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Structural, Morphological, Optical and Electrical Study of Sol-Gel Spin Coated Zinc Oxide Thin Film

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Abstract
The characteristic analysis of pure zinc oxide thin film was conducted by fabricating it on the ITO glass plate using spin coating technique .The structural, morphological ,optical and electrical analysis had done with SEM, XRD ,UV and electrical measurements . The thin film was formed on the ITO coated glass plate by spin coating and annealed with different temperature. The SEM micrograph analysed for thin film with two different cycles of coating . The X-Ray diffraction results shows c-axis orientation with peak along (002) plane and grain size 15.84nm. The transmittance and absorption coefficients are analysed using UV spectrometer. The electrical characteristic are also studied.

Keywords*: spin coating, SEM, XRD, UV, Transmittance, absorption,Band gap energy.*

I. Introduction

Zinc Oxide is commonly used in medical field in ointments used or skin irritations. It can also be used in cigarette filters ,paint pigments, paint coatings, laser diodes, light emitting diodes, Spintronics, sensors, memories, identification tags [1].It is traditionally used as a white pigment and an additive to rubber [2].It is a promising material for applications such as transparent electrodes in displays, window layers for solar cells, photo detectors, piezoelectricity and bio-sensors [3]. It is found in the earth crust as a mineral zincite. But most of the part or commercial use is fabricated synthetically. Crystalline ZnO changes its colour from white to yellow when it is applied heat and reverse back to white when cooling. It is thermochromic compound[4]. It is a distinctive electronic and photonic ,wurtzite n type semiconductor material with wide direct band gap energy 3.37eV and excitonic energy is 60meV at room temperature[5] .The excitonic transitions can take place at room temperature. This shows the high radiation efficiency from spontaneous emission and low threshold voltage. Zinc Oxide thin films are fabricated using coating techniques like sol-gel-spin coating, sol-gel-dip coating, atomic layer deposition, pulsed laser deposition, radio frequency magnetron sputtering, chemical vapour deposition, physical vapour deposition [6] . Spin coating is the widely used method to abdicate functional layers on glass or single crystal substrate using sol-gel precursors and it is cost effective.

II. Experimental Techniques

The substrate used in this method to fabricate thin film of zinc oxide is Indium Tin Oxide (ITO) coated glass substrate. The glass substrate used or spin coating is ultrasonically cleaned well using acetone and methanol or 5 minutes each. The sonicated glass substrate is then rinsed using distilled water many times and finally dried at 660^0C for 2hrs. ZnO solution is then prepared

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using zinc acetate dehydrate $Zn(CH_3COO)_2.2h_2O$ is mixed with 2Methoxyethanol $((CH)_3CHOH)$ containing monoethanolamine (MEA)(H_2NCH_2 H_2CH_2OH). Molar ratio of Zinc Acetate Dehydrate ,the precursor with MEA the stabilizer is 1:1. The concentration of the precursor is kept as 0.5mol/L and 2-Methoxy Ethanol ,the solvent can control the temperature by absorbing heat generated by the exothermic reaction and MEA is used to prevent the formation of the colloidal from aggregating the solution. After that stirred the solution well or 3hrs at 60^0 C using magnetic stirrer ,which helps to improve the reaction process between all the materials in the solution. The solution stirred well again at room temperature or 6hrs to produce a clear homogeneous and transparent solution.

The solution then poured on the glass substrate with a rotational speed of 3000rpm for 30sec and pre-heated to a 250^0 C or 5 minutes. This helps to evaporate the solvents and organic residuals . The process is repeated for ten times and thin films are post heated for 3hrs at 400^0 C.

III. Results and Analysis

The structural characterization can be done using XRD and surface morphology is obtained from Scanning Electron Microscopy (SEM). .The optical spectra is obtained using UV/V spectrometer. The current and voltage for analysing V-I characteristics is measured using source meter (Kiethley4200) The thickness of ZnO thin film is measured using a surface profilometer using Detak surface profiler

IV. Surface Analysis

The scanning Electron Microscope (SEM) provides topographical and elemental information at magnifications of 10x to 100000x with virtually unlimited depth of field . SEM micrographs with different magnifications of x13000 and x1000000 are shown in fig.1a &1.b respectively . When investigated it is found that the surface of the thin films are flat and homogeneous. It is noted that the particles are granular in nature with uniformly deposited spherical(200nm diameter) and rod shaped(400nm diameter) particles. When the thickness in the range of μm the particles tried to project up and form micro ring structure. It is observed that the smaller grains makes the surface smooth and transparent.

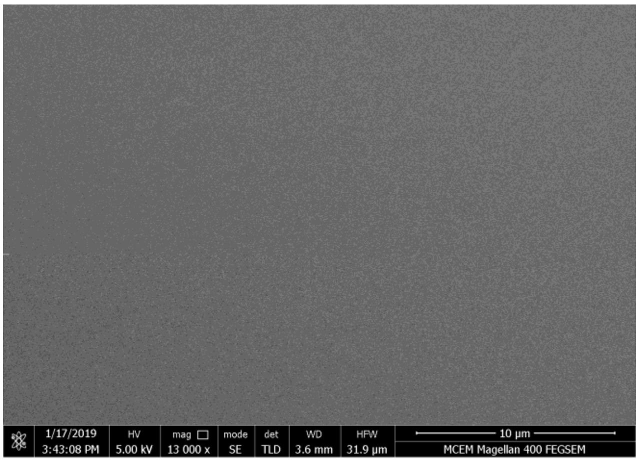

Fig.1 (a) SEM image with 13000x magnification

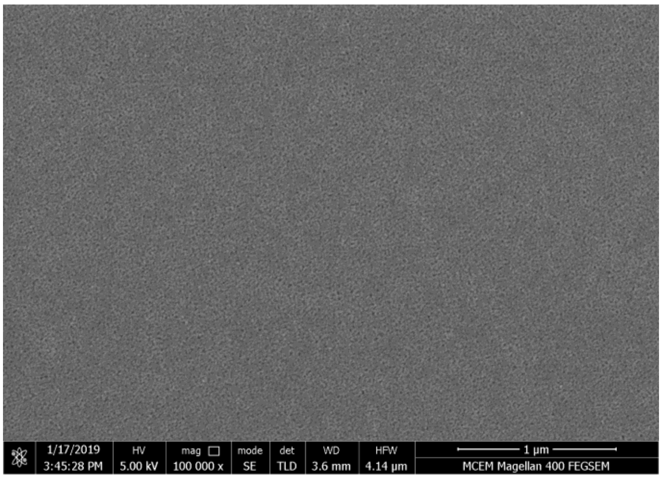

Fig.1(b)SEM micrograph with 100000x magnification

V. Structural Analysis

The crystal quality and orientation of synthesized ZnO thin film can be studied using XRD analysis. The XRD pattern of spin coated ZnO thin film with 0.50μm thickness is shown in Fig.2. (100), (002) and (101) directions are the diffraction peaks of the sample, obtained from

XRD pattern. A strong preferential structural growth is found along the c axis in (002) plane which confirms that ZnO shows hexagonal wurtzite structure and the peak appeared at 2θ= 34.52° [7].

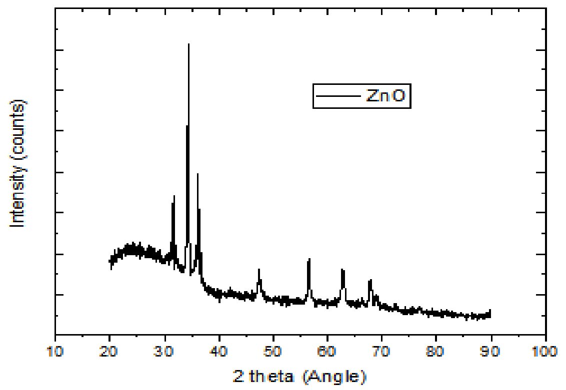

Fig.2 XRD pattern of spin coated ZnO thin film

X-ray diffraction (XRD) is used for structural characterization of ZnO thin films.. At the time of measurement, the current and the voltage of XRD are maintained at 30 mA, 45 kV respectively. The mean christallite size D was calculated using DeBye-Scherrer formula [8], D=0.9λ/βcosθ using where λ , is the x-ray wavelenghth with value 1.54A ^{0}, β is the full width at half maximum and (FWHM) of (002) peak in radians and θ is the Bragg's diffraction angle .When calculated the average value of grain size is obtained as 15.84nm and it shown in the table below

plane	β	2θ	Dnm	**δ (nm)**	**εx10 -2**
(002)	0.5	34.3561	15.84838217	0.003981	2.0851

VI. Optical Properties

The optical transmittance and absorbance were measured using UV spectrometer in the wavelength range of 300nm to 900nm. Fig.3a explains the transmittance spectra of ZnO thin films with different annealing temperature 200 ^{0} C and 400^{0}C. Good transmittance is obtained at 390nm and 90% of the transmittance is obtained above 400nm range. The wave length of good transmittance increases when annealing temperature increases. But above 85% and 80% transmittance occur in the wavelength range above 400nm. Fig. 3b shows the optical absorption and spectra of ZnO thin films annealed at 200^{0}C,400^0 C. The investigation shows that the absorption increases with annealing temperature is in the range of 300nm to 800nm .The absorbed photon energy is maximum in the 300nm to 400nm range . The end of the sharp absorption region is found at 370nm region in the spectrum as ZnO is a direct band gap material and it is increasing when annealing temperature increases. The investigations show that when annealing temperature increases the band gap decreases.

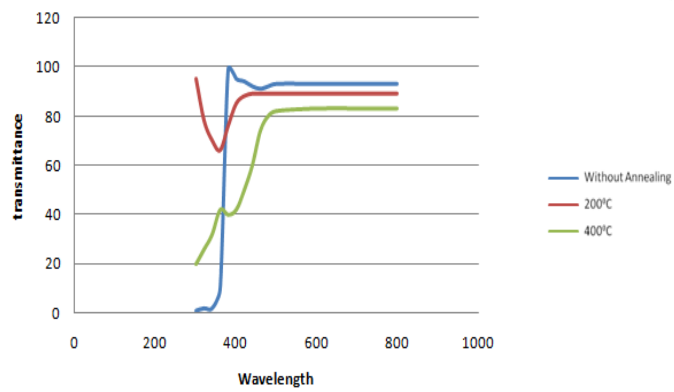

Fig.3b Absorption Spectra o ZnO thin film annealed with different temperature

Absorption coefficient α can be determined from the transmitted spectrum with photon energy E is

$$(\alpha E)^2 = E - Eg \; [10]$$

where Eg is the energy band gap of the semiconductor. A graph is plotted with photon energy (E) versus $(\alpha E)^2$.It is a stright line which crosses the photon energy X-axis at the energy band gap point .According to the graph 3.93eV is the band gap energy of the bulk ZnO thin film. When repeated with thin films after annealing at

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200^0 C and 400^0 C it is found that the energy band gap decreases to 3.40eV and 2.98eV respectively.

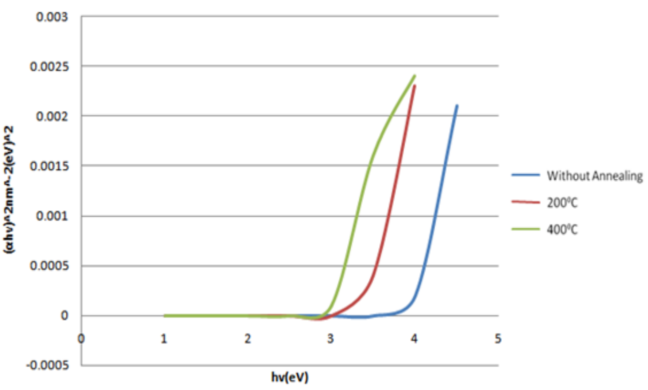

Fig.3c Plot for $(\alpha E)^2$ versus E of ZnO thin film annealed with different temperature

VII. Electrical Analysis

The voltage and current variations were measured using Keethly Source Meter. The VI characteristic of the bulk ZnO and the films annealed with 200^0 C and 400^0 C were plotted below. From the analysis it is found that the variation of the current is almost linear 12]as per the direct band gap materials where the voltage varies from -1V to+1 V. When annealing the range of the current widens on both sides

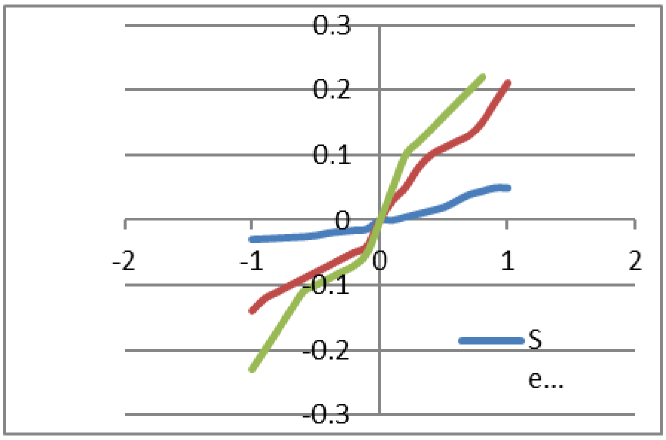

Fig.4 Plot o V-I characteristics o ZnO thin ilm annealed with dierent temperature

VIII. Conclusion

The investigations on the ZnO thin film coated on the glass substrate with ITO by sol-gel process is polycrystalline in nature. We analysed that the parameters like precursor concentration, rotation speed, annealing temperature ect .influence the quality of the film. The XRD results shows that the peak orientation is along (002) direction and SEM micrograph analysis shows the small grains and the surface is smooth and transparent. The optical transmittance is above 80% for the three samples 400nm to 800nm range. The absorption ranges from 300nm to 400nm. The optical analysis shows that when annealing temperature increases the band gap energy decreases. The electrical analysis also shows that the band gap energy decreases when increasing annealing temperature. As per these investigations annealing improves the performance of the thin film.

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