Deposition and Optical Characterization of ZnO Thin films on Glass Substrate

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Abstract. ZnO is a wide band gap (3.37 eV) compound semiconductor which can be used in short wavelength optoelectronic devices. Here in this work we chose spin coating method as growth mechanism as it is simple, less expensive and in addition film uniformity is maintained in this method. In the growth process zinc acetate dihydrate, iso-propanol and monoethanolamine were used for producing Sol-gel Solution. The prepared solution was kept for 3 days (44 h) and 7 days (188 h) for aging. After deposition, optical characterization has been performed by UV-VIS-Spectrometry. The Transmittance values of the films deposited at the speeds of 2500 rpm (with 44 h aged solution) and 3500 rpm (with 188 h aged solution) are at the range of 70-73% and the Energy band gaps of the films are 3.1 eV and 3.25 eV, respectively. Whereas films deposited at the speed of 4000 rpm shows 86% transmittance and band gap energy of 3.3 eV which is much closer to the optimum value of 3.37 eV. Lower absorption values have been shown for higher coating speed. So with the increase in coating speed, the transmittance and the band gap both are increased. Also we can see that there is very negligible effect of aging time on optical properties of deposited films.

1. Introduction:
Transparent conducting oxide layers have been studied widely because of their far-reaching range of applications. Recently, ZnO thin films have urged a great interest as transparent conductor, owing to their favorable properties. ZnO is a key technological material which has wide band-gap energy of 3.37 eV[1]. Advantages associated with a large band gap include higher breakdown voltages [2], ability to sustain large electric fields [3], lower electronic noise [2], high-temperature and high-power operation [4].

ZnO thin films are low cost, nontoxic and highly durable against hydrogen plasma compared to ITO [5]. ZnO-based nanostructures including nanowire arrays hold a host of opportunities for flat screen displays, field emission sources, gas, chemical [6] and biological sensors, and as UV light emitters and switches [6-8]. The high exciton binding energy (60meV) [1] in ZnO crystal can ensure efficient excitonic emission at room temperature. Furthermore, these nanostructures are easily formed even on cheap substrates such as glass and hence they have auspicious potential in the nanotechnology future.

ZnO films have been fabricated using various kinds of deposition techniques. Among them molecular beam epitaxy, chemical vapor deposition, chemical bath deposition and spin coating are prevalent. It seems that the vacuum based technology is costly which might not be suitable for many applications. Thus low cost techniques such as chemical bath deposition and spin coating are...
promising for different applications. In our study we have chosen Sol-gel Spin Coating as our deposition method because of controllability of composition, simplicity in processing, cost effectiveness and Film Uniformity. Moreover this process has been widely used in the manufacture of integrated circuits [9], optical mirrors, color television screens and magnetic disk for data storage [10].

In this paper we provide a meticulous overview on optical properties of ZnO nanostructures. Production of high quality films at relatively lower annealing temperature, optical characterization of ZnO deposited films to understand their optical properties and investigation of the optimum film on the basis of characterization results are the prime concern here. The assessment is organized as follows: At first we discussed a complete review of sample grounding, sol preparation and fabrication of films of ZnO. Next optical characterization results and discussion on optical properties are introduced. Finally some conclusion and viewpoint for the future are given.

2. Experimental Method:
For preparing sol, we have used Zinc acetate dehydrate Zn(CH$_3$COO)$_2$·2H$_2$O (ZAD) as the precursor material and chosen the concentration of the solution 0.5 M. In order to produce the solution of required concentration, we have taken 4.39 g of Zinc Acetate Dehydrate. We weighted the required amount of Zn(CH$_3$COO)$_2$ using a balancing instrument. 4.39 g of Zinc acetate dehydrate was mixed with 100 ml of Iso-propanol. Then we started boiling the prepared solution at 65 °C under constant stirring using a magnetic stirrer. The color of the solution turns milky after 15 minutes of stirring and heating. After 30 minutes of continuous stirring and heating, we have added 6-10 drops of monoethanolamine to the solution by a 5 ml dropper. Monoethanolamine acted as sol stabilizer. The solution turned transparent, but its heating and stirring was continued for further 90 minutes. Then the solution under stirring was allowed to cool. The whole process of Sol preparation took 2 hours and we have used CBD machine for preparing this Solution of Deposition.

Aging mechanisms have a great influence on the formation of good quality ZnO nanostructure. So we have decided to vary the aging time to see its effect on the formation of the films. We have kept the solution for 44 hours (almost 3 days) and 188 hours (almost 7 days) at room temperature to produce aged solution. We haven’t prepared any film from freshly prepared solution. Once the fabrication has been done, the fabricated films were taken to the vacuum heat chamber for annealing treatment. Here, a pre-heat treatment of 200°C was applied for 1 hour. Post heat treatment temperature was 250°C and the duration of the treatment was 1 hour.

3. Results and Discussion:
After the preparation of the samples, the optical properties were investigated. We have fabricated eight Samples varying aging time and coating speed. Among them we have chosen four samples for characterization. We have listed the samples in the table 1 that are being characterized-

| Sample ID | Aging time | Coating Speed |
|-----------|------------|---------------|
| S1        | 44 hours   | 2500 rpm      |
| S2        | 44 hours   | 4000 rpm      |
| S3        | 188 hours  | 3500 rpm      |
| S4        | 188 hours  | 4000 rpm      |

(a) Transmittance Analysis:
Transmittance of the surface of a thin film is its effectiveness in transmitting radiant energy. Fig 1 (a) and (b) shows the variation of transmittance with respect to wavelength. These showed variations are for films of different speeds produced by 44 h and 188 h aged solutions.
In Fig 1 (a), it is seen that films with different rpm speed (aging Time 44 h) have almost same transmittance pattern. It is also observed that transmittance rises very rapidly after 350 nm, attain at maximum value and then stay in between 70-75% up to 800 nm. When the coating speed is 2500 rpm, the maximum transmittance value is 70% whereas at the speed of 4000 rpm the value is reported 75%. Similarly if we look at Fig 1(b), we can observe that in case of 3500 rpm coating speed, the value of transmittance is reported 76% but at the speed of 4000 rpm a dramatic increase in transmittance value has been observed and that was up to 87%.

(b) Absorbance Analysis:
The term absorption refers to the physical process of absorbing light, while absorbance does not always measure absorption: it measures attenuation (of transmitted radiant power). Fig 2(a) and (b) shows the absorbance spectra of ZnO thin films (different aging time) with respect to wavelength-
If we look at Fig 2 (a) and (b) we can see that, absorbance value rises very rapidly before 300 nm, attains at maximum value and then decreases rapidly up to 380nm. It is also observed that in case of films produced by 44 h aged solution the absorbance range is in between (0.3~1.8) and for the films produced by 188 h aged solution, the absorbance ranges in between (0.2~1.6). From Fig 4.8 and 4.9, it is clear to us that, with the increase in coating speed, absorbance decreases.

(c) Band Gap Measurement:
In Fig 3 (a) and (b), $(\alpha h\nu)^2$ as a function of photon energy is plotted to obtain band gap energy for different ZnO films. Table 2 summarizes the band gap of different films.
If we look at the band gap values, it has been observed that the plots of $(\alpha h\nu)^2$ versus $h\nu$ are linear over a wide range of photon energies. In case of films produced by 44 h aged solution, we can see that at 2500 rpm speed the obtainable band gap value is 3.2 eV. On the other hand when the speed increases up to 4000 rpm the band gap value increases to 3.3 eV which is much closer to the optimum value 3.37 eV. Same thing has been observed in films when aging time is 188 h. The band gap value improves as we increase the coating speed. At 4000 rpm coating speed, 3.3 eV band gap has been observed which matches the actual band gap value.

We can also evaluate from the above table that, the changes in the value of band gap energies with the change in aging time is very much negligible. With the same speed of 4000 rpm, we have got band gap energy of 3.3 eV regardless of aging time. That means whether we take 44 h aged solution or 188 h aged solution, prepared films will give almost same optical band gap unless we change the coating speed.

4. Conclusions
Investigating the effects of coating speed and aging time on diverse properties of ZnO thin films and hence finding the optimized result is the prime concern of our work. The Transmittance values of the films deposited at the speeds of 2500 rpm (with 44 h aged solution) and 3500 rpm (with 188h aged solution) are at the range of 70-73% and the Energy band gaps of the films are 3.1 and 3.25 respectively. Whereas films deposited at the speed of 4000 rpm shows 86% transmittance and band gap energy of 3.3 eV. So After scrutinizing all the characterization results, it is clear to all that film quality greatly depends on coating speed. On the other hand aging time hardly affects the quality of the fabricated films. Films deposited at 4000 rpm exhibit higher quality and could be used in short wavelength optoelectronic devices.

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| Sample ID | Coating Speed | Aging Time | Band gap (eV) |
|-----------|---------------|------------|---------------|
| S1        | 2500 rpm      | 44 h       | 3.2           |
| S2        | 4000 rpm      | 44 h       | 3.3           |
| S3        | 3500 rpm      | 188 h      | 3.25          |
| S4        | 4000 rpm      | 188 h      | 3.3           |