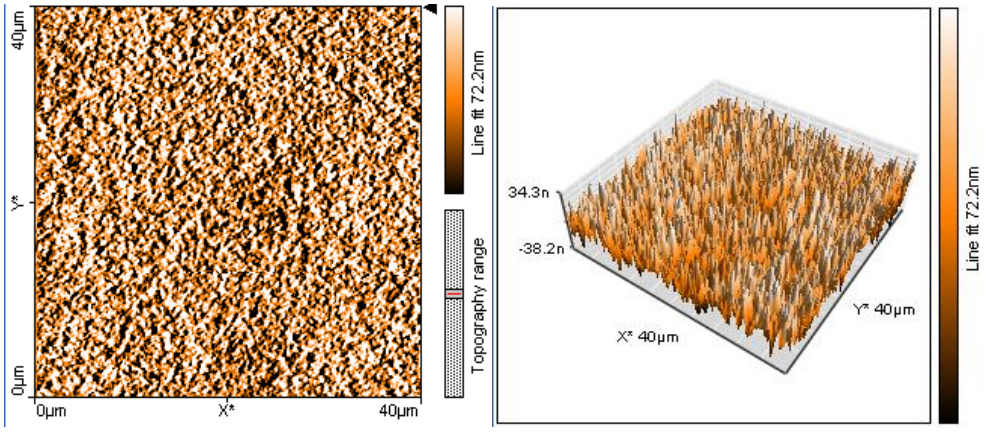
Fig.3 (a) shows a two dimensional surface morphology and Fig. 3(b) 3D image of the thin films prepared at optimum level ZnO sol ($A_3B_2C_2D_1$). The images were obtained using Atomic Force Microscope by contact mode. The scanning area was 40 µm x 40 µm. Fig.3 (b) reveals that the sample surface is relatively rough and grain sizes are uniform. The measured values of coating thickness and surface roughness were 492 nm and 3.31 nm respectively.



3(a) 3(b)

Figure 3: (a) and 3(b) AFM Micrographs of ZnO thin films for optimum condition for coating thickness.

Fig.4 (a) and 4(b) show AFM micrographs of the ZnO thin films obtained for the factor level combinations of $A_3B_1C_2D_1$. The RMS value of surface roughness is 3.27nm and the coating thickness was 508nm.



4(a) 4(b)

Figure 4: 4 (a) and 4 (b) AFM Micrographs of ZnO thin films for optimum condition for surface roughness.

Table 5 shows the experimental results of coating thickness and surface roughness obtained for the optimum parametric combination, performed as confirmation experiments.

Table 5: Experimental results for the optimum parametric combination.

Combination	Coating thickness (nm)	Surface roughness(nm)
$A_3B_2C_2D_1$	492	3.31
$A_3B_1C_2D_1$	508	3.27

Table 5 shows that the lowest coating thickness of the thin film can be obtained by adopting the parametric combination $A_3B_2C_2D_1$ and the best surface roughness by adopting $A_3B_1C_2D_1$ combination.

3.4.2 X-ray Diffraction (XRD)

XRD pattern of ZnO thin film obtained by adopting optimum levels of parameter combinations is shown in Fig. 5. Three strongest diffraction peaks were detected at Bragg angles of 31.8^0, 34.4^0 and 36.3^0 indicating that the films are polycrystalline with a hexagonal wurtzite structure and preferred orientation along (100), (002) and (101) planes. No characteristic peak was observed for impurities.

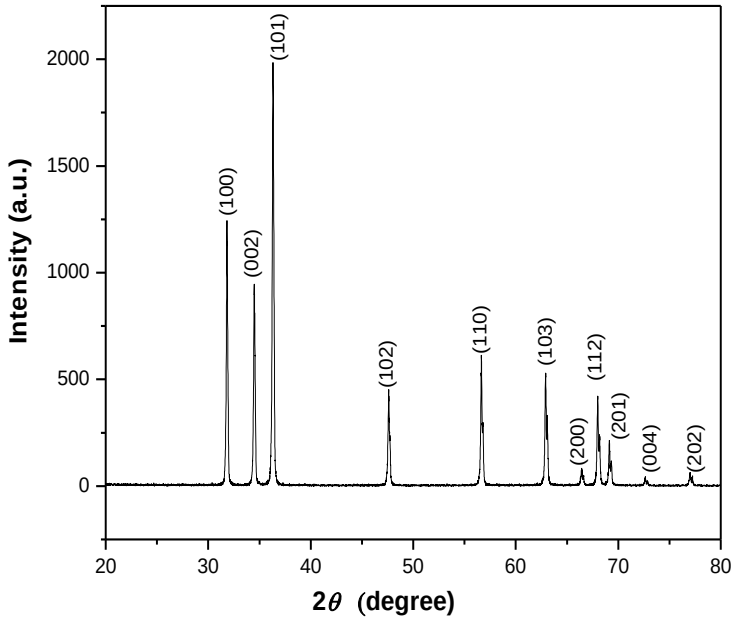


Figure 5: XRD pattern of Zinc Oxide thin film obtained for optimum parametric combination.

3.4.3 Scanning Electron Microscopy (SEM)

SEM micrograph of Fig.6. revealed the nanostructure of the ZnO thin film for optimum combination with an average grain size of 45 nm. Irregular grains of the film on the surface of the substrate were due to the shortage of hydroxyl or alkoxy group in ZnO solution which was evaporated due to the shorter time for drying of the solution.

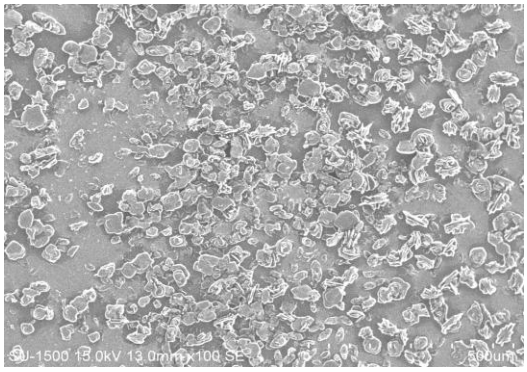


Figure 6: SEM micrograph of ZnO thin film obtained at for optimum parametric combination.

AFM, XRD and SEM results confirmed the optimum parameters of spin coating which are important for the quality of ZnO thin films for achieving the specified coating thickness and surface roughness of the film.

4. Conclusions

Based on the experimental investigation of spin coating process for synthesizing ZnO thin films the following conclusions were arrived at:

- Lowest coating thickness of 492 nm was obtained at spinning speed 5000 rpm, spinning duration 30 seconds, volume of solution 0.75 ml and Molar concentration of the precursor 0.4 M the least coating thickness obtained was.
- Best surface roughness of 3.27 nm was also obtained at the same parameter combinations except for the spinning duration of 60 seconds.
- Three strongest diffraction peaks were detected at Bragg angles of 31.80, 34.40 and 36.30 indicating that the films are polycrystalline with a hexagonal wurtzite structure.
- The coating thickness and surface roughness were measured by surface profilometer and AFM respectively.

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