Sol gel Spin Coated ZnO Thin Films for Biosensing Applications

Edmund P Samuel, Hemalata Bhadane, Umesh Chandra, D. K. Gautam

***Abstract*—Zinc oxide thin films deposited through sol-gel spin coating method for glucose biosensor applications. The surface morphology of film has been studied through AFM and SEM. Surface morphology investigation clearly reveals the enhancment of the surface area due to porous nature fo the thin films. The increment in surface area leads to a possiblity of improvement of sensitivity through sensing elements. The study has been mainly focused on optimization of annealing temperature and it has been realized that the better crystalline nature of zinc oxide films are obtained at 450 ^{0}C. Thin film annealed at 450 ^{0}C was found to be having thickness of around 800 Å with refractive index almost 1.86.**

***Index Terms*—Zinc Oxide, Glucose Biosensor, Sol-gel**

I. Introduction

Biosensors are significant tool in detection and diagnosis of various diseases with ease and efficiently [1, 2]. The electrode made of Zinc oxide (ZnO) loaded with enzymes which are very highly responsive, makes ZnO most remarkably known material for biosensor applications. Particularly, the ZnO nanorods have unique advantages due to high specific surface area, good conductivity, high electron mobility and biocompatibility with the biological molecules [3]. ZnO gained significant attention as it has direct energy band gap of 3.37eV, and most importantly the ZnO thin films can be fabricated using sol-gel technique [4]. The sol-gel technique provides better chemical inertness along with photochemical stability. Through sol-gel one can tune the porosity which is very significant in tailoring the bandgap energy and refractive index of ZnO thin films in accordance to achieve better sensitivity of ZnO based glucose biosensor. ZnO is a very promising material for various applications such as light emitting devices, ultra violet wavelength detection, solar cell with more improved efficiency then polymer based cells, gas sensors etc. [5-8]. Recently, in biosensors, the nanostructured ZnO layers are used due to its, chemical stability, non-toxicity [9]. The Figure 1 shows the schematic representations of the ZnO based biosensors which are having better sensitivity toward biological molecules detection.

In the recent years ZnO and MgZnO has been investigated intensively because of their immense potential in biosensor, light emitting devices, piezoelectric transducers and gas sensors. However, the crystalline structure is the key for achieving the better performance and sensitivity through ZnO thin films. The crystal structure and orientation along with the porosity, highly depends on annealing temperature. Therefore, annealing temperature was considered to be significant for the optimization of ZnO thin film deposition conditions and studied in detailed for its impact over various properties such as refractive index, thickness, surface morphology and crystal orientation. The paper reports thickness and refractive index variation with changes in annealing temperature and the optimized best thin film with its surface morphology and XRD analysis has been included in results and discussion section. The experimental procedure is in section II and the overall discussion of results are presented in section III and finally the conclusion has been presented.

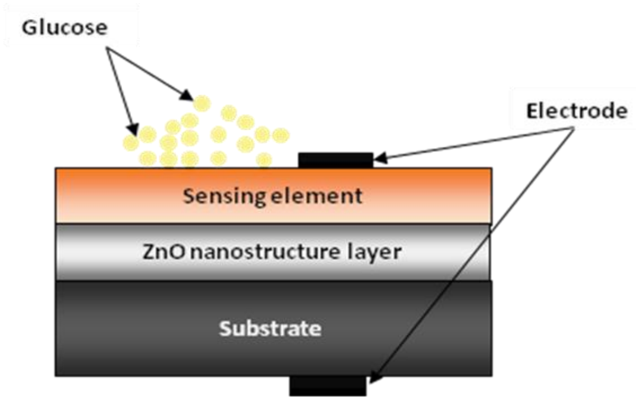

Figure 1 Biosensor structure

II. Experimental

Zinc Oxide thin films have been deposited by sol-gel spin coating method by using precursor Zinc Acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), 2- Methoxyethanol as solvent and Monoethanolamine as the stabilizer. The 0.5M of Zinc acetate (ZnAc) has been dissolved in 2-Methoxyethanol and further monoethanolamine has been added drop wise at room temperature under constant stirring. The concentration of monoethanolamine has been kept 1:1 with the Zinc acetate. This resultant solution has been stirred further at 50°C for 45 min to obtain a homogeneous, clear and transparent solution. The glass substrates have been cleaned with the dilute hydrochloric acid, ethanol and distilled water. The p-type Silicon <100> substrates have been ultrasonically cleaned into acetone and isopropanol in order to remove unwanted

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native oxide layer on the wafer surface. Finally, the silicon wafer has been rinsed and cleaned with deionized (DI) water. For the deposition of thin film, the prepared ZnAc transparent solution dropped on the pre cleaned glass substrate and spinning was done with 3000 rpm for 30 sec for uniform deposition of thin film. These deposited ZnO films were preheated at 110°C for 10 min to evaporate any remaining solvent and organic compound. The process of deposition of films and preheating were repeated for ten times to obtain the desired thickness. The films were also deposited on silicon substrate for thickness and refractive index measurement. The prepared thin films were further annealed at the different temperature from 300 to 500 °C using muffle furnace.

The thickness and refractive index (RI) were measured by Ellipsometer (Philips SD-1000). The structural property of thin films was studied using the X-ray diffraction (XRD, Rigaku Japan). The surface morphologies and roughness of the spin coated ZnO film was studied using a scanning electron microscope (SEM; JEOL, JSM-6610) and atomic force microscope (AFM; XE-100, Park Systems Corp., Suwon, Korea) respectively.

III. Results and Discussion

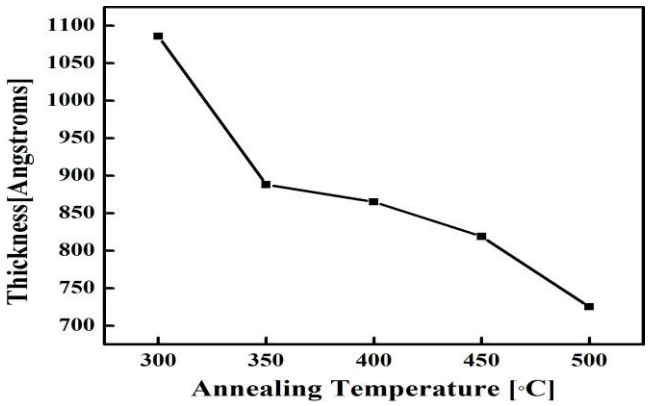

Figure 2 (a) Effect of annealing temperature on thickness of films

The films deposited on Si substrate were characterized by Ellipsometery for measurement of thickness and refractive index in order to study the effect of annealing temperature as shown in Figure 2(a) & (b).The thickness of films (Fig. 2(a)) are observed to be decreasing from 1080 Å to 725 Å. The lowering in thickness is because of reduction in the hydroxyl groups and other volatile impurities from films due to the annealing. Thus, it can be said that, the annealing significantly removes the water molecules trapped in films. The refractive index has been increased from 1.66 to 1.96. This is due to increase in density of films as well as improved crystallinity. It is observed that the thickness of films is getting lowered with annealing temperature and it is well known that the higher annealing temperature improves crystallinity of films [10] and reduces the surface area. The higher surface area is more beneficial for sensing application, thus, the optimized temperature in this case is 450˚C. Hence, further, characterization such are XRD, SEM and AFM have been carried out for ZnO thin film annealed at 450 ˚C

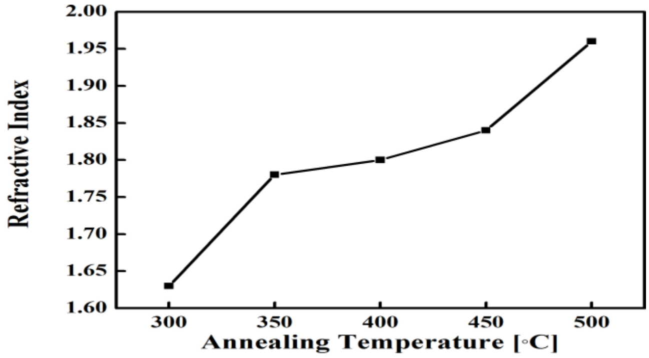

Figure 2 (b) Effect of annealing temperature on refractive index of films

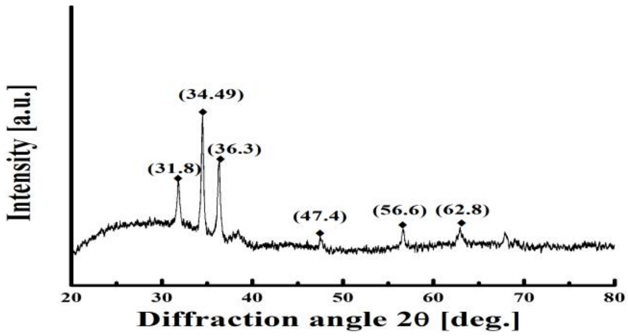

Figure 3 XRD pattern of ZnO thin film annealed at 450˚C temperature

The XRD have been used to determine the crystal structure of the ZnO thin film in the range of 20°<2θ<80°. Figure 3 shows the XRD pattern of ZnO thin film annealed at 450°C. It has been seen from the pattern that all major diffraction peaks correspond to the ZnO crystal faces. The diffraction peaks denoted by diamonds (♦) indicates absence of any preferential orientation that reveals the ZnO film is polycrystalline in nature. The peaks are consistent with the diffraction planes of the hexagonal wurtzite structure of ZnO, as confirmed by JCPDS data card no.36-1451. XRD pattern show six primary peaks at 31.8, 34.49, 36.3, 47.4, 56.6 and 62.8 which can be attributed to the (100), (002), (101), (102), (110) and (103) planes respectively. The average crystal size of film was measured to be ~33 nm using the Debye- Scherrer [11] formula that also demonstrates nanocrystallinity (<100 nm) in film. The evaluated *a* and *c*-axis lattice constants of the film are 0.318 and 0.519 nm respectively, which are slightly smaller than standard values presented in JCPDS 36-1451.

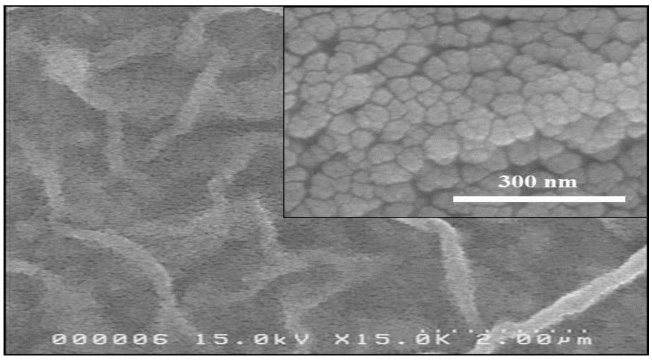

Figure 4 SEM of the ZnO thin film annealed at 450°C. Inset image shows ZnO grains at higher resolution

The SEM image presented in Figure 4 shows the morphology of the ZnO thin film. The ganglia-like hills of typical width of about 0.2 µm have been observed in SEM. At higher resolution the grains of ZnO are clearly observed as shown in inset of figure 4.

Three dimensional (3D) AFM image of ZnO thin film is presented in Figure 5. Average roughness (R_a) values determined from the XEI data processing analysis software available with the AFM system. The R_a value that is acquired from a 5 µm X 5 µm scanned area of films is 6.4 nm.

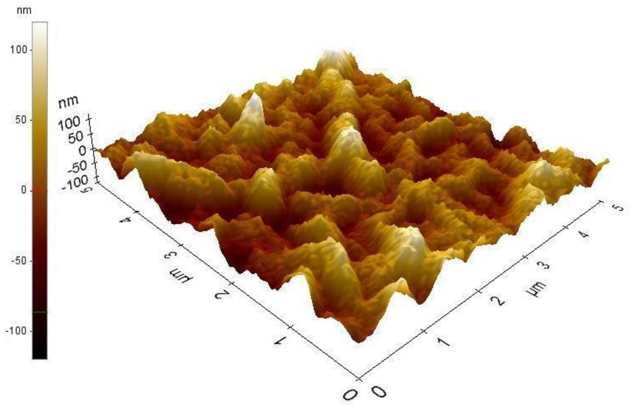

Figure 5. 3D AFM image

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IV. Conclusion

The nanocrystalline ZnO thin films are deposited successfully on glass substrates by sol gel spin coating technique. The thickness of ZnO thin films were observed to be decreasing with increase in annealing temperature, however, RI is observed to be increasing. The XRD pattern of ZnO thin film annealed at 450˚C shows polycrystalline wurtzite structure. The AFM and SEM support the porous morphology of film which also suggests increased surface area of films making them useful for biosensing applications.

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