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EVIDENCE OF POSITIONAL DOPING EFFECTS ON THE OPTICAL PROPERTIES OF DOPED TIN DIOXIDE (SnO_2) WITH ZINC (Zn)

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Films of pure SnO_2 were doped with zinc ($Zn.SnO_2$) via chemical spray pyrolysis method. Its deposition on the glass slide with different doping concentration values of 1 wt.%, 2 wt.%, 3 wt.% and 4 wt.% Zn on SnO_2. The optical properties were investigated. The average transmittance, reflectance intensity and optical band gap of the Zn doped SnO_2, showed that the results gotten were due to the dopant affinity for any sites on the sample structure which defines the properties of the doped samples. This concept explains the strange functionality noticed in some metallic oxides.

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Keywords: Spray pyrolysis, SnO_2 thin film, Optical properties, Doping

1. Introduction

The tin dioxide (SnO_2) thin film is classified as an n-type semiconductor with broad-band gap of about 3.6eV and low IR reflectivity which is due to its high order in the optical transparency- in the electromagnetic spectrum(Li et al., 2011). The optical properties of the tin oxide can be seen as it applies to opto-electronic devices (solar cells and thin film transistors), window layers, light emitting diode, flat panel displays (Gordon, 2000) e.t.c.

The tin dioxide has a non cubic or hexagonal structure with stable d-orbital. This unique feature allows the influence of dopants to change its stoichiometry, electrical and optical properties. The Zinc doped tin oxide thin film is not a new concept (Delgado et al., 2003; Jiang et al., 2011), our experimental emphasis was on the method of deposition and its consequences for higher application in the tin oxide technology. We propose that the location of the dopant (represented by positions 1-5 in figure 1) within the tin oxide structure determines or defines its nature of the sample. For example, we propose that if the dopant is at the position 1 in its structure (see figure 1), its nature and definition may change if the dopant is located in position 5. This may be one of the reasons behind the emergence of different results even if the fabrication techniques is the same. Therefore the percentage doping may not be as important as the location of the dopant within the tin oxide structures. This idea can be seen in the strange characteristics of metallic oxides in recent times (Zutic et al., 2005). Major improvements on the Tin thin films (like other metallic thin films) are unarguably are in its fabrication techniques. Researchers have argued on the various techniques for thin film preparation and inferred necessary solutions (Drobny, 1979; Ogwu et al., 201; Emetere et al., 2013).

There are numerous techniques for fabricating thin films e.g. evaporation, sputtering, pulsed laser ablation, spray pyrolysis technique. The chemical spray pyrolysis (Ayouchia et al., 2003) is simple, reproducible and cheap for large area applications. There had been other types of pyrolysis (spray hydrolysis, corona spray pyrolysis, electrostatic spray pyrolysis and

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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.

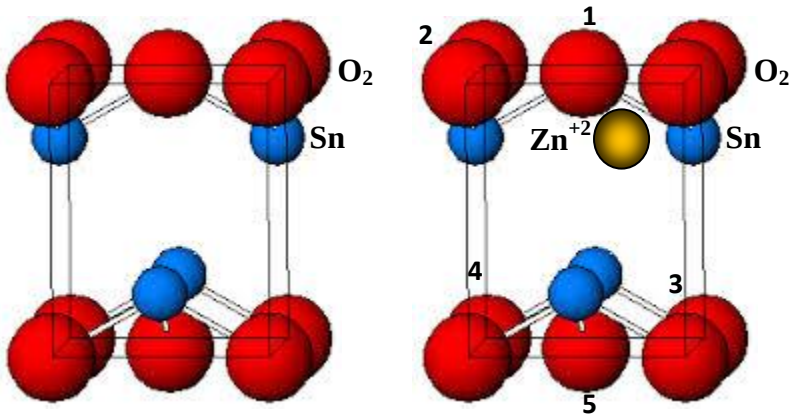

Fig. 1. Logical positions of dopant within the tin oxide structure

In this paper, the established specification for growing tin dioxide thin film was maintained to prove the positional effects of dopants on the sample structure and properties. The various optical parameters e.g. optical band gap, transmittance spectra, reflectivity, absorption coefficient, extensive coefficient were investigated to ascertain the improvement on the technique of thin film preparation. The evidence of dopant position effect on the structure of the tin dioxide thin film was enacted for further research.

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

2.2 UV Spectrometer Characterizations

The UV spectrometer analysis gives information on the transmittance and reflectance values of the Zn doped and undoped SnO_2, it also gives information on the absorption and energy values of the Zn doped and undoped SnO_2. The reflectance and transmittance characterized the main optical properties of virtually all materials. Transmittance measures the ratio of transmitted and incident light from the sample.

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

The optical band gap which defines the optical relevance of a material of the thin film samples were discovered via the mathematical relationship.

$$\alpha hv = K(hv - E_g)^{\frac{1}{2}} \quad (1)$$

K is the energy-independent constant, E_g is the optical band gap. Practically, is obtained from the plot of $(\alpha hv)^2$ against hv as shown in the figure 2-4. The optical band gap was estimated in lower wave length region and it was found to be 3.5eV for the undoped SnO_2 and 3.4eV, and 3.2eV for 1 wt.% and 4 wt.% Zn doped SnO_2 respectively.

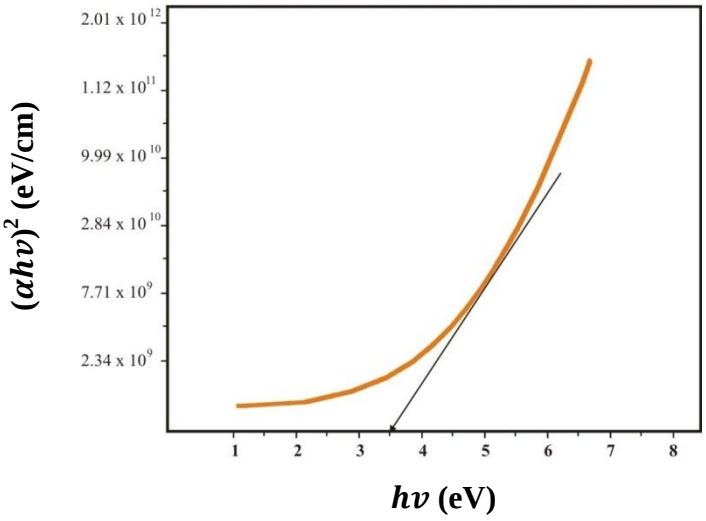

Fig.2. Optical band gap of undoped SnO_2

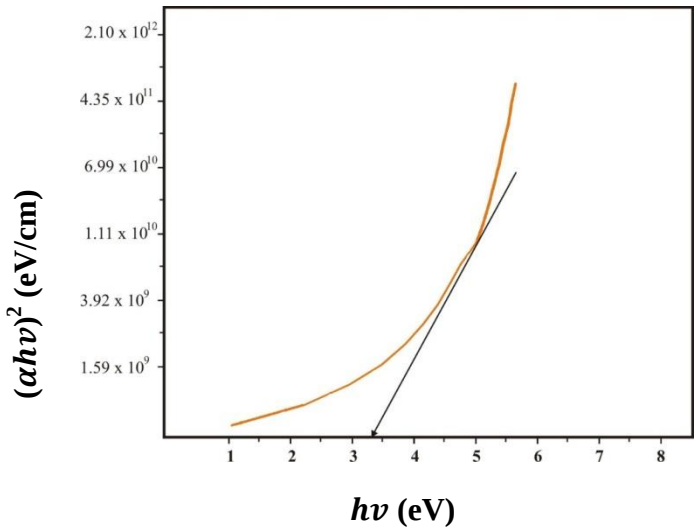

Fig.3. Optical band gap of 1 wt.% Zn doped SnO_2

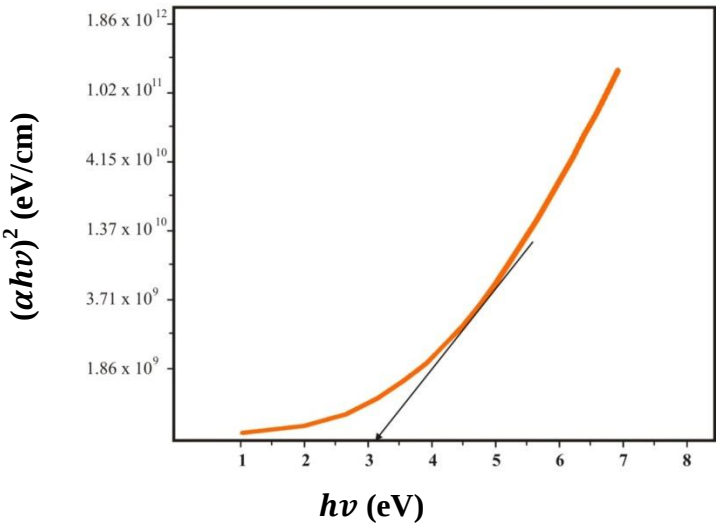

Fig.4. Optical band gap of 4 wt.% Zn doped SnO_2

The optical band range within the doped sample suggests the presence of dopants positional shift which is supported by table 1. At higher doping, the fluctuation in the d-space and position creates a non-linear band gap which defines the optical and electrical nature of any sample. We tried to mathematically express a formular that would incorporate the model as

$$E_g = \sum_1^i K_1 \frac{p_i}{d_i} - K_2 \quad (2)$$

Where E_g is the optical band gap, p_i is the position, d_i is the d spacing, K_1 and K_2 are the energy-independent constant given as $K_1 \leq 1$, $K_2 > 1$, $\frac{K_1}{K_2} \leq 1$. Equation (2) showed accuracy with the samples. However, the validity of equation (2) has not been proven for other doped metallic oxides. This is not in the scope of these findings.

Table 2: The fluctuations in the position and d-spacing

1% doping		2% doping		3% doping		4% doping	
Pos. [°2Th.]	d-spacing [Å]	Pos. [°2Th.]	d-spacing [Å]	Pos. [°2Th.]	d-spacing [Å]	Pos. [°2Th.]	d-spacing [Å]
26.5232	3.36070	26.5232	3.36070	26.5258	3.36039	26.5128	3.36199
31.6708	2.82524	31.6708	2.82524	31.6700	2.82531	31.6754	2.82484
38.0089	2.36744	38.0089	2.36744	38.0780	2.36331	38.0371	2.36575
51.7248	1.76735	51.7248	1.76735	51.7491	1.76658	51.7522	1.76648
61.8342	1.50047	61.8342	1.50047	54.6641	1.67907	61.8771	1.49953
66.2368	1.40985	66.2368	1.40985	66.2376	1.40983	66.1434	1.41161

The optical transmittance spectra of the deposited film were recorded. It was found that the average transmittance of the undoped SnO_2 film is 59.2% and for the 1 wt.% and 4 wt.%, Zn doped SnO_2 film to be 61.2% and 70.9% respectively. The average reflectance of the undoped SnO_2 film is 33.6% and for the 1 wt.% and 4wt%, Zn doped SnO_2 film to be 45.2% and 52.6% respectively. This increase in optical transmittance spectra and average reflectance as the dopant increases may be as a result of the increase in grain size and the reduction in light scattering effect (Sankara, N.S., et al., 2006). Though, this is a general concept. A closer look on Fig. 5, shows the evidence of the corresponding effects of positional dopant location on the transmittance. While sample A(1 wt.% zinc dopings) and sample B (2 wt.% zinc dopings) follow-almost the same trend but at varying magnitudes, sample C(3 wt.% zinc dopings) and sample D (4 wt.% zinc dopings) exhibited different optical properties. These values are evidently different from past research (Delgado et al., 2003; Jiang et al., 2011). The reflectance showed that sample A,B,C and D can function as good optical devices. The emphases were on the out of phase sinusoidal forms exhibited by individual samples. The sharp difference between magnitudes of reflectance and absorbance between sample C and D is also an evidence that the functionality of any device is not only dependent on the percentage doping but on the location or position occupied by the dopant within the sample structure.

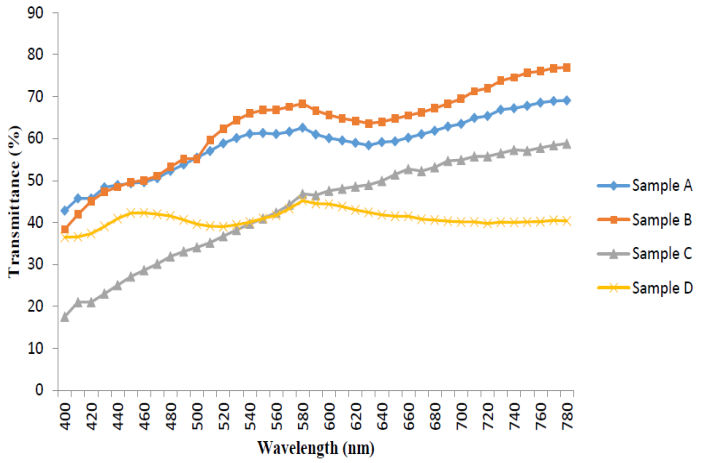

Fig. 5.Transmittance spectra for Samples A, B, C and D

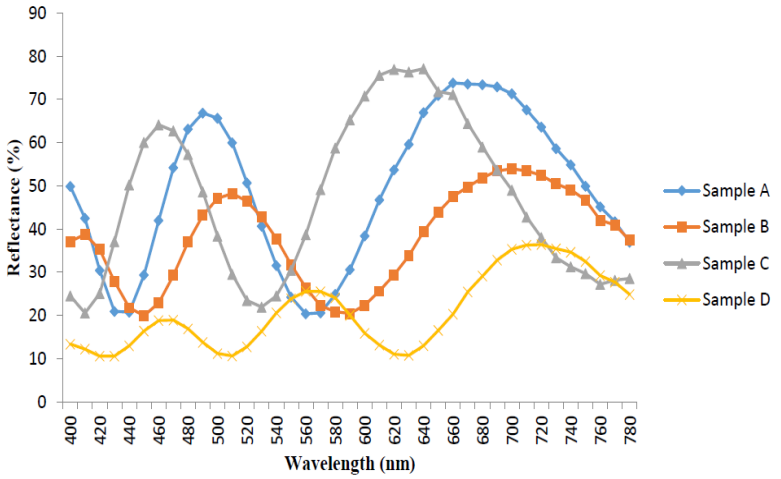

Fig. 6 Reflectance spectra for Samples A, B, C and D

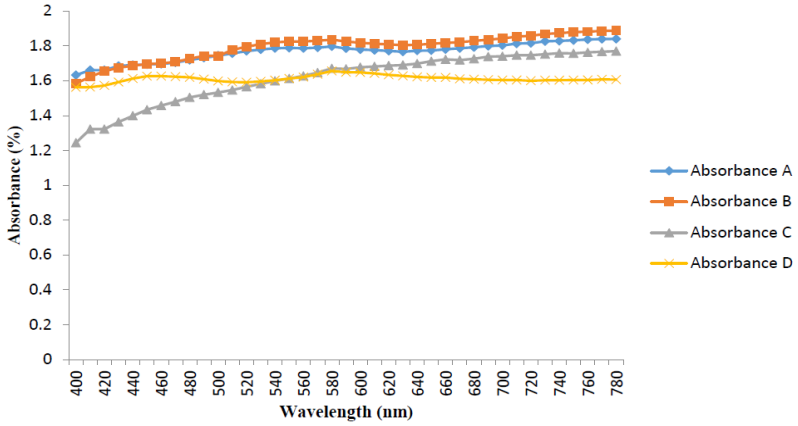

Fig. 7. Absorption spectra for Samples A, B, C and D

Further on the fluctuations created by displaced dopant within the sample structure, we highlighted in Table 2 its effects on the optical properties of each doped samples.

Table 2 Summary of the characterized optical properties

Sample	Temperature T (^{o}C)	Transmittance T_v (%)	Absorption A_v (%)	Absorption Coefficient α (cm^{-1})	Extinction Coefficient (k)	Refractive Index (n)	Band gap E_g (eV)
A	325	59.77	1.77	8.94 x10^5	0.039	3.12	1.88
B	358	64.40	1.79			2.91	
C	382	41.76	1.61	2.91 x10^6	0.127	3.52	1.90
D	408	41.73	1.61			2.42	

From Table 2, the thermally-associated bonding was perceived to be the factor-responsible for the affinity of dopant to bond at any location of the sample structure. The even/equilibrium thermal treatment is proposed to be responsible for the positional shifts in different samples.

4. Conclusion

The optical band gap was estimated in lower wave length region and it was found to be 3.5eV for the undoped SnO_2 and 3.4eV, and 3.2eV for 1 wt.%, and 4 wt.% Zn doped SnO_2 respectively. The average transmittance of the undoped SnO_2 film is 59.2% and for the 1%, and 4%, Zn doped SnO_2 film to be 61.2%, and 70.9% respectively. The average reflectance of the undoped SnO_2 film is 33.6% and for the 1 wt.% and 4 wt.%, Zn doped SnO_2 film to be 45.2% and 52.6% respectively. These results are due to the dopant affinity for any sites on the sample structure. This events defines the properties of the doped samples. This concept might be the explanation to obtaining different results even if the experimental process is repeated. The preparation of doped metallic oxide should be modified to understand the strange behavior of some metallic oxide at certain conditions.

Acknowledgements

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