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CRYSTALLINE GRAIN SIZE EFFECTS ON THE CONDUCTIVITY OF THE DOPED TIN DIOXIDE (SnO_2) WITH ZINC (Zn)

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Spray pyrolysis technique was used for the fabrication of the sample. A series of SnO_2 and Zn doped SnO_2 (Zn. SnO_2) have been deposited on the glass slide with different doping concentration values of 1 wt.% , 2 wt.% ,3 wt.% and 4 wt.% Zn on SnO_2. The average grain size of the Zn doped SnO_2, compare to the average grain size of SnO_2 film is clearly increasing upon increase in doping concentration. However, grain boundary theories were obeyed except for the 4 wt.% Zn on SnO_2 which showed a high level of doping incompatibility. At 1 wt.% Zn on SnO_2 exhibited the characteristics of a homogenous and stable p-type semiconductor. At 3 wt.% Zn on SnO_2, the direction change in the orientation of two adjacent grains was shown to localize at a site equidistant to the grains.

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1. Introduction

The major physical properties of thin films of SnO_2 possess is high electrical conductivity (1) which makes it a good material for recent electronics inventions (2). Its high electrical conductivity presumes that it has low resistivity and high transmittance. SnO_2 thin films have been found to be very useful in the fabrication of window layers and heat reflectors in solar cells(3), various gas sensors(4) etc. Therefore the improvement on the Tin thin film is a novel idea (5) because its properties have not been totally explored for better technological inventions. The hydrogenated amorphous Tin (1) is typical case study of Tin thin film improvement i.e. it improved on the reduction in semiconductor thickness and photo sensitivity. Major improvements on the Tin thin films (like other metallic thin films) are unarguably are in its fabrication. Researchers have argued on the various thin film preparation processes and inferred necessary solutions (2-4). Among major known techniques used to fabricate tin oxide films (evaporation, sputtering, pulsed laser ablation, spray pyrolysis technique), the chemical spray pyrolysis (5) has proven to be simple, reproducible and cheap for large area applications. There had been other types of pyrolysis (spray hydrolysis, corona spray pyrolysis, electrostatic spray pyrolysis and microprocessor based spray pyrolysis) used to obtain good quality thin film by optimizing preparative conditions e.g. substrate temperature, spray rate, characterization, concentration of solution, effects of precursor, dopants, substrate temperature, post annealing treatments, solution concentration etc.

In this paper, we explored the properties of Zn doped SnO_2 films. Generally, the Zn doped SnO_2 films have been reported to be used as solar cells and thin film transistors, due to their unique properties of high electrical conductivity. However, the crystalline particle grain size and the electrical properties of pure and zinc doped tin oxide thin films have not been efficiently explored for better results. The aim is to examine the conductivity of the undoped and Zn doped SnO_2 by measuring the resistivity. Also to examine the structural properties of the undoped and Zn doped SnO_2 by X-ray diffractormeter (XRD) analysis.

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2. Methodology

2.1. Fabrication of the Tin Dioxide Thin Film

The fabrication of the undoped Tin dioxide (SnO_2) was carried out using Tin (IV) Chloride ($SnCl_4$) solution as the source element. One molar solution of Tin (IV) Chloride was used and it contains 260.50g of the Tin (IV) Chloride. During the fabrication 10ml of the solution of Tin (IV) Chloride and 10ml of distilled water was used and the thin films form of Tin (IV) Oxide (SnO_2) were deposited on a glass substrate. The 10ml solution of the Tin (IV) Chloride has a density of 0.0368g/cm^3. The optimum temperature, which was kept constant throughout the fabrications is 450^{0}C and the room temperature was 30^{0}C. The distance between the substrate and the atomizer was fixed at 15cm through the fabrication process. The consumption rate or the spray rate of the vapour was 1.92ml/min. The time of deposition of the film on the glass slide was five minutes. During the fabrication 10ml of doped Tin (IV) Chloride solution and 10ml of distilled water was used and the thin film forms of Tin (IV) Oxide doped with zinc, (Zn.SnO2) were deposited on a glass substrate.

Thin films of undoped and zinc doped tin oxide were prepared on glass substrates at 30^{0}C room temperature and 450°C which is equivalent to 13.415 millivolts on the reference table by spray pyrolysis technique of type K Thermocouple. Zinc acetate dehydrate Zn $(CH_3COO)_2.2H_2O$ was used as a source for zinc (Zn) in doped films while Tin (IV) Chloride ($SnCl_4$) as the source of Tin dioxide (SnO_2). To obtain an optimum result, thin films were first deposited with different tin chloride concentration in start solution that was varied from 0.05M to 1M. The optimum amount of molarities was used for preparing SnO_2 thin films with different zinc doping levels.

2.2. XRD Characterisation

The deposited SnO2 film is characterized by XRD measurement using PANalytical editor and diffractometer type 0000000011066165 of Focus-Divergent Slit of 100mm. The XRD analysis gives information on the hkl values of the Zn doped and undoped SnO_2, it also gives information on the d-values and the Full Width and Half Maxima (FWHM) values of the Zn doped and undoped SnO_2 at 25^{0}C.

2.3. The Four Point Probe Characterization

A QUADPRO-301-6 four point probe meter was used to carry out the electrical characterization measurements. A four way probe operational process upon which QUADPRO-301-6 works includes the two outer probes measure the current I (source measure units SMU 1 & 2) and two inner probes sense the voltage V (SMU 3 and ground unit GNDU). This method is a non-destructive way of determining the resistivity of the samples and eliminates measurement errors due to the probe resistance. One source measure units (SMU1) and the GNDU (ground unit) are used to source current between the outer two probes. Two other SMUs (SMU2 and SMU3) are used to measure the voltage drop between the two inner probes. The space 's' is given as 200A^o (4).

3. Results and discussion

Tin (IV) Oxide (SnO_2) doped with Zinc was fabricated by doping from 1wt.% to 4 wt.% of Zn in the source material (SnO_2) using the relation, $\frac{Zn(g)}{\{Zn(g)+Sn(g)\}}$ which forms 1%, to 4% of the Zn by weight. The table below gives the detail of the doping process.

Table 1: Details of SnO_2 doped with Zinc.

Wt. of Sn	Wt. of Zn	% of Zn	Vol. of ZnAc	Vol. of $SnCl_4$
0.37g	0.0037g	1	0.476ml	10ml
0.37g	0.0074g	2	0.663ml	10ml
0.37g	0.0111g	3	1.401ml	10ml
0.37g	0.0148g	4	1.847ml	10ml

Structural analysis of the deposited undoped and Zn doped SnO_2 film was carried out by using CuKα radiation source having wavelength 1.54060Å. The diffractormeter (0000000011066165 type) was used and a fixed divergence slit type of size 0.2177^0. The X-ray diffraction pattern of the film is recorded (figure 1-5). Figure. (1-4) shows the XRD patterns of spray deposited undoped and Zn doped tin dioxide (SnO_2) thin film with well-defined peaks that match standard interplanar spacing JCPDS card no. 01-072-1147 and hkl values.

The film formation is dependent on substrate temperature. We considered the substrate temperature below 290^0C, the spray falling on the substrate will undergo incomplete thermal decomposition giving foggy film whose transparency as well as electrical conductivity will be very poor. This is due to the Bauschinger effect which is responsible for thermal gradient truncation in some heterogeneous compounds. The Bauschinger effect refers to the effects of microscopic stress distribution as a result of characteristic changes in the material's stress/strain relationship. When the substrate temperature is about 400^0C, the spray gets vaporized before reaching the substrate and the film becomes almost powder. At optimum substrate temperature of 450^0C the spray reaches the substrate surface in the semi-vapour state and complete oxidation takes place. The X-ray diffraction pattern of the film at the optimum substrate temperature of 450^0C for the pure Tin thin film and doped film (1% - 4%) are presented in figure 1-5 below.

The blue circle of figure (1-5) gives the orientation of the grain growth in the SnO_2 thin film and the number of grain boundaries. Like ordinary thin film, SnO_2 in its pure form has its grain growth defect, but unlike other thin film the defects extended through a positional range of 20-36 [^{o}2Th]. This shows that SnO_2 thin film in its pure form has higher susceptibility for doping. The growth defects in the 1% zinc doping were reduced. Much more, the feature shows homogenous and stable p-type doping as seen in ZnO thin film (12). The growth defects in the 2% zinc doping were almost synonymous to the pure form of SnO_2 thin film, though the difference was the reduced grain boundary. The kind of doping is the fundamentals for multi-quantum well structure (13). The growth defects in the 3% zinc doping possess a unique feature which shows an unusual peak in the midst of pinning point. This is very unusual in grain boundary strengthening technique. The direction change in the orientation of two adjacent grains localizes the dislocation to a site equidistant to the grains. The growth defects in the 4% zinc doping shows a high level of doping incompatibility (14). This means that the sample would have a reduced thermal conductivity at room temperature. By elementary physics, materials with high thermal conductivity possess also a high electrical conductivity. In this case, the sample possesses a high electrical conductivity and low thermal conductivity. This suggested a 4% zinc doped sample of SnO_2 thin film is more of a superconductor than a semiconductor or normal metal. Though the sample possesses same positional range as in the pure form, it is evident that it possesses a reduced grain boundary.

The XRD pattern was analyzed with Gaussian function where full width and half maxima [FWHM] was determined. Undoped film were found to exhibit six diffraction peaks associated (figure 6) with (110), (101), (200), (211), (220) and (310). The 1% Zn doped SnO_2 were found to exhibit two diffraction peaks associated (figure 7) with (102), (200). The 4% Zn doped SnO_2 were found to exhibit six diffraction peaks associated (figure 8) with (110), (101), (111), (211), (310) and (221). The grain size of the undoped SnO_2 thin film and the Zn doped SnO_2 thin film was estimated i.e. using the Debye-Scherrer formula (11) which gave the average grain size of the undoped SnO_2 deposited film as approximately 132nm and for the 1% and 4% Zn doped SnO_2 to be 164nm and 223nm respectively.

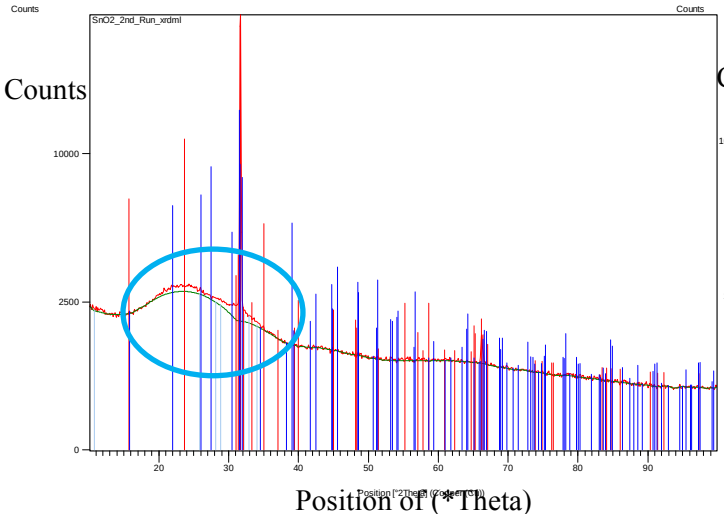

Fig 1: X-ray diffraction pattern of pure tin dioxide thin film

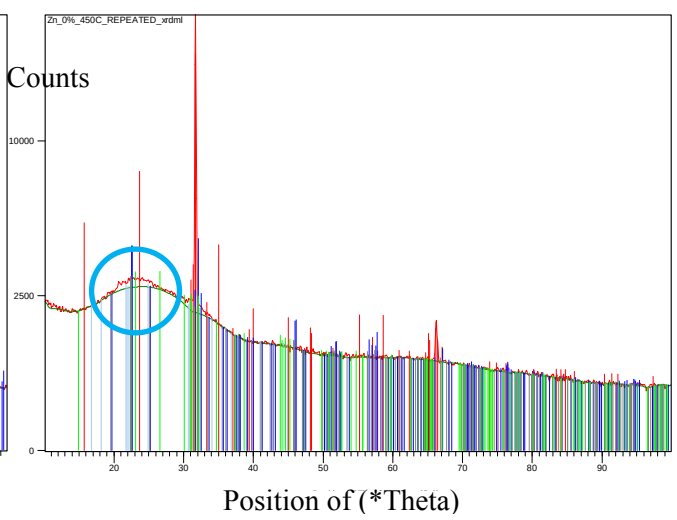

Fig 2: X-ray diffraction pattern of doped tin dioxide thin film with 1% Zn

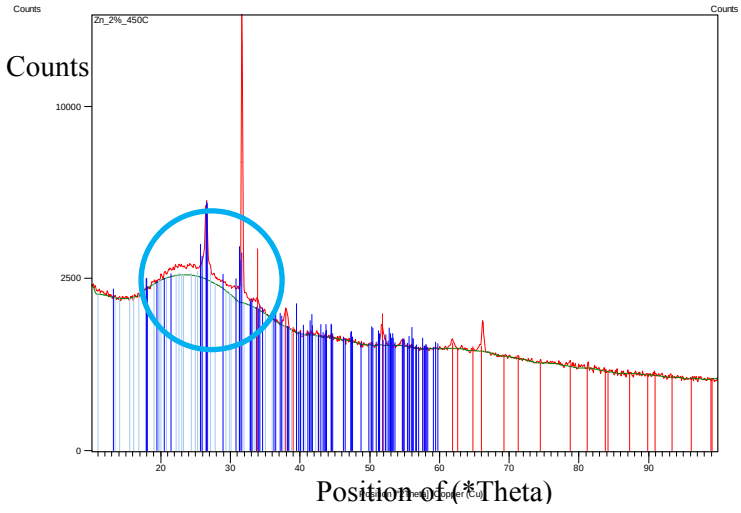

Fig 3: X-ray diffraction pattern of doped tin dioxide thin film with 2% Zn

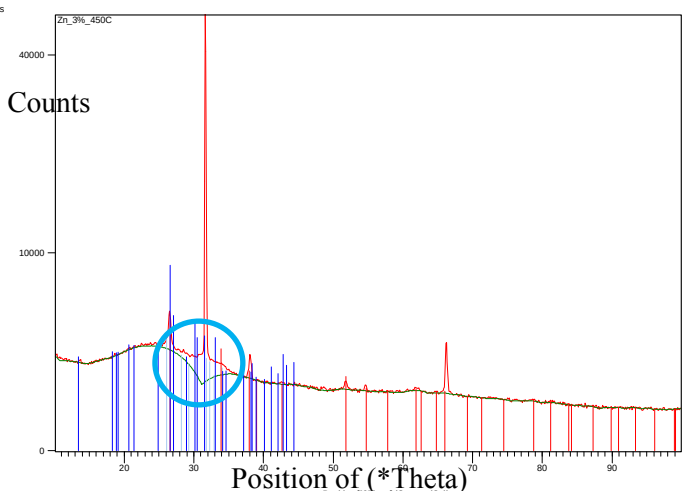

Fig 4: X-ray diffraction pattern of doped tin dioxide thin film with 3% Zn

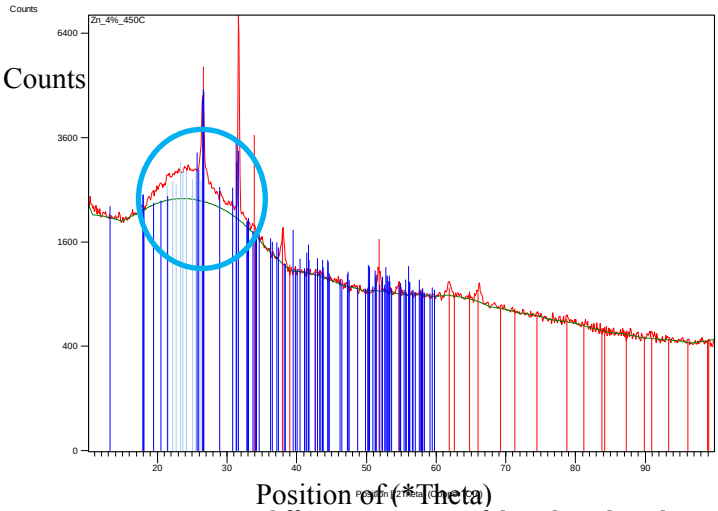

Fig 5: X-ray diffraction pattern of doped tin dioxide thin film with 4% Zn

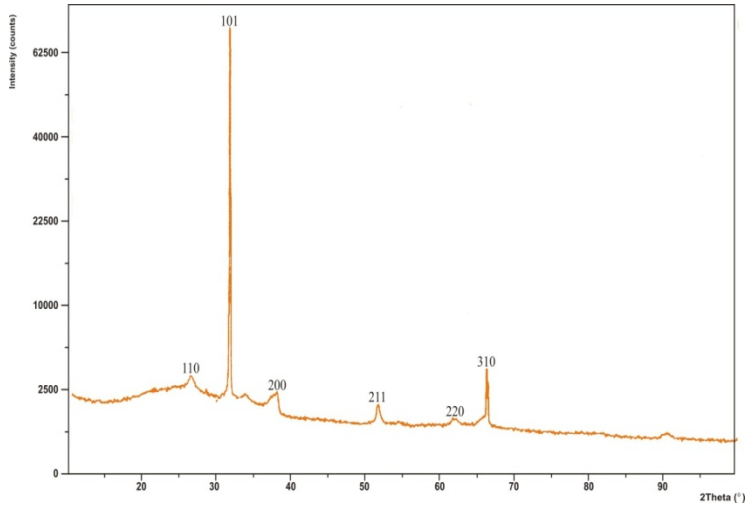

Fig.6 XRD Patterns of undoped SnO_2

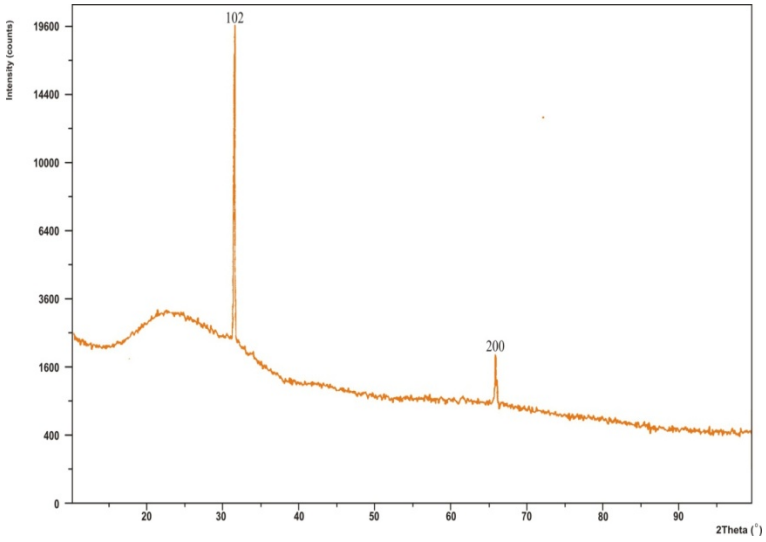

Fig.7 XRD Patterns of 1 wt.% Zn doped SnO_2

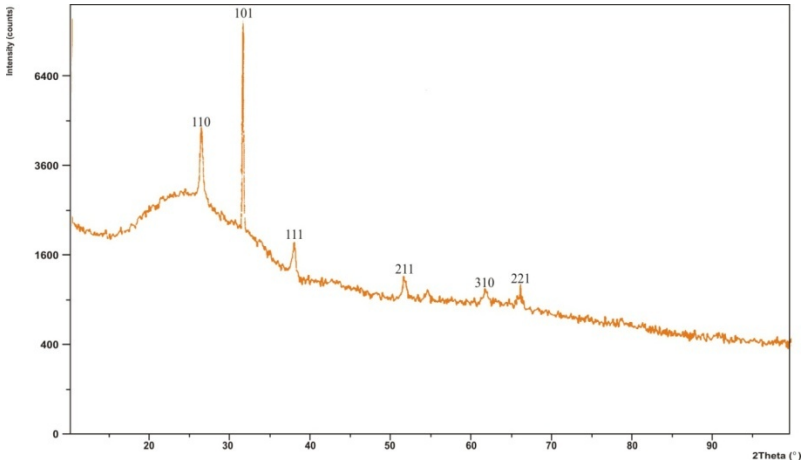

Fig.3 XRD Patterns of 4 wt.% Zn doped SnO_2

The resistivity of the undoped and Zn doped SnO_2 was estimated using the four point probe technique. The resistivity value for the undoped SnO_2 was estimated to be 826.588Ωcm and for the 1 wt.%, 2 wt.%, 3 wt.%, and 4wt.% Zn doped SnO_2 are 779.142 Ωcm, 571.898 Ωcm, 526.389 Ωcm, and 218.680 Ωcm respectively.

4. Conclusion

The average grain size of the undoped SnO_2 deposited film was calculated to be 132nm and for the 1 wt.% and 4 wt.% Zn doped SnO_2 to be 164nm and 223nm respectively. This indicates that the increase in doping concentration of Zn increases the average crystalline grain size. The functionality of the doped SnO_2 sample reveals at highest doping i.e.4 wt.% , the sample exihibits more as superconductor. At this stage, the doping incompatibility is more evidence. At 1 wt.% Zn doping, the sample is a homogenous and stable p-type semiconductor. From the four point characterization, the resistivity values for the undoped SnO_2 was estimated to be 826.588Ωcm and for the 1 wt.%, 2wt.%, 3wt.% and 4 wt.% Zn doped SnO_2 are 779.142 Ωcm, 571.898 Ωcm, 526.389 Ωcm, and 218.680 Ωcm respectively. It can be concluded that, the resistivity values decreases upon increase in doping concentration of the Zn because the metallic nature of the film increases and causes a clear decrease in resistivity, and this can be explain in terms of the different oxidation states of zinc. This implies increase in doping concentration increases the conductivity of the semiconductor.

Acknowledgements

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