Asian Journal of Chemistry; Vol. 29, No. 9 (2017), 1990-1994

ASIAN JOURNAL OF CHEMISTRY

<https://doi.org/10.14233/ajchem.2017.20712>

Characterization of Doped and Undoped Tin Oxide Thin Films Prepared by Sol Gel Spin Coating Technique

AMANDEEP KAUR* and RAJESH KUMAR

Department of Physics, Lovely Professional University, Phagwara-144 411, India

*Corresponding author: E-mail: amandeepkchak@gmail.com

Received: 14 April 2017;

Accepted: 11 May 2017;

Published online: 15 July 2017;

AJC-18481

Optical and structural characterization of Cu-doped and pure SnO_2 thin films were performed as a part of this investigation. In this respect, the effects of changing the concentration of the precursors on the thin film properties were investigated. Tin dioxide thin films both in pure and doped form were prepared by a sol gel spin coating technique. The metallic oxide (SnO_2) films deposited were characterized using the UV Spectrophotometer and XRD studies. The average band gap for tin dioxide thin films was found to be approximately 3.80 eV. As far as direct band gap is concerned that copper doping appears to have no effect on the direct band gap which is in accordance with the literature. The indirect band gap for thin films was found to be approximately 3.48, 3.32 and 3.20 eV for different concentrations of the solutions, respectively. The indirect energy gap of the Cu doped thin films decreases as 3.76, 3.73 and 3.16 eV, respectively for different concentrations of the precursor solutions. The less value may be due to the addition of Cu-dopant and may also be due to growth of grain and improvement of the degree of crystallization.

Keywords: SnO_2 thin films, Spin coating, Band gap, Surface structure.

INTRODUCTION

Thin films are used for variety of applications in different fields of scientific research and investigations nowadays [1-5]. Thin films based on metal oxides are very good materials for different applications [6]. Out of these metal oxides, tin oxide is a wonderful material in the sense that its properties can be tailored by adding suitable impurities in it to suit the particular needs of an application [4]. Tin oxide is a wide band gap n-type semiconductor (3.6 eV) material which shows good transmission properties in the visible region and high reflection in IR region [7-12]. These properties make it a perfect candidate for use in the solar cells and antireflective coatings [2,13]. The doped SnO_2 owes its properties to the dopant introduced and undoped to the concentration of oxygen vacancies on its surface [8,11,14]. Tin oxide thin films have been prepared by a variety of methods by different research investigators since 1962. These methods are reactive thermal evaporation, electron beam evaporation, spray pyrolysis, sputtering, *etc.* [15,16]. These methods are costly and require complicated apparatus. Out of these methods, we have used a cost effective and relatively simple method of thin film preparation, sol gel spin coating [9,17,18]. The advantages of this method include low cost, simple and good film morphology of prepared thin films [7,15,19].

EXPERIMENTAL

Undoped SnO_2 thin films: $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was used as the precursor for the preparation of sol gel. Methanol and glacial acetic acid were used as the solvent and chelating agent for dissolving the precursor material in a beaker. The solution was prepared for different concentrations 0.2, 0.4 and 0.6 M, respectively. The stirring of prepared solution was done at room temperature by using magnetic stirrer in order to achieve the transparent and homogeneous solution.

Doped SnO_2 thin films: Tin(IV) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) was used as the precursor for the preparation of sol gel. Methanol, copper acetate and glacial acetic acid were used as the solvent and chelating agent for dissolving the precursor material in a beaker. The solution was prepared for different concentrations 0.2, 0.4 and 0.6 M, respectively. The stirring of prepared solution was done at room temperature by using magnetic stirrer in order to achieve the transparent and homo-geneous solution

General procedure: The glass substrates were cleaned with cleaning soap, distilled water and acetone in order to remove the solution organic impurities. The cleaned glass substrates were dried in a furnace at 200 °C for 10 min. After drying, the glass substrates were used for depositing the films from the prepared solution. The film was deposited by the use

of a spin coater (Apex instruments make) model no. Spin NXG-P1. The thin film was deposited on the glass substrates by applying 1 mL of the solution on the surface of glass substrates. The films were deposited with the spin coater having spin duration for each cycle of 60 s, spin speed of 3000 rpm and acceleration of 2 m/s^2 [6].

Detection method: The optical properties of thin films have been studied from UV spectrographs from a UV-visible spectrophotometer (Model No. UV-1800 Shimadzu) in the wavelength range of 200–800 nm. The structural properties were analyzed by using X-ray diffraction spectra using $\text{CuK}\alpha$ (wavelength = $1.5405 \text{ \AA}$) radiation (model no. X' Pert PRO, PANalytical Netherland).

RESULTS AND DISCUSSION

The absorbance spectra of thin films with different concentrations are shown in Fig. 1. The trend of absorption spectra is same for all the grown thin films. Absorbance spectra show that the absorbance decreases with the increase in wavelength for all the samples. The absorption decreases almost same for 0.4 and 0.6 M samples whereas it is comparatively greater for 0.2 M sample. This shows that the thickness of 0.2 M sample is higher than the other samples. Absorption is very high in the UV region, lowest absorbance in the visible region. In the NIR region, absorbance became steady. Absorbance decreases as precursor concentration increases for thin films. The transmittance spectra of films with different concentrations are shown in Fig. 2. The transmittance spectra have the same trend for all the films. The transmittance is highest in the visible region for 0.4 and 0.6 M solutions and is lowest for 0.2 M solution. This is because lower thickness of 0.4 and 0.6 M solution samples. In the NIR region, transmittance became steady. Transmittance increases with the increase in precursor concentrations. The absorption coefficient of SnO_2 thin films with different concentrations is shown in Fig. 3. The absorption coefficient (α) of SnO_2 thin films were calculated using the following equation:

$$\alpha = \frac{2.303A}{t}$$

Fig. 1. Absorbance spectra for SnO_2 thin films as a function of wavelength

Fig. 2. Transmittance spectra for SnO_2 thin films as a function of wavelength

Fig. 3. Absorption coefficient of SnO_2 thin films as a function of photon energy

where α is the absorption coefficient, t is the thickness of the film and A is the absorbance. The thicknesses of thin films have been found to be in the range of 2–10 μm .

The absorbance coefficient of SnO_2 thin film was plotted against the photon energy. The pattern is same for all the films with different concentrations. The films have lower absorption for longer wavelengths; absorption is highest for smaller wavelengths.

The direct and indirect optical band gap energy of thin films was extrapolated from the plot of $(\alpha hf)^2$ and $(\alpha hf)^{1/2}$ against photon energy (eV) shown in Figs. 4a–c and 5a–d, respectively. The band gap energy values were determined by plotting intercept with energy axis. The direct and indirect band gap energies are affected by precursor concentrations. The direct energy band gaps for thin films were found to be in the range of about 3.77–3.83 eV, respectively. These thin films are preferred to be used in optoelectronic devices due to the greater energy difference between valence band and conduction band. The indirect band gap for thin film was found to be approximately 3.48, 3.32 and 3.20 eV for different concentrations of the solutions, respectively.

Fig. 4a. Optical energy gap for the direct allowed transition of SnO_2 films for the sample prepared by of 0.2 M concentration

Fig. 5a. Optical energy gap for the indirect allowed transition of SnO_2 films for the sample prepared for three concentrations

Fig. 4b. Optical energy gap for the direct allowed transition of SnO_2 films for the sample prepared by of 0.4 M concentration

Fig. 5b. Indirect band gap of Cu doped SnO_2

Fig. 4c. Optical energy gap for the direct allowed transition of SnO_2 films for the sample prepared by of 0.6M concentration

Fig. 5c. Indirect band gap for Cu doped SnO_2 (0.4 M)

Fig. 5d. Indirect band gap for Cu doped SnO_2 (0.6 M)

Figs. 5b-d shows the UV spectra for Cu doped SnO_2 thin films with copper concentration of 2.5 % in 0.2, 0.4 and 0.6 M solutions. From these spectra, it is observed that the indirect energy gap of the thin films decreases as 3.76, 3.73 and 3.16 eV, respectively for different concentrations of the precursor solutions. The less value may be due to the addition of Cu- dopant and may also be due to growth of grain and improvement of the degree of crystallization. As for as direct band gap is concerned that the Cu doping appears to have no effect on the direct band gap which is in accordance with as reported in the literature [13].

Fig. 6a and 6b show the XRD patterns of tin oxide and Cu doped tin oxide thin films, respectively. Fig. 6a shows that tin oxide thin films have crystalline nature. The peaks at [101] and [022] planes were present. The peaks corresponding to angles 6.87° and 13° was unidentified. The lattice parameters for tin oxide thin films were calculated. It was found that the lattice parameter 'a' for tin oxide thin films was 6.75 and the value of 'c' came out to be 4.53 which are different from the values mentioned in the literature. However for Cu doped tin oxide thin films, the peaks having planes [022] and [101] were examined in Fig. 6b. The peak corresponding to 10.97° was unidentified [8]. The lattice

Fig. 6a. XRD spectra of tin oxide thin film prepared with 0.2 M concentration

Fig. 6b. XRD spectra of Cu doped tin oxide thin film prepared with 0.2 M concentration

parameter 'a' and 'c' for Cu doped tin oxide thin films were 6.03 and 4.05, respectively. The tin oxide thin films had tetragonal rutile structure. The calculated XRD parameters for tin oxide and Cu doped tin oxide thin films are shown in Tables 1 and 2, respectively.

TABLE-1
XRD DATA FOR TIN OXIDE THIN FILMS

hkl	2θ ($^\circ$)	Intensity (I)	d	a	c
(101)	15.85	145.110	5.58	7.891311678	5.302961448
(020)	31.73	124.078	2.81	5.62	3.77664

TABLE-2
XRD DATA FOR COPPER DOPED TIN OXIDE THIN FILMS

hkl values	2θ ($^\circ$)	Intensity (I)	d	$\text{\AA}$	c
(022)	21.73	174.679	4.085	8.16	5.48
(101)	32.25	260.447	2.772	3.92	2.63

Conclusion

Tin oxide thin films have been successfully deposited on the glass substrates by using sol gel spin coating technique. Thin films were fabricated by taking the different concentrations of precursor solutions of tin(IV) chloride dihydrate and copper acetate. From the absorbance spectra, it has been concluded that the absorbance is low and transmittance is high. This is due to the greater thickness of the films which is in μm . The prepared thin films have wide energy band gap in the range of 3.77-3.83 eV which is in agreement with the energy band gap values reported in the literature. Due to more absorbance in the UV region and low absorbance in the visible region, these films can be used to stop UV radiations and admit the visible light. These films appear to have potential to be used in optoelectronic devices.

ACKNOWLEDGEMENTS

The authors sincerely thank the cooperation extended by Mr. Navjot Singh and Mr. Jagtar Singh of Sophisticated Analytical instrumentation Facility (SAIF), Panjab University, Chandigarh for X-ray diffraction studies of the samples.

REFERENCES

1. S.K. Tripathy, B.P. Hota and P.V. Rajeswari, *Afr. Rev. Phys.*, **7**, 265 (2012).
2. F. Zahedi, R.S. Dariani and S.M. Rozati, *Bull. Mater. Sci.*, **3**, 433 (2014); <https://doi.org/10.1007/s12034-014-0696-8>.
3. K.L. Jarvis and P.J. Evans, *Thin Solid Films*, **624**, 111 (2017); <https://doi.org/10.1016/j.tsf.2016.12.055>.
4. J.-S. Park, H. Chae, H.K. Chung and S.I. Lee, *Semicond. Sci. Technol.*, **26**, 034001 (2011); <https://doi.org/10.1088/0268-1242/26/3/034001>.
5. S.S. Lekshmy, I.J. Berlin, L.V. Maneeshya, Anitha and K. Joy, *IOP Conf. Ser.: Mater. Sci. Eng.*, **73**, 012018 (2015). <https://doi.org/10.1088/1757-899X/73/1/012018>.
6. F. Gu, S.F. Wang, M.K. Lü, X.F. Cheng, S.W. Liu, G.J. Zhou, D. Xu and D.R. Yuan, *J. Cryst. Growth*, **262**, 182 (2004); <https://doi.org/10.1016/j.jcrysgro.2003.10.028>.
7. S.-C. Lee, J.-H. Lee, T.-S. Oh and Y.-H. Kim, *Sol. Energy Mater. Sol. Cells*, **75**, 481 (2003); [https://doi.org/10.1016/S0927-0248\(02\)00201-5](https://doi.org/10.1016/S0927-0248(02)00201-5).
8. S.K. Tripathy, B.P. Hota and P.V. Rajeswari, *Bull. Mater. Sci.*, **36**, 1231 (2013); <https://doi.org/10.1007/s12034-013-0582-9>.
9. B. Yarmand, *Int. Mater. Phys. J.*, **2**, 20 (2014).
10. M. Marikkannan, V. Vishnukanthan, A. Vijayshankar, J. Mayandi and J.M. Pearce, *AIP Adv.*, **5**, 027122 (2015); <http://dx.doi.org/10.1063/1.4909542>.
11. J.O. Ajayi and D.B. Agunbiade, *Int. J. Res. Appl. Sci. Eng. Technol.*, **3**, 821 (2015).
12. A.D. Bhagwat, S.S. Sawant, B.G. Ankamwar and C.M. Mahajan, *J. Nano Electron. Phys.*, **7**, 04037 (2015).
13. P.G.L. Baker, R.D. Sanderson and A.M. Crouch, *Thin Solid Films*, **515**, 6691 (2007); <https://doi.org/10.1016/j.tsf.2007.01.042>.
14. S.K. Tripathy, R. Prabeena, V.S. Jahnavi and N.V.P.R. Thirumala, *Int. J. Sci. Res.*, **2**, 101 (2013).
15. E. Savarimuthu, N. Sankarasubramanian, B. Subramanian, M. Jayachandran, C. Sanjeeviraja and S. Ramamurthy, *Surf. Eng.*, **22**, 268 (2006); <https://doi.org/10.1179/174329406X122838>.
16. S. Saipriya, M. Sultan and R. Singh, *Physica B*, **406**, 812 (2011); <https://doi.org/10.1016/j.physb.2010.12.003>.
17. M. Shaban, G.F. Attia, M.A. Basyooni and H. Hamdy, *Int. J. Eng. Adv. Res. Technol.*, **1**, 11 (2015).
18. I.H. Kadhim and H.A. Hassan, *J. Appl. Sci. Agric.*, **10**, 159 (2015).
19. S.S. Oluyamo and D.B. Agunbiade, *Int. J. Innov. Res. Adv. Stud.*, **3**, 2394 (2016).