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Effect of Doping Concentration on the Structural Properties of Zn: SnO_2

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Abstract: *Undoped tin Oxide and Zinc doped tin oxide thin film were prepared by Chemical spray pyrolysis on soda lime glass substrate. The effects of doping concentration (1wt%, 2wt%, 3wt% and4wt%) on the structural properties of the films were investigated. X-ray diffraction analysis indicates that the films were polycrystalline, having tetragonal rutile structure irrespective of their doping concentration and exhibits a preferred orientation along the (101) plane while the crystallinity was enhanced with increased in doping concentration to an optimum value at 4 wt %. The structural parameters such as particle size, strain and dislocation density were affected and calculated. The particle size of $SnO_2$is 27.9 nm while that of Zn:SnO_2 thin film was found to be within the range of 26.2 nm to 11.2 nm. The thickness of the film decreases with increase in doping concentrations within the range of 0.030 to 0.018µm.*
Key words: *TCO, Thin film, Doping*.

I. Introduction

Transparent conducting oxides (TCOs) are solid- state oxides with low resistance and high transparency in the visible range of the electromagnetic spectrum. Most inorganic films typically are made up of a layer of transparent conducting oxides, generally in the form of Indium doped Tin IV Oxide (ITO), Fluorine doped Tin IV Oxide (FTO), Zinc doped Tin IV Oxide (ZTO), [1]. TCOs are wide band-gap semiconductors that have relatively high concentration of free electrons in their conduction band. These arise either from defects in the material or from extrinsic dopants, the impurity levels of which lie near the conduction band edge. Reduction of the resistivity involves either an increase in the carrier concentration or in the mobility [2]. The high-electron-carrier concentration causes absorption of electromagnetic radiation in both the visible and infrared portions of the spectrum. For the present purposes, it is the former that is the more important.

Transparent conducting oxides haveband gaps with energies corresponding to wavelength which are shorter than the visible range of 380 nm to 700 nm. As such, photon with energies below the band gaps are not collected by these materials and these visible lights passes through [3].

Tin dioxide (SnO_2) is an n-type broad-band gap (3.6eV) oxide semiconductor with high chemical and mechanical stability. SnO_2 which has exceptional optical, electrical and mechanical properties because of the low resistivity and high transmittance, It is a multipurpose material and has wide usage as the most smart material for gas sensor applications, as a catalyst during the oxidation of organic compounds, as a crucial component in rechargeable Li batteries and as a master element in opto-electronic devices [4].Tin (IV) Oxide is an inorganic compound.The mineral form of SnO_2 is called cassiteritte and this is the main ore of tin. Tin dioxide is white, diamagnetic and amphoteric in nature. It is also a non- flammable substance.

However such Zinc dopant requires a high degree of deposition control or the optimization of dopant concentration to obtain a carrier concentration suitable for use as a TCO in thin film solar cell due to the high reactivity of SnO_2 with oxygen. Above a certain level, the excess Zn atoms exist in the films as interstitial atoms or tend to segregate into grain boundaries and poor crystallized area there by working as electrically inactive sites with a build-up of an energy barrier limiting carrier transport and decreasing carrier concentration. As such we investigate the effects of doping concentration on the structural properties of Tin dioxide (SnO_2) doped with Zinc thin film.

II. Materials And Methods

2.1 Deposition Parameters

In this work, the quality of films deposited depends on the following deposition parameters; the substrate temperature, spray rate and the height of the nozzle from the substrates. Chemical spray pyrolysis technique depositor of K-type thermocouple is used. Rate of flow is 1.92 ml/min and height of nozzle from substrate is 12cm.When the substrate temperature is below 290 ^{0}C, the spray falling on the substrate will produce foggy film as a result of incomplete thermal decomposition (oxidation) as a result; will give rise to a film whose transparency as well as electrical conductivity is very poor. When the substrate temperature is in the range of 400 – 500 ^{0}C the spray reaches the substrate surface in the semi vapour state and complete oxidation

takes place forming clear SnO_2thin film. If the substrate temperature is greater than 500^0C the spray gets vaporized before reaching the substrate and the film becomes almost powdery. As such in this work a temperature of 420 ^{0}C was used for the deposition.

2.2 Fabrication of Undoped SnO_2

The fabrication of the undoped Tin dioxide (SnO_2) was carried out using Tin (IV) Chloride ($SnCl_4$) solution as the source element.During the fabrication of undoped tin (IV) Oxide, 10ml of Tin (IV) Chloride solution, and 10ml of distilled water were added to the solution container of the spray pyrolysis equipment after which is was switch on for the thin film deposition to begin. The thin films of Tin (IV) Oxide (SnO_2) were deposited on a glass substrate.During the fabrication of the doped thin film, 10ml of the doped Tin (IV) Chloride solution with zinc acetate ($Zn(CH_3COOH)_2.2H_2O$) as the dopant and 10 ml of distilled water was used and the thin film form of tin (IV) Oxide doped with zinc, ($Zn.SnO_2$) were deposited on a glass substrate. The temperature of thermocouple of the chemical spray pyrolysis depositor set-up which was kept constant throughout the fabrications process was 420 ^{0}C and the room temperature was 30 ^{0}C. The distance between the substrate and the spray nozzle was fixed at 12 cm through the fabrication process. The consumption rate or the spray rate was 1.92 ml/min. The time of deposition of the film on the glass slide was five minutes because at that time, quality thin film, good for characterisation have already being deposited on the glass slide.

2.3 Fabrication of Tin (IV) Oxide Doped With Zinc

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;

$\frac{Zn\,(g)}{\{Zn\,(g)+Sn\,(g)\}}$ = 1%, 2%, 3% and 4% of the Zn by weight used for the doping.1000ml $SnCl_4$ solution used contained 36.83g of $SnCl_4$; this implies 10ml of$SnCl_4$ solution used for the fabrication contain $\frac{10}{1000} \times 36.83 = 0.368$ g.

Table 1 SnO_2 doped with Zinc

Wt. of Sn (g)	Wt. of Zn(g)	% of Zn	Zinc Acetate(ml)	$SnCl_4$(ml)
0.37	0.0037	1	0.269	9.731
0.37	0.0074	2	0.533	9.467
0.37	0.0111	3	0.790	9.210
0.37	0.0148	4	1.045	8.955

III. Results And Discussion On Surface Thickness Of The Film

The surface thickness of the films was carried out using Profilometer with stylus of 12.5 µm, length of 2000 µm, resolution of 0.333µm and duration of 10.0 second. The results are shown in table 2 for the undoped SnO_2 and 1 wt.% to 4 wt.% Zn doped SnO_2 respectively.The values of the thickness of the thin films are then used to calculate the resistivity values of the thin film. Table 2 gives the result of the thickness of the thin film.

Table 2 Shows the Result of thickness for the thin film

Sample	Thickness of thin film (µm)
Undopped SnO_2	0.150
1 wt.% Zn doped SnO_2	0.030
2 wt.% Zn doped SnO_2	0.025
3 wt.% Zn doped SnO_2	0.020
4 wt.% Zn doped SnO_2	0.018

Table 2 shows the result of the thickness of the undoped SnO_2 thin film and the 1 wt.% to 4 wt.% Zn doped SnO_2 thin film. It was observed that the thickness of the thin film decreases with increase in doping concentration of Zn. This is due to the decrease in grain size of the thin film which as a result of increase in the grain boundary of thin film. The decrease in the thickness of the thin film is also attributed to Beer Lambert's law which shows that as the transmittance increase the thin film thickness decrease at wavelength range of the visible portion of the electromagnetic spectrum between 400 nm and 780 nm for transparent conducting oxides.

3.1 Discussion on XRD analysis

The X-ray diffraction pattern of the thin film is recorded in Figure 1 From the result, it shows that both the doped and the undopedTin (IV) Oxide (SnO_2) thin film have tetragonal rutile-type structure with lattice parameters a = 4.7370Å, c = 3.1850Å. The XRD pattern was analyzed with Gaussian function where full width half maxima [FWHM] were determined. Undoped film were found to exhibit six diffraction peaks associated in figure 1 with (110), (101), (200), (211), (220) and (310) planes. The 1% Zn doped SnO_2 were found to exhibit five diffraction peaks with (110), (101), (111), (211) and (301) planes. The 2% Zn doped SnO_2 were found to exhibit six diffraction peaks with (110), (101), (111), (211), (221) and (301) planes. The 3% Zn doped SnO_2

were found to exhibit two diffraction peaks with (101) and (200) planes. The 4% Zn doped SnO_2 were found to exhibit six diffraction peaks with (110), (101), (111), (211), (310) and (221) planes.

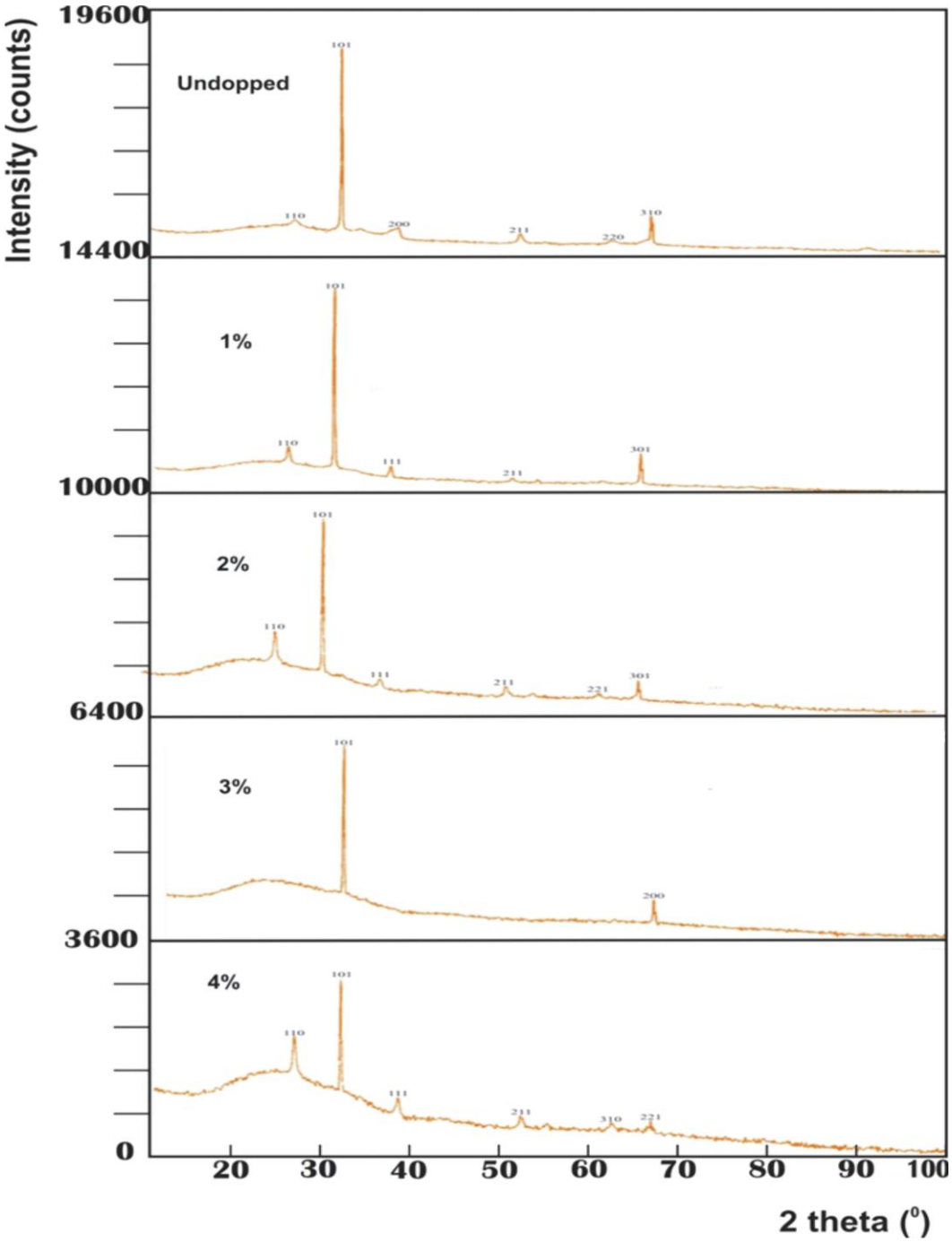

Figure 1: XRD patterns of undoped $SnO_2$and Zn doped SnO_2 thin film

From figure 1 it was observed that deposited films have preferred orientation along (101) plane in all the Zn doped SnO_2 films deposited at doping concentration 1wt.% to 4 wt.%, this is because the 101 plane has relatively high intensity for all the samples irrespective of the doping concentration. The low intensity and a broad diffraction peak were identified, corresponding to an early crystallization of the Zn doped SnO_2 in the oriented structure and such peaks are, (111), (211), (221), (200) and (310) as shown in figure 1 this decrease in the peak intensity is also attributed to the increase in the number of defects or reduction in the atomic weight as a result of the substitution of the Sn^{2+}ion (0.071Å) with the Zn^{2+} ion (0.074Å). As the doping concentration increased, the increase in peak intensity is associated with 101 plane, the narrowness of the (101) diffraction peak indicates growth of the (101) oriented crystallites. At 4 wt.%, there are very small diffraction at around 70^0

and 80^0 2θ scan whose match were not found. The decrease in peak intensity which results to broadness in diffraction peaks might also be due to change in electron density in the conduction band or due to point defect. The crystal structure of SnO_2did not change because the lattice parameters were not change by the Zn doping, the reason is, Sn^{+4} ion have close radii to the Zn^{+2} ion, that is; the ionic radius of $Sn^{4+}$is r= 0.71 Å and Zn^{2+} is r = 0.74 Å. This might also be due to the substitution of metal ions in the crystallite structure and therefore result to no structural strain in the Zn:SnO_2

3.2 Discussion on grain size

The grain size of the thin film was calculated using Debye Scherer formula

$$D = \frac{0.9\lambda}{\beta \cos \boldsymbol{\theta}} \qquad (1)$$

Where D is the grain size, λ is wavelength of the CuKα radiation source(1.54060 Å) wavelength, β is the Full Width Half Maxima (FWHM) and θ is the diffraction angle.

Table 1: Shows the Result of grain size for the thin film.

Sample	Grain size of thin film (nm)
Undopped SnO_2	27.9
1 wt.% Zn doped SnO_2	26.2
2 wt.% Zn doped SnO_2	22.3
3 wt.% Zn doped SnO_2	17.9
4 wt.% Zn doped SnO_2	11.2

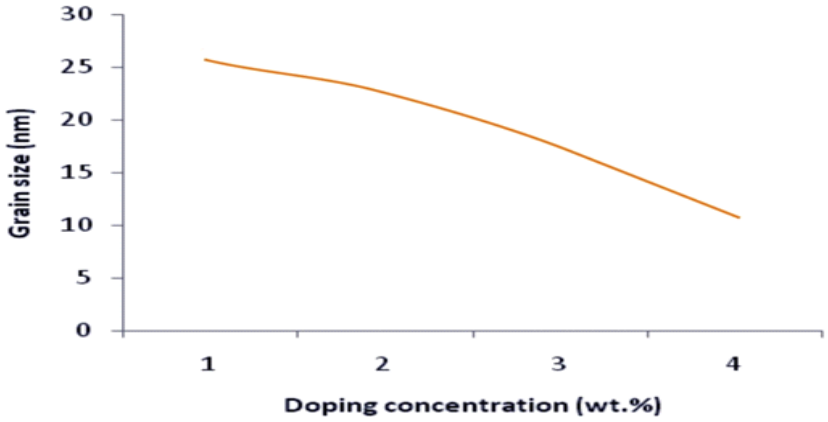

Figure 2: graph of grain size against doping concentration.

From figure 2 Increasing in doping concentration to 4 wt.% causes decrease in the grain size, this is because increase in doping concentration increases the FWHM of the diffraction peak which is an indication of decrease in particle size. This is a clear reason for the decrease in peak intensity with increase in doping concentration. The grain size could also have decrease with increase in doping concentration due to the effect Zn ion on the nucleation during the process of film growth.

3.3. Discussion on SEM analysis

The Scanning Electron Microscopy (SEM) characterisation reveals that all the SnO_2 thin films are almost uniform. The SEM micrographs of pure SnO_2 thin films and 1 to 4 wt.% Zn doped SnO_2 is shown in figure 3 and figure 4

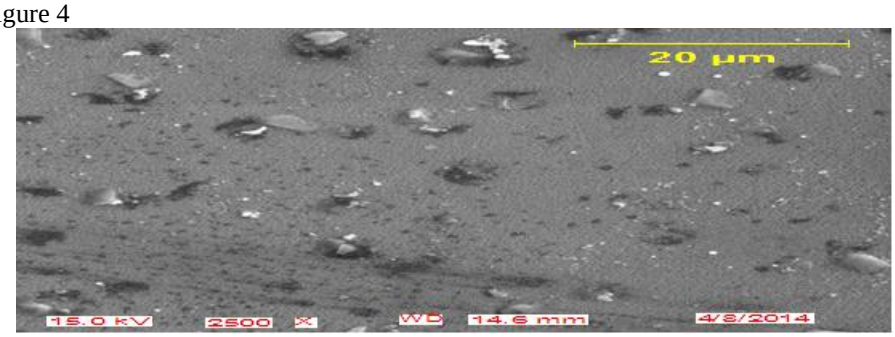

Figure 3: Scanning Electron Micrograph (SEM) of SnO_2

The SEM pictures in figure 3 exhibit the view of the thin film surface which consists of very thin network of SnO_2 nanoparticles.Surface morphology of the SEM micrograph showed fine tiny nanoparticles, with certain clustering.

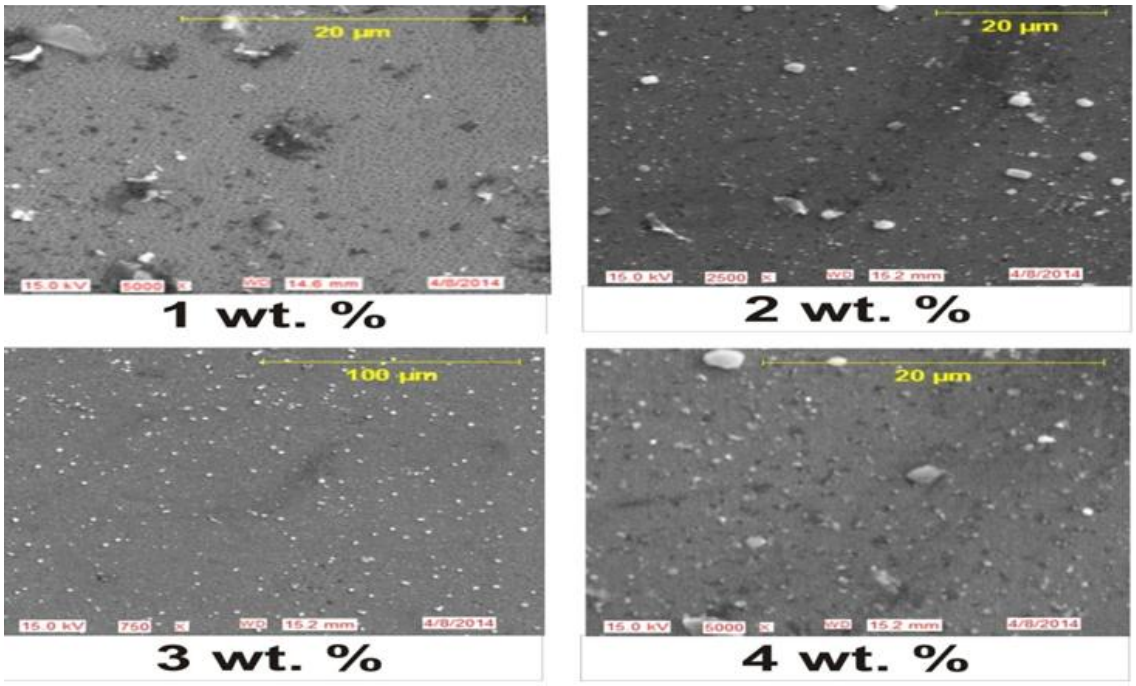

Figure 4: Scanning Electron Micrograph of Zn doped SnO_2

The SEM pictures in figure 4 consist of very thin network of Zn doped SnO_2nanopaticles. With increase in doping concentration, the SEM micrographs of the thin films were found to be almost uniform. This uniformity in the SEM micrograph is due to the fact that on substitution of Zn ion in the crystal structure of the SnO_2 thin film, no structural strain was generated because of the closeness of the ionic radius of Zn and Sn atom.

IV. Conclusion

On doping Tin IV Oxide with Zinc at doping concentration of 1 wt.% to 4 wt.%, the XRD result shows the plane 101 to have the most preferred orientation at all doping concentration. The thickness of the doped Tin IV Oxide decrease with increase in doping concentration and theSEM micrographs of the thin films were found to be almost uniform at all doping concentration.

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