Effect of Coating Thickness on the Mechanical Behavior of ZnO Thin Films on Stainless Steel Prepared by Sol-gel Route

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Abstract— *ZnO has high bandgap with high excitation binding energy which make it a powerful candidate for many future applications. This work consist of testing mechanical behaviour of ZnO thin film deposited on stainless steel substrate of variable thickness. ZnO thin films were grown using sol-gel process with multiple iterations to vary the thickness. Thickness of film were measured using surface profilometer. Nanoindentation method is used to get the mechanical properties (hardness and young's modulus) of ZnO film series prepared by sol-gel process.*

1. INTRODUCTION

ZnO has gained high interest of research community in past decade. ZnO[1] has many properties such as semiconductivity, high bandgap with high excitation binding energy, piezoelectricity, room-temperature ferromagnetism, huge magneto-optic and chemical-sensing effects. ZnO cover many application field with all its property so it felt very interesting to test the structural and mechanical properties of ZnO. This work is based on structural (crystal morphology, surface roughness etc) and mechanical (hardness and young modulus) of thin film. ZnO film was prepared by various other techniques like CVD[2], molecular beam epitaxy[3], pulsed laser deposition[4],[5], RF magnetron sputtering[6]. After analysing all these methods, we found sol-gel technique[7],[8] be the best one to prepare ZnO thin film as sol gel technique is simple, cheap, variation in thickness of film is possible and film is uniform. In this paper, we show preparation of ZnO thin film using sol-gel method with multiple thickness and then the variation in its properties as a function of thickness.

2. MATERIALS AND METHODS

2.1 Preparation of ZnO solution

For the preparation of the ZnO sol, 99%pure Zinc acetate dehydrate and iso-propanol were used as a precursor material and diethanolamine was used as a sol stabilizer/surfactant. To prepare 0.1 M of sol, 0.432g of zinc acetate dehydrate($ZnC_4H_6O_4$) was weighed and then dissolved in 20 ml of iso-propanol. Then the solution was stirred continuously at 84°C for 30 minutes at 500 rpm on themagnetic stirrer. The solution turned milky after 10 minutes of stirring and heating. After this step, the equimolar of surfactant i.e. diethanolamine was taken in the 100µl pipetteand it was added drop by drop into the milky solution. The solution became transparent after sometime and was continuously stirred around 1 hour at the same rpm and temperature. The transparent sol was prepared and it was kept aside for 24 h for the ageing process so that the bonds between the zinc and oxygen becomes stronger. After ageing the gel is prepared for the film formation.

2.2 Film Formation

The deposition of the film on the stainless steel was done by using spin coater. Firstly, the stainless steel(SS316) was taken as a substrate. The dimension of the substrate was 1.5×1.5×1 cm. Before depositing the film, the substrate was cleaned by using sonicator. The substrate was first sonicated in acetone for 10 minutes, then in ethanol for 5 minutes and then again in distilled water for 10 minutes. After this, the sample was dried for the coating in an oven at 100°C.The substrate was put at the centre of the spin coater and for the holding of the substrate vacuum pump was on. Then, 60 ml of gel was taken in pipette and put on the centre of the substrate for uniform layer of coating. The spin coater was then allowed to rotate at the speed of 3000 rpm for 20 seconds. Now, the film is deposited on the substrate and then the film was allowed to dry at 100ºC in an oven for 10 minutes.This is done to remove the organic solvents from the film and to make the crack free coating.After this, the annealing was done on the sample in air in the furnace at 500°C for 1 hour to obtain the crystallinity of the film.This process is repeated for several times to study the thickness effect on the ZnO thin film.The summary of the ZnO thin film preparation by sol gel process is shown in **Fig.2.1**in the form of flow chart. Different thickness samples were prepared by doing 5,6,7 and 8 number of coating.

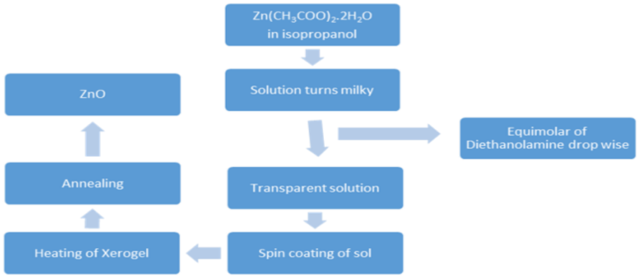

Fig. 2.1: The flow chart of the process used in the preparation of ZnO solution.

3. RESULTS AND DISCUSSION

The thin film was deposited on the stainless steel SS 316 substrate and characterization techniques were done which confirmed the formation of ZnO. Four samples were prepared, by changing the number of coating, the thickness of films varied. The coating was repeated for the 5,6,7 & 8 number of times and desired thickness were obtained. The thickness was measured through surface profilometer, the measuredthicknesses were 300, 350, 450 & 580 nm.The films were tested by XRD, FE SEM,AFM,. The mechanical properties of the films were studied by Nanoindentation techniques.It gives the value of hardness and the young's modulus of the film.

3.1 XRD ANALYSIS

The crystallinity of the ZnO thin films were analyzed by XRD. Fig. 3.1 showing the XRD pattern of ZnO thin films where the standard peaks of ZnO were analyzed. Study of the standard JCPDS 021-1486 illustrated that the synthesized materials are hexagonal ZnO phase (wurtzite structure) with (100),(002),(101) crystal planes peaks of ZnO. Study of the JCPDS 033-0397 confirmed the peaks of stainless steel present in the XRD pattern. The deviation of lattice parameter was also observed which is due to the presence of various point defects such as zinc interstitials, oxygen vacancies. It is demonstrated that with the increase in the thickness of the thin film, there was not any significant effect on the peak height and on the crystallinity of the structure.

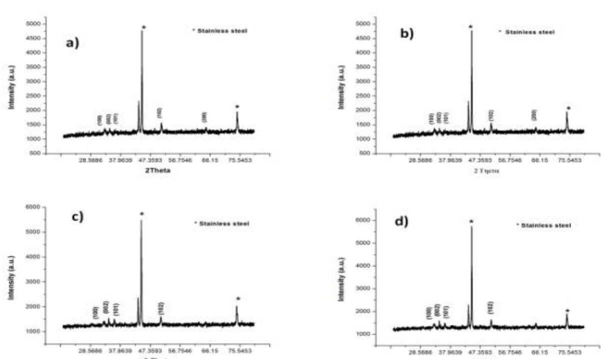

Fig .3.1 showing XRD plots of (a)300, (b) 380,(c)450 & (d) 580 nm.

3.2 AFM ANALYSIS

To analyze the grain size and to study the effect of surface roughness of the filmagainst mechanical properties, AFM analysis was done. **Fig.3.2** shows the 2D AFM images of the films grown on the stainless steel SS 316 substrate with different thickness.The results demonstrated that the ZnO film with thickness 300, 380, 450, 580 nm has surface roughness of 30.24, 26.197,21.501 and 20.72 nm respectively. The film with higher thickness was much smoother than the film having less thickness. And the grain size of the film is decreasing with the increase in the thickness of the film.The grain size of the film was ranging from 122.67 to96.447 nm.With the increase in the thickness of the film, the grains were becoming more denser and they were uniformly distributed over the surface.

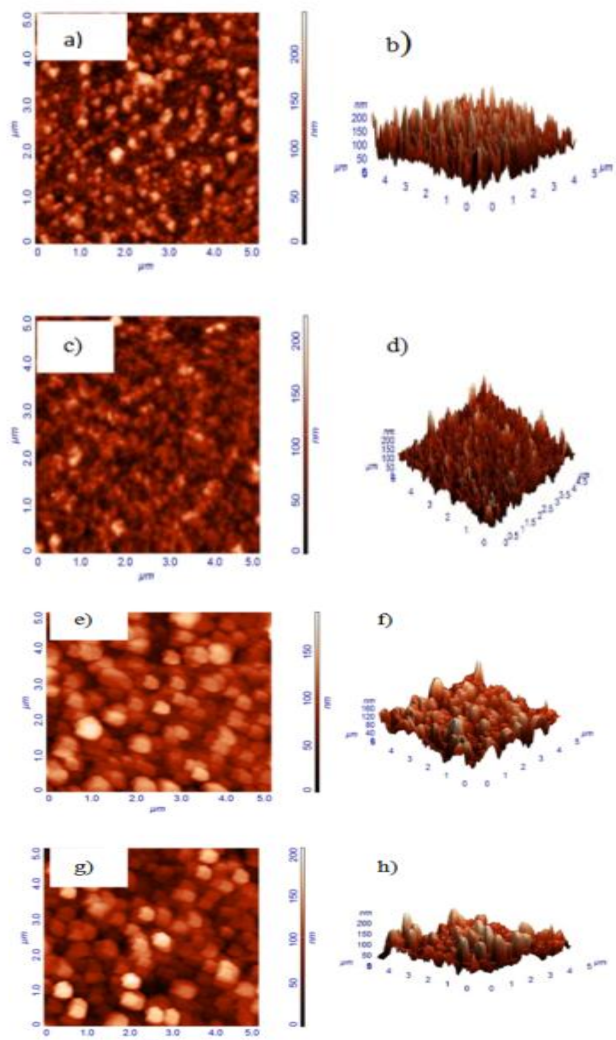

Fig. 3.2: (a), (c), (g) and (f) are the AFM images of ZnO film for roughness analysis with different thickness 300, 380, 450 and 580 nm, respectively; (b),(d), (e) and (h) are the three dimensional images of ZnO film.

3.3 FE SEM ANALYSIS

The surface morphology of the coating was confirmed by FE SEM analysis. **Fig.3.3** shows the different FE SEM micrographs of the samples prepared with different coating thickness. Four samples were prepared having 5,6,7 and 8 numbers of coating with increase in thickness approx 300 nm, 380 nm, 450 nm and 580 nm respectively. The figure clearly demonstrates the formation of hexagonal ZnO nanostructure and the change of grain size with the coating thickness. It is also understood that there is no porosity in the coating, and the grains are uniformly distributed over the surface. It is also clearly visible that as the number of coating increases, the thickness increases and hence grain size is decreasing. From **Fig. (a) to Fig. (d)** it can be concluded that the density of the smaller grains is increasing over the surface with the increase in the coating thickness.

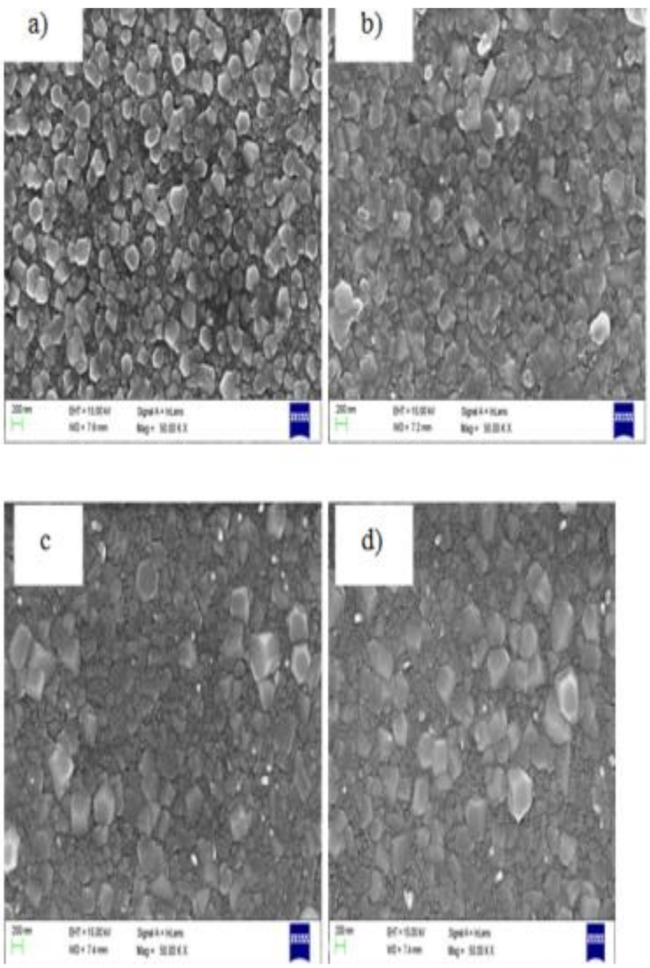

Fig.3.3: FE SEM images of the films annealed at 500°C with (a)300 nm (b) 380 nm (c) 450 nm (d) 580 nm coating thickness respectively.

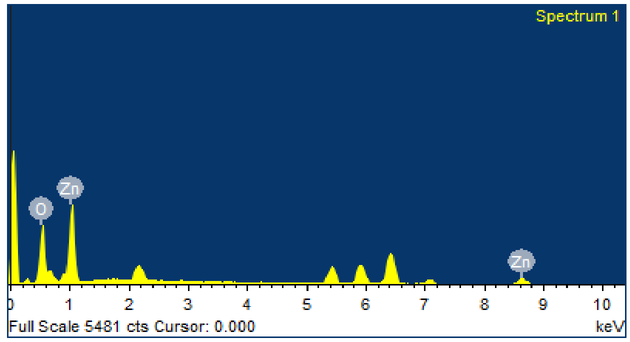

Fig. 3.3.1: Showing the confirmation oftheformation of the ZnO nanostructure through EDX analysis.

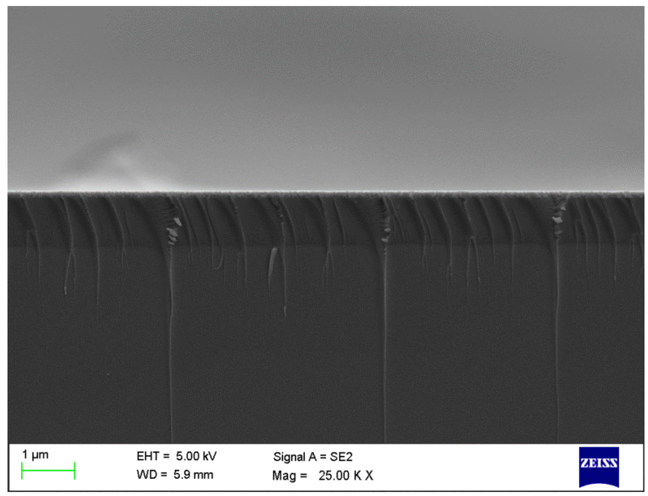

Fig. 3.3.2: Showing the cross sectional view of the coating.

3.4 NANOINDENTATION RESULTS

To analyze the mechanical properties of ZnO coating fabricated by sol gel method, nanoindentation technique was used. **Fig. 3.4** is the loading and unloading curves obtained when doing nanoindentation and showing the hardness and young's modulus value of the film coated on the stainless steel substrate with different thickness approx 300 nm, 380 nm, 450 nm and 580 nm.500μN load was applied on the film to cause effective plastic deformation during indentation neglecting substrate effect. The nanoindentation results demonstrated that the hardness of the ZnO film was 6.7 GPa and it decreases to 5.98 GPa as the thickness of the coatingincreases. It was recommended that the decrease in hardness was due to the residual stresses present. These residual stresses were relaxed by the annealing process. Nanoindentation measures both thehardness and the modulus, and these are affected by theresidual stress. The increase in modulus could be due to the residual stress induced by the substrate. However, the decrease in the hardness and modulus could not be only explained by the residual stress effect. It is reported that, according to Hall-Petch relationship of the metals and metal alloys, the yield strength and the hardness of the film increases when grain size decreases. It was foundthat the grain sizewas decreasing with the increase in the thickness of the coating which is in accordance to the Hall Petch relationship also. It is also reported, that the hardness of the film not only depends on grain size but it also depends on the ratio of the grain size to the indentation size during indentation process[9].

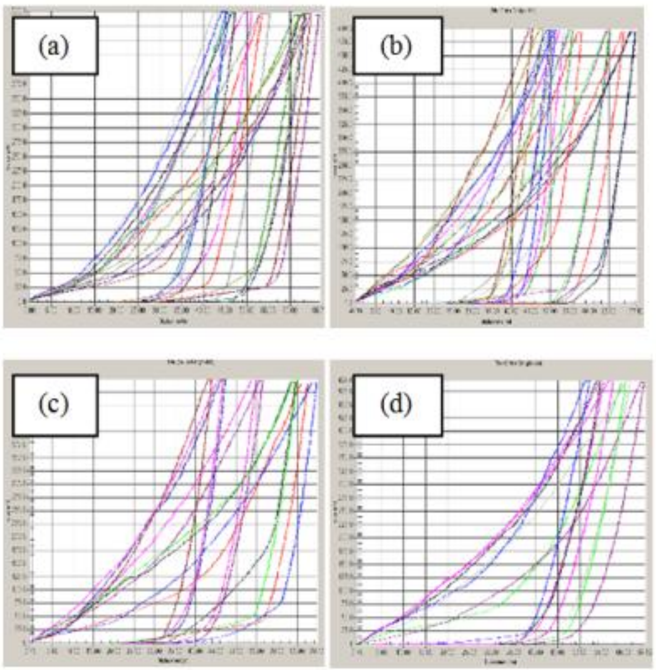

Fig. 3.4: Loading and unloading indentation curve of the film with thickness(a) 300,(b) 380 (c) 450 and (d) 580 nm respectively.

Table 3.4.1: Showing the values of Young's Modulus and hardness of the ZnO.

Sample	Young's modulus Gpa	Hardness (GPa)
ZnO_5	202.08±49.39	5.91±0.2
ZnO_6	200.65±40.50	5.98±0.78
ZnO_7	211.21±50.41	5.98±0.05
ZnO_8	151.53±14.17	6.7±0.963

4. CONCLUSION

In summary, the ZnO thin films were fabricated by the use of the low cost effective method. The ZnO thin films were fabricated by sol-gel process using spin coating. The films were annealed at 500°C for 1 hr in air. All the characterization results confirmed the synthesis of ZnO.Crystal orientation, grain size, hardness and young's modulus were calculated using XRD, AFM and Nanoindentation respectively.ZnO also exhibits good mechanical properties with high hardness at nanoscale, which tells that ZnO offers some potential to be used where load is applied.ZnO provides a new path in the field of large scale device fabrication.All the results state that ZnO has unique properties and it can be used in various application by using it in energy harvesting techniques which will provide a new direction to the coming world in saving the energy and it would be cost effective also.

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