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Effect of copper doping on optical and structural properties of sprayed tin oxide thin films

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In this paper, Effect of doping with copper on optical and structural properties of tin oxide (SnO_2) thin films was investigated. the effect. SnO_2 as transparent conductive oxide (TCO) was prepared using spray pyrolysis technique. Optical and structural properties of the product were investigated using UV-Vis spectrometry and XRD techniques. It was observed that the thin films have a high transmittance in visible range: 80% transmittance at undoped state and increased by copper doping to reach 84.8% at 0.6% level. The band gap energy ranges from 3.925 to 3.965 eV. It increases, with slight fluctuation, upon doping level increasing. Crystalline structure of thin films grew preferably along the (211) plan on a tetragonal system. Lattice parameter *a* has increased to a maximum value at 0.2% doping, and then decreased beyond. Unit cell volume followed the same trend as lattice parameter *a*. Similarly, the grain size of crystallite increases to a maximum at 0.2% doping, and then decreases with further doping. As results height quality thin films with high transmittance and regular thickness were obtained.

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1. Introduction

Transparent conducting oxides (TCOs) are optically transparent to visible light and electronically conductive. Owing to these properties, they have broad industrial applications in many fields such as optoelectronic devices and solar cells as electrodes. SnO_2 is a transparent conductive oxide with interesting thermal and gas sensing properties. The pure mineral form is known as cassiterite and the mineral is a wide band gap semiconductor (>3.7 eV) but exhibits conductivity due to oxygen deficiencies in the crystal lattice [1]. Though transparent in the visible frequencies, SnO_2 is reflective in the infrared and it is often used as a coating on glass to produce thermally insulating windows [2].

Based on the effect that introducing oxygen vacancy defects into the formed layers improves its conductivity [2], several complicate and expensive methods are employed to elaborate SnO_2 thin films. In this work, yielding better film conductivity compared to other deposition methods, a spray pyrolysis with moving nozzle as a simple and inexpensive technique was employed to prepare pure and Cu-doped SnO_2 thin films.

Films were prepared from an aqueous solution of tin chloride dihydrate on 500°C heated glass substrates. Copper doping is achieved by adding a small amount of copper chloride to the starting solution which is mixed thoroughly prior to spraying. The objective of this paper is to evaluate the influence of (0.2-1.0 at% Cu/Sn) copper doping on the optical and structural properties of Cu-doped SnO_2 thin films.

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2. Experimental

2.1. Thin film preparation

Stannic oxides prepared by adding few droplets of HCl to 5g of Stannous chloride dihydrate ($SnCl_2$, $2H_2O$) powder. The resultant was dissolved in a mixture of 30 ml of distilled water and 20 ml of Ethanol. Solution was left to mix under agitation over the night [3].

In the second hand, Copper dopant is prepared by dissolving 0.3g of ($CuCl_2$, $2H_2O$) in 40 ml of double distilled water, and then diluted further by a factor of 10 to yield the required concentration of doping purpose. Every 1 cc of copper solution makes 0.2 mole percent of SnO_2 base solution prepared in first step. Thus, doping at different concentration can be simplified to adding multiple number of 1 cc from copper solution.

5 samples of SnO_2 were prepared with following copper concentration: 0% (undoped), 0.2%, 0.4%, 0.6%, 0.8% and 1.0 at% Cu/Sn. Every time copper dopant is added to SnO_2 mother solution and the blend is agitated for 45 minutes prior to spraying.

Thin films of SnO_2 with different doping percentages were deposited on 500°C heated glass substrate using spray pyrolysis technique. Number of passes and distant of nozzle-substrate were optimized to give the lowest resistivity of thin films from undoped solution. For this experiment, 4 passes at 2 cm distance between nozzle and glass substrate were sufficient to achieve a low resistivity of 80 Ohm between 1 mm distant electrodes. The sprayed thin films on heated glass substrate were left to cool down at ambient temperature.

2.2. UV-Vis measurement

Optical properties of the thin film are evaluated using Shimadzu UV–Visible 1800 spectrophotometer. UV-Visible light beams are sent through the glass substrates with thin film, and transmittance is recorded as function of wavelength. Light spectrum used in this experiment ranges from 200nm to 900 nm. Measured transmittance from different samples is shown in Fig. 1.

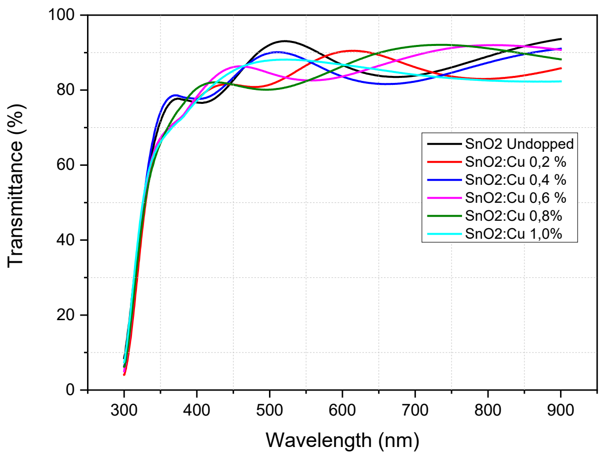

Fig. 1. Thin film transmittance for different doping percentage.

Interference fringes are observed on all samples, this is an indication of smooth surface and regular thickness of thin layers. These fringes will be used to extract all optical properties, such as refraction index, absorbance, and eventually gap energy.

2.3. XRD measurement

Thin film structure was investigated using X-ray diffraction technique. The instrument used in this experiment was RIGAKU MiniFlex 300/600, using Theta/2-Theta measurement method. Incident angle spanning was from 20 to 90 deg, at 0.03 deg resolution. Background noise was subtracted from raw data so peak can easily be analyzed, see Fig .2.

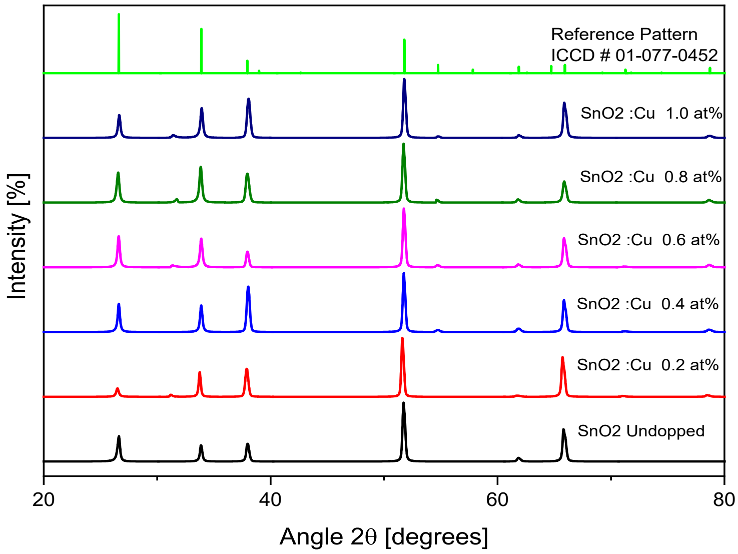

Fig. 2. XRD results for SnO_2 doping with copper.

3. Results

Transmittance data exhibit interference fringes due to multiple reflection through thin film medium. Envelop technique was used to extract optical properties of thin layer from transmittance curve [4 – 6]. Where two asymptote curves TM and Tm are drawn to covers the Maximum and Minimum amplitudes of the curve.

The Spectrum domain is divided into three regions based on light absorption: Region1, Transparent region, where absorption coefficient α is zero. Region-2: weak to medium absorption, and Region3: high absorption.

Substrate refraction index (s) is estimated from transparent region.

where

$$s=\frac{1}{T_s}+\sqrt{\left(\frac{1}{T_s^2}+1\right)} \tag{1}$$

T_s is the highest value of transmittance in the transparent region. Refraction index n, and absorbance x is computed as function of wavelength in the Region-2 as follow:

$$n(\lambda) = \sqrt{N + \sqrt{N^2 - s^2}} \tag{2}$$

$$N = 2s\frac{T_M - T_m}{T_M T_m} + \frac{s^2+1}{2} \tag{3}$$

$$x(\lambda) = \frac{E_M - \sqrt{E_M^2 - (n^2-1)^3(n^2-s^4)}}{(n-1)^3(n-s^2)} \tag{4}$$

$$E_M = \frac{8n^2 s}{T_M} + (n^2-1)(n^2-s^2) \tag{5}$$

In region3 high light absorbance occurs, therefore interference fringes disappear, T_m and T_M curves converge to single curve T_0. Refractive index is extrapolated from region 2. Absorbance in region 3 is computed as follow.

$$x(\lambda) \cong \frac{(n-1)^3(n+s^2)}{16n^2 s} \tag{6}$$

Thin layer thickness (d) is estimated using the following equation:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (7)$$

where λ_1, λ_2 are two adjacent peaks wavelengths, and n1, n2 are their respective refractive indices.

Absorption coefficient α (λ) is inferred from absorbance using the relation:

$$x = e^{-\alpha d} \quad (8)$$

Gap energy E_g is computed from Tauc'splot [7], where$(\alpha h\nu)^2$is plotted vs $h\nu$. Linear portion of the curve is extrapolated to zero to give the value of E_g. Fig 3. Gap energy for different doping percentage is represented in Fig 4.

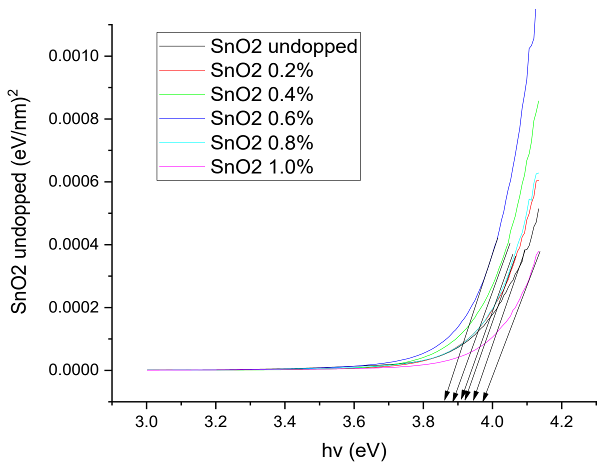

Fig. 2. Gap energy determination using Tauc's plot.

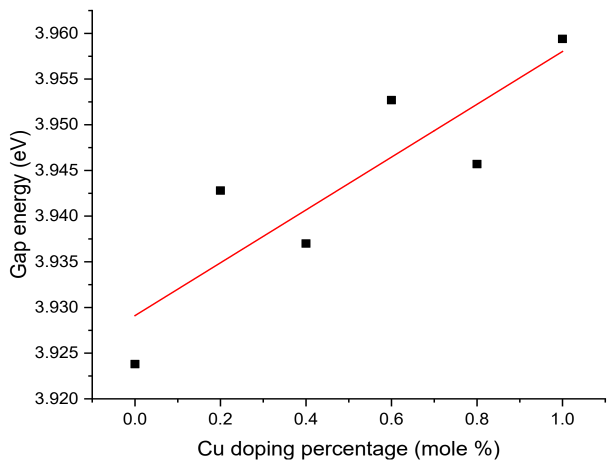

Fig. 3. Eg vs doping percentage.

Structural properties of thin films are obtained from XRD results. Thin layer response is matching very well to the reference pattern 00-041-1445 from JCPDS database which corresponds to tetragonal crystal system. Crystal growth is preferably in (211) plan. Lattice parameters: a, b and c are computed using the formula [8]:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (9)$$

Average grain size is estimated from peak broadening using Scherrer's formula [9]:

$$G = \frac{0.9\,\lambda}{\beta cos\theta} \tag{10}$$

where G is the grain size, λ: wavelength of incident X-ray, β: peak broadening at full width half maximum and θ is the Bragg angle. Plan (211), and (101) were used to estimate lattice parameters.

FWHM Broadening from the major peak corresponding to plan (211) is used to estimate grain size. Table-1 below summaries computed parameters as function of doping.

Table 1. Lattice parameters and Grain size computation as function of doping.

Doping %	Plan (*110*)		Plan (211)		Lattice Parameters (Å)			Volume	(FWHM) B(rad)	G (nm)
	2θ (°)	d_{110}(Å)	2θ (°)	d_{211}(Å)	a	b	c	V(Å^3)	B_{211}(rad)	
0.0	26.63	3.3449	51.72	1.7661	4.7304	4.7304	3.2082	71.7889	0.2613	33.79
0.2	26.50	3.3610	51.61	1.7694	4.7532	4.7532	3.1928	72.1333	0.2391	36.91
0.4	26.62	3.3465	51.74	1.7653	4.7327	4.7327	3.1999	71.6719	0.2507	35.22
0.6	26.60	3.3481	51.74	1.7653	4.7417	4.7417	3.1964	71.8678	0.2598	33.98
0.8	26.56	3.3481	51.72	1.7661	4.7417	4.7417	3.1908	71.7406	0.2638	33.46
1.0	26.65	3.3417	51.78	1.7640	4.7259	4.7259	3.2027	71.5282	0.2598	33.99

Grain size, and lattice parameters variation as function of doping percentage is presented in Fig 5 and Fig 6.

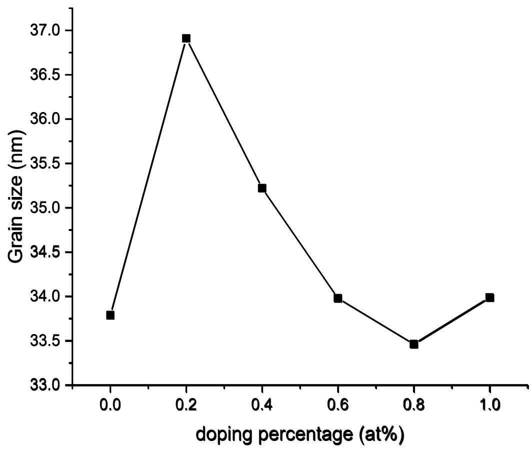

Fig. 5. Grain size vs doping.

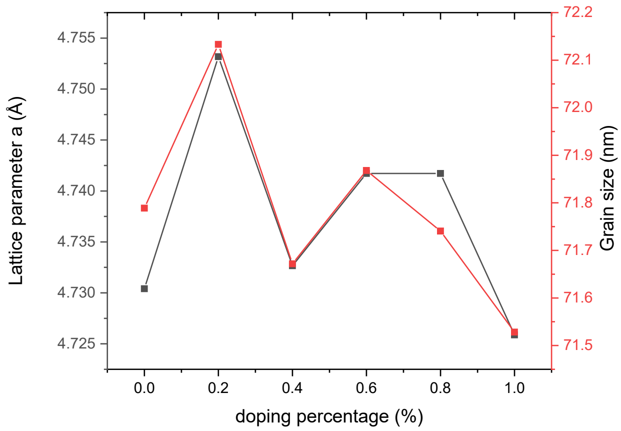

Fig. 6. Lattice parameter, unit cell volume vs doping.

4. Discussions

Good quality thin films were formed using spray pyrolysis technique with moving nozzle. Transmittance of thin layers in visible region was above 80%, smoothness of its surface and homogeneity in its thickness resulted in strong interference fringes on UV-Vis transmittance spectrum. It is observed that all samples exhibit high transmittance in the visible region (more than 80%). Undoped SnO_2 average transmittance in visible range is 80%, doping with copper increased transmittance upwards to reach maximum of 84.8% at 0.6% doping. Gap energy of SnO_2:Cu varies from 3.925 to 3.965 eV. It seems to increase – with slight fluctuation – with increase of doping percentage.

XRD analysis reveals tetragonal crystalline system of thin layer deposits, with preferred growth in (211) plan. Doping with copper seems the increase Grain size from 33.79nm at undoped state to a maximum of 36.91 at 0.2%, further doping decreases the grain size. Slight increase of grain size at 1.0% doping might be an experimental artifact. Analysis of doping effect beyond 1.0% would be useful to understand the reverse of the decreasing trend.

Similarly, doping with copper is increasing lattice parameter *a*, and also the unit cell volume from undoped status to a maximum at 0.2% doping, further doping decrease lattice parameter and unit cell volume. The linked variation of the lattices parameters to the grain size may find its origin from the effect that low grain leads to stressed unit cell volume and consequently to lower lattices parameters as it was carried out in this study.

5. Conclusion

In this paper, Transparent Conductive Oxide 0-1 at % Cu/Sn doped SnO_2 was prepared using spray pyrolysis technique. Good quality thin films of SnO_2 were obtained. Effect of doping with copper on optical and structural properties was investigated by UV-Vis spectrometry and XRD techniques. It was observed that the thin films have a high transmittance in visible range: 80% transmittance at undoped state and increased by copper doping to reach 84.8% at 0.6% level. The Gap energy ranges from 3.925 to 3.965 eV. It seems to increase - with slight fluctuation- with increase of doping level. Crystalline structure of thin films grew preferably along the (211) plan with a tetragonal system structure. Lattice parameter *a* has increased to a maximum value at 0.2% doping and then decreased afterwards. The grain size of crystallite reveals a similar trend as the lattice parameters. In further studies electrical and opto-electrical investigation will be take our focus in the future.

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