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# HIGHLY EFFICIENT OPTOELECTRONIC PROPERTIES OF DOUBLY DOPED $SnO_2$ THIN FILM DEPOSITED BY SPIN COATING TECHNIQUE

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In this study, we investigated structural and optical properties of doubly doped $SnO_2$ thin films prepared successfully by sol-gel spin coating technique on optical glass substrates. Low cost precursor $SnCl_2.2H_2O$ for host precursor and $Sbcl_3$ and $NH_4F$ dopant source are used (for 4 % wt. Sb and 30 % wt. F). X-ray Diffractometer, UV-Vis spectrophotometer, scanning electron microscope (SEM) and atomic force microscopy (AFM) were performed on AFTO (Antimony and Fluorine Doped $SnO_2$) films. Structural studies reveals the presence of orthorhombic structure with preferential orientation of (021) and (042). The dislocation density of the doubly doped film is smaller than densities mentioned in the literature for doubly doped $SnO_2$. SEM and AFM studies reveal the surface of AFTO to be made of nanocrystalline particles. The transmittance of the films in the visible range is 85-97 %, the best transparent film for doubly doped tin oxide films in the literature. $E_g$ values are quite wide, 4.45 eV and better linearity was obtained in the $(\alpha h\nu)^2$ vs. $(h\nu)$ plots for $E_g$ values. The band gap attained for the doubly doped films in this study is higher than the values reported for doubly doped tin oxide films prepared from prophanol solution of $SnCl_2.2H_2O$ precursor. Our experimental results indicated that AFTO thin films with high optical quality could be synthesized by sol-gel spin coating techniques.

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*Keywords*: $SnO_2$: Sb: F thin films, Spin coating method, Optoelectronic devices, Solar cell

## 1. Introduction

Transparent conducting oxides are materials providing both high optical transmittance and high electrical conductivity simultaneously. Antimony and fluorine doped tin oxide (AFTO) films are an n-type semiconductors. Semiconductor materials have been extensively investigated because of their unique size dependent electronic, magnetic, optical, and electrochemical properties [1–5]. As an n-type semiconductor with a wide band gap energy, tin oxide spans a wide range of applications from conductive electrodes and transparent coatings to heterojunction solar cells and chemical sensors [6,7]. Tin oxide is a semiconductor material highly transparent and with high mechanical and chemical stability, except for their interactions with oxygen atoms at high temperature [8]. In addition to its high optical transmission due to a wide optical band gap nearly 3.8 eV, SnO2 thin films have high n-type conductivity, which is due to their non-stoichiometric character associated with oxygen vacancies and interstitial tin in the lattice [9, 10, 11].

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Many dopants, such as antimony (Sb), arsenic (As), fluorine (F), indium (In), molybdenum (Mo), and phosphorus (P) have been used to improve the electrical properties of tin oxide films [12]. Among these, Sb and F are found to be the most commonly used dopants for solar cell layers.

Tin oxide films with low resistivity can be realized by doping either Sb or F. Undoped and doped tin oxide films have been deposited by various methods [12-17]. The conventional techniques such as CVD, PVD have been widely followed [18-20] to study the effect of high dopant concentration on structural, optical and electrical properties of the doped material. The number of studies [21–23] on the sol–gel based antimony or flor doped $SnO_2$ films have been extremely rare. The sol–gel processing exhibits good uniformity and better-controlled composition [24] for thin film deposition by the spinning method. In this study, an attempt is made to find different layers effect by simultaneously doping antimony and fluorine. Even though, Thangaraju and Ravichandran et al. have reported [13, 25, 26, 27] some properties of the doubly doped TO films, detailed report on these films are hardly available in the literature.

In the present work, antimony and fluorine doped tin oxide (AFTO) films were fabricated using $SnCl_2.2H_2O$ (98 % purity, Merck), $Sbcl_3$ (99 % purity, Merck), and $NH_4F$ (98 % purity, Sigma-Aldrich) as precursor. The aim of this work is to investigate the relationship between the multilayers and the structural and optical properties of $SnO_2$: Sb: F thin films, deposited by spin coating technique. The results obtained have been compared with the specified results by several researchers and the reason was discussed.

## 2. Experimental

$SnCl_2.2H_2O$ (0.05 M) 0.564 g added to prophanol and $NH_4F$ (30 % wt.), $SbCl_3$ ( 4 % wt.) was then added as dopant source in the solvent. 10 ml HCl were then added to the solvent and completed to 50 ml. This solvent was stirred and heated 1 hour for solution phase. Solution became transparent and was then added spin coater (Laurell WS-650 series spin processor) with static method at 3000 rpm. The substrates were cleaned in washing machine using bidistilled water, and then heated in oven at 250$^o$C for 1 h. Multilayer coatings were spun at a speed of 3000 rpm for 10 s. The layers were first dried in air then sintered in oven at 150$^o$C for 1 h. At the end film annealed for one hour at 400 $^o$C in tube furnace.

X-ray diffraction patterns were recorded using X-ray diffractometer (Rigaku D Max-IIIC) which was operated at 40kV and 30mA with X-ray source of CuKα radiation having wavelength 1.5406˚ A. The surface morphology of the coating was imaged using a high resolution scanning electron microscopy (SEM) and atomic force microscopy (AFM). SEM images were obtained by employing Zeiss Evo-LS-10 model scanning electron microscope and AFM, which was produced by nanomagnetics instrument. Perkin Elmer UV–Vis-NIR double beam spectrophotometer (Lambda-35) is used to record the transmission spectra in the range of 300–1100nm.

## 3. Result and discussion

### 3.1.Structural properties

X-Ray Diffraction (XRD) patterns of doubly doped $SnO_2$ ($SnO_2$: Sb: F) thin films depict that films are crystalline in nature. XRD patterns reveal that films are not good crystalline for low layers but high layers are good crystalline. XRD graph showed that films have grown orthorhombic structure with the (021) and (042) preferential orientation (ICDD Card No: 78-1063). No other peaks have emerged. The obtained graph is rather original, because the films are single crystalline and have not been found in the literature. A similar conclusion has been given by Radheshyam Rai et al. for $SnCuO_3$ [28]. The high intensity of the peak suggests that these thin films mainly consist of the crystalline phase. As the number of layers is increased, the crystallinity of the thin films is enhanced as manifested by the intensity and sharpness of the XRD peaks of the AFTO thin films as shown in Fig. **1**. The crystallinity increases with increasing layer number because of amount of tin oxide in the surface of the films. Lower layers (2 and 4) don't exhibit well crystalline in nature.

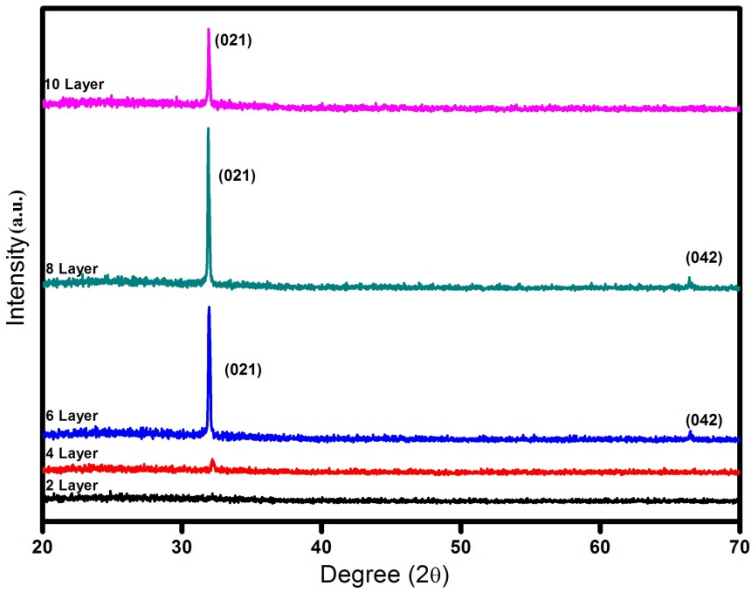


*Fig. 1: XRD patterns of doubly doped thin film for different layers*

The quantitative improvement in the crystallinity can be understood from the calculation of the grain size. The grain size D is determined from the full width half maximum (FWHM) value of the dominant (021) reflection, using Scherrer's formula [29]: $D = 0.9\ \lambda/(\beta\ cos\theta)$ where λ is the x-ray wavelength (1,5406 Å for CuKα), θ is the diffraction angle and β is the FWHM. The calculated values are tabulated in Table **1**. It is seen that the grain size decreased with increasing layers number and reached minimum at 6 layers then increased with the increasing deposition layer. AFTO nanoparticle size sharply decreases from 222.31 nm (at room temperature) to smaller than 58.7 nm at size layers. It finally slowly increases to 72.6 nm at higher layers. It is explained that amount of tin oxide in the surface of the films increases with increasing deposition and decreases grain size. Different researcher find changes the grain size for annealing temperature. They generally said that grain size increases with increasing annealing temperature [30, 31, 32]. In this study deposition layer effect investigated and found that grain sizes nearly decreases with increasing deposition layer.

The dislocation density (δ), defined as the length of dislocation lines per unit volume, has been estimated using the equation, $\delta=1/D^2$ [33]. Since δ is the measure of the amount of defects in a crystal, the small values of δ obtained in the present study confirmed the good crystallinity of the doubly doped TO films deposited by spin coating. These conclusions also were given Table **1**.

*Table 1. Structural parameters table of different layer deposition of doubly doped tin oxide*

| Layer Numbers | 2θ (Degree) | FWHM | D(nm) | $\delta x10^{18}$ (lines/m$^2$) | RMS(nm) |
|---|---|---|---|---|---|
| 2 | 32,18 | 0,042 | 222,31 | 0,066 | 230,15 |
| 4 | 32,14 | 0,054 | 174,07 | 0,108 | 172,14 |
| 6 | 31,94 | 0,161 | 58,02 | 0,976 | 156,91 |
| 8 | 31,88 | 0,134 | 69,71 | 0,677 | 174,81 |
| 10 | 31,90 | 0,129 | 72,67 | 0,623 | 255,86 |

2θ- The Diffraction Angle; FWHM- Full width half maximum; D-Grain size; δ-Dislocation density

The surface morphologies of the $SnO_2$: Sb: F thin films, was also investigated by using Scanning electron microscope (SEM) and atomic force microscopy (AFM). Scanning electron microscope (SEM) images were given in Fig. **2** for different layers. These images revealed that films

are uniform and homogenous. These observations strongly support the results obtained from XRD data. It has been observed that increasing deposition layer increases homogeneity and uniformity. It has also been observed that nanoparticles of the films increase with increasing layer deposition and grain size decreases. Good crystallinity of the films obtained for high number of layer could be seen SEM images. It is observed that there are cube and pyramid shaped nanostructures in the surface. This is attributed to the orthorhombic structure of $SnO_2$ and SnO in the given literature [34]. These images have not been observed in the literature for tin oxide films.

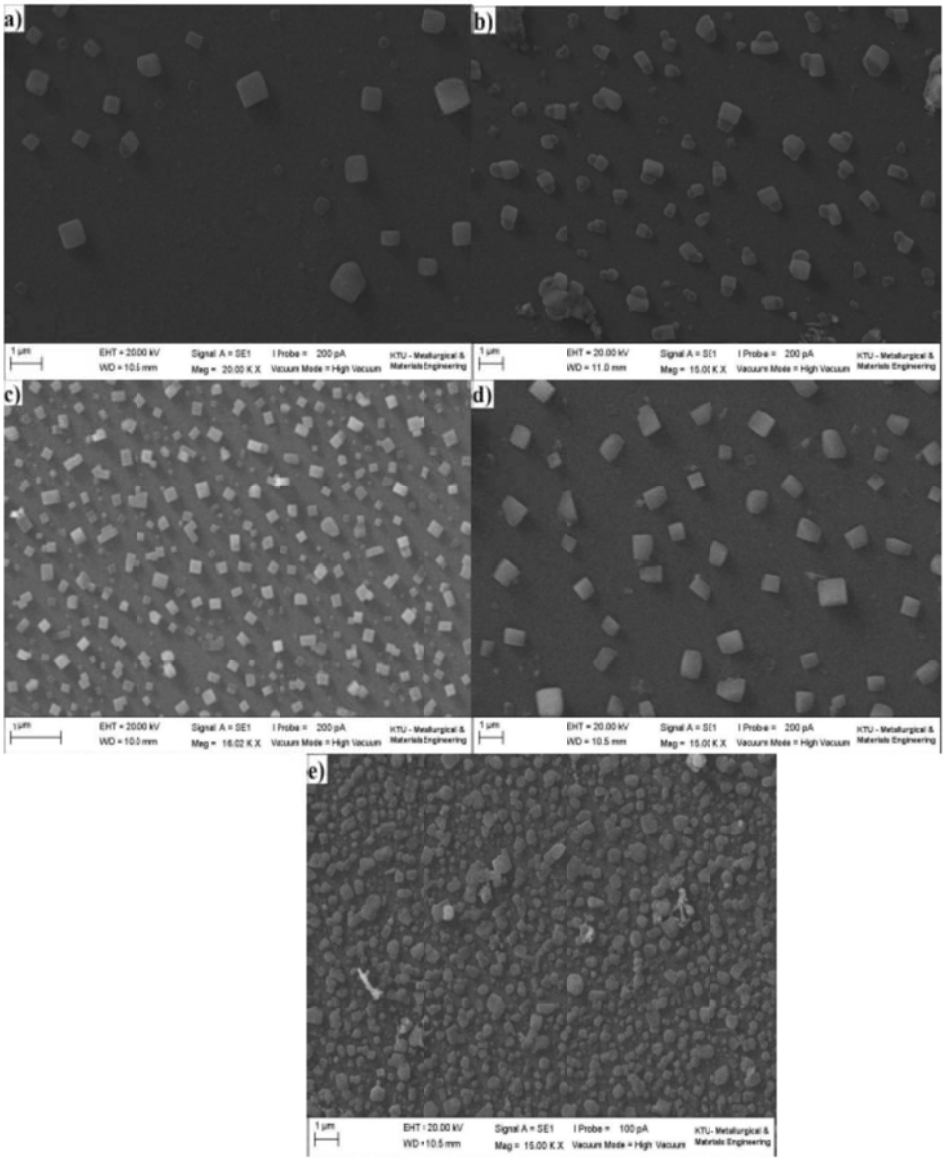


*Fig. 2: SEM micrographs of doubly doped tin oxide thin films*
*a) 2, b) 4, c) 6, d) 8, e) 10 layers deposition*

The atomic force microscopy surface 3D images were obtained for $SnO_2$:Sb:F films prepared with different deposited layers. Fig. 3(a)-(e) show 3D atomic force microscopy images of doubly (from 2 layers to 10 layers) doped $SnO_2$ films and Fig. 3(f) showed the surface roughness variations of $SnO_2$:Sb:F films as a function of the layer number. The number of smaller grains increased with the increase in layer number. The grains can be seen almost all over the substrate. The distribution of grains is uniform on the substrate surface. The root mean square (RMS) values of surface roughness is found to be 156.91 to 255.86 nm doubly doped film. The root mean square roughness of the films with 6 layers is the lowest in comparison with other films (Table 1). As the layer numbers increased from 1

to 6, the roughness of the films decreased from 230.15 to 156.91 nm, then increased to 255.86 nm. The AFM microphotographs of the $SnO_2$:Sb:F films were also shown that the grain size of the films decreased with the increase in the layer numbers. Detailed atomic force microscopy study revealed that the roughness of the film was dependent on the layer numbers.

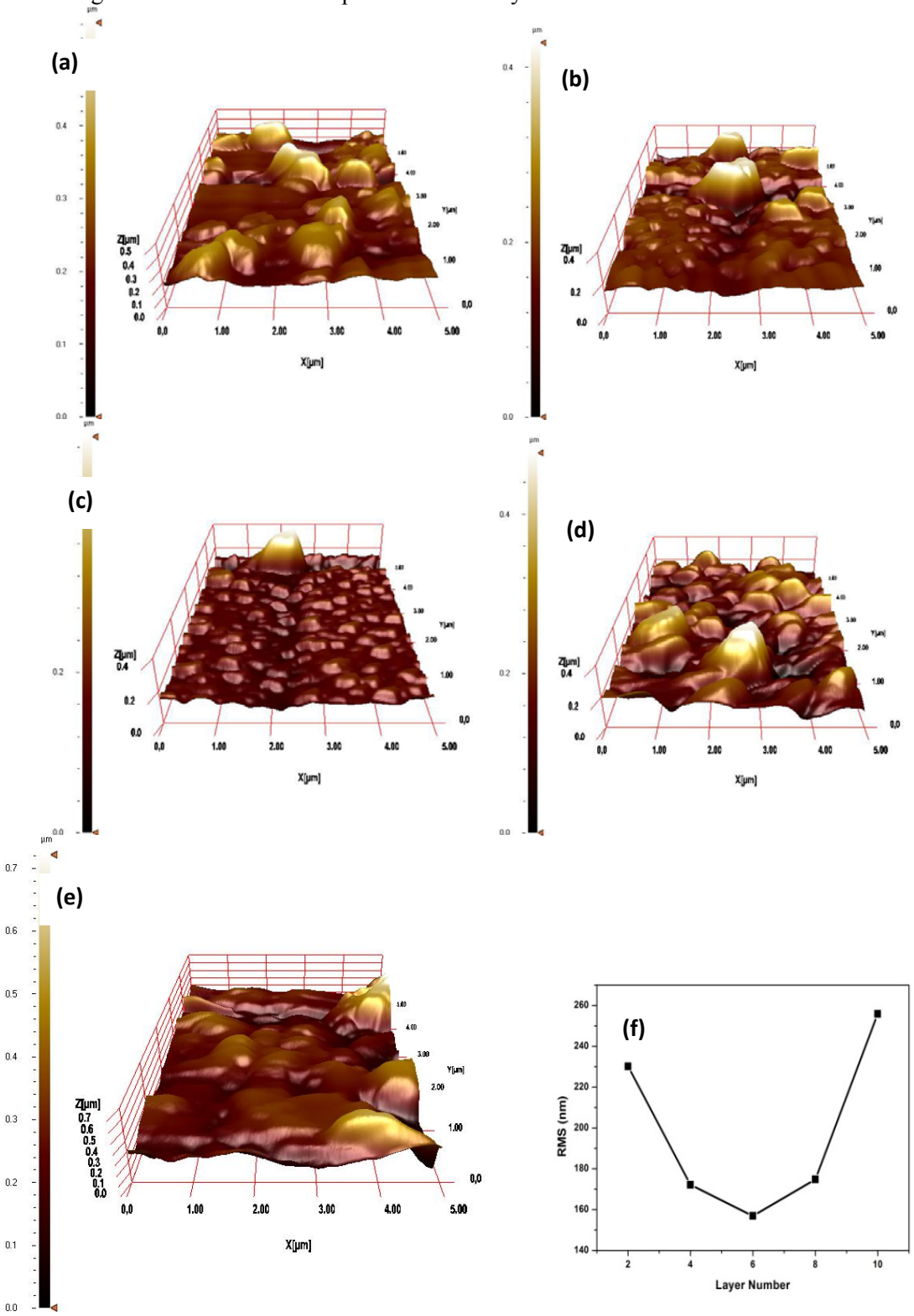


*Fig. 3: Fig. 3. AFM surface 3D images of doubly doped films as a function of layer number: (a) 2, (b) 4, (c) 6, (d) 8, (e) 10, (f) the surface RMS roughness variation of doubly doped films as a function of layer number*

### 3.2. Optical properties

The optical properties of AFTO coating were characterized by measuring the optical transmittance (T) spectrum in the range 300–1100 nm (Fig.4(a)). The layers were deposited at spinning speed of 3000 rpm for 10 s. The thickness of the layers is supposed to increase linearly by increasing the number of deposited layers but the optical properties (transmittance) was found to decrease (Fig.4(b)). The information of optical transmittance is important in evaluating the optical performance of semiconducting oxide thin films. From the spectra it is observed that the transmittance in the visible range is 85-97 % for the doubly doped TO films grown by spin coating technique at different layer deposition. Although it is quite difficult to deposit doubly doped tin oxide films with this method, we successfully deposited and obtained quite homogeneous and transparent films in the literature. The transmittance measurements indicated that present AFTO thin films can be used as a window material for solar cell application due to their best transmittance of films is around 95%. The value obtained for AFTO films is the highest value compared to other studies that use other methods.

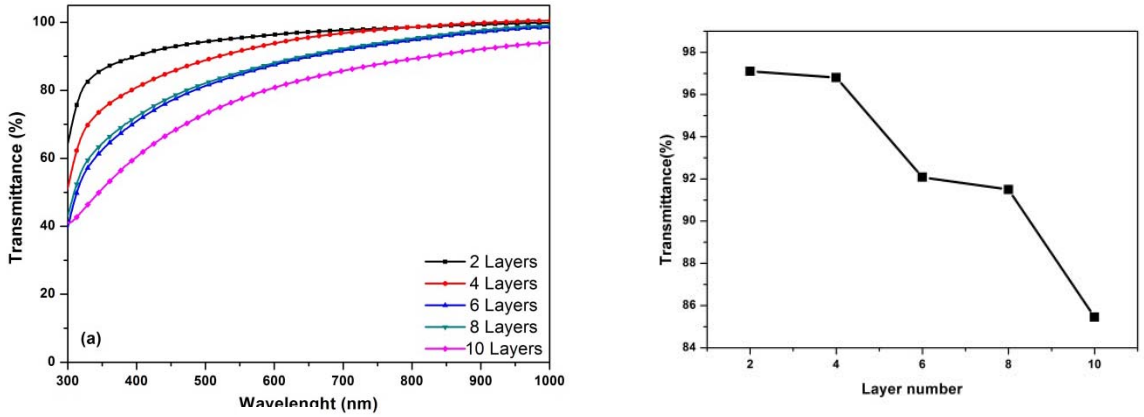


*Fig. 4: (a) Optical transmission spectra of doubly doped tin oxide thin films for different layer deposition (b) The optical transmittance values doubly doped films as a function of layer number*

The absorption coefficient (α) can be calculated from the transmittance (T) values at the absorption edge from the Lambert's law $\alpha = \ln (1/T)/t$ [35]. The variation of absorption coefficient against photon energy (hν) has the form of $\alpha = A (h\nu - Eg)^{n/2}$, where $E_g$ is the band gap, A is a constant related to the effective masses associated with the bands and n is a constant which is equal to one for a direct-gap material and four for an indirect-gap material [35].

*Table 2. Transmittance and Band gap energy values for different layer deposition*

| Layer Numbers | T (%) (λ~700 nm) | $E_g$ (eV) |
|---|---|---|
| 2 | 97,10 | 4,25 |
| 4 | 96,80 | 4,25 |
| 6 | 92,08 | 4,45 |
| 8 | 91,50 | 4,41 |
| 10 | 85,45 | 4,25 |

T- the transmittance at 700 nm; Eg-Energy band gap

To determine whether the doubly doped TO films deposited using spin coating method have direct or indirect band gap, $(\alpha h\nu)^2$ vs. (hν) and $(\alpha h\nu)^{1/2}$ vs. (hν) plots were drawn. Since better linearity was obtained in the $(\alpha h\nu)^2$ vs. (hν) plots, the direct band gap values were determined by extrapolating the linear portion of these plots to the energy axis. The optical band gap values are also estimated using the dT/ dλ vs λ plots. The average optical transmittance and the estimated $E_g$ values are summarized in Table **2**. $E_g$ values did not chang for different layer deposition, as can be seen better in Figure **5.** But it was found that the value obtained for the films deposited with 6 layers doubly doped tin oxide is the highest value obtained in the present study (4.45 eV).

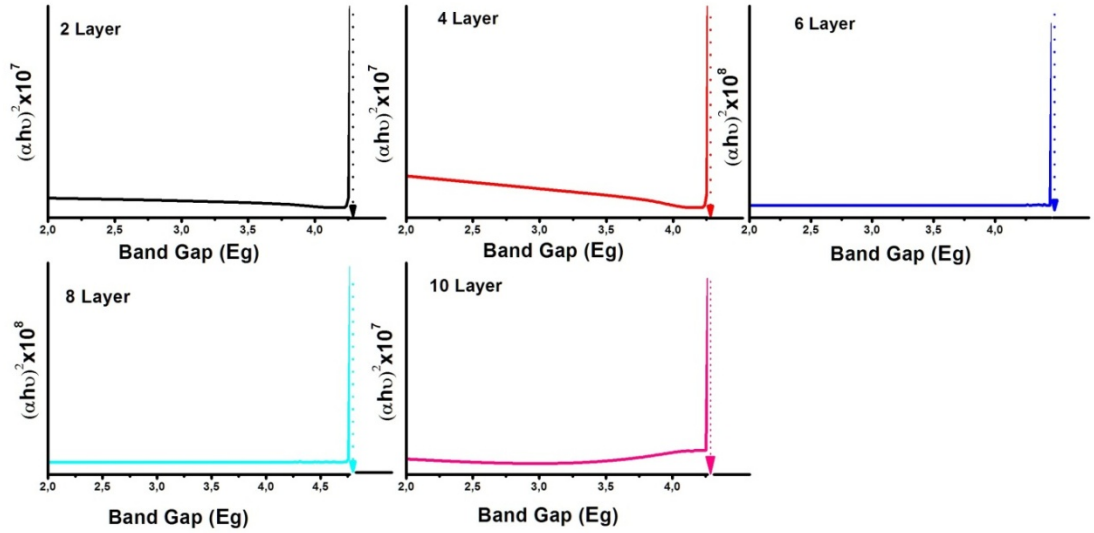


*Fig. 5: Band gap graphs of doubly doped tin oxide films for different layer deposition*

## 4. Conclusion

Doubly doped $SnO_2$ thin films were successfully prepared by sol-gel spin coating techniques. Films were deposited on optical glass and annealed at 400°C. The microstructural and optical properties of AFTO thin films were investigated different layer number in the layer range from 2 to 10. Optical properties as well as the structure and morphology of the films were found to depend on the multilayer. XRD patterns revealed that films are single crystal in nature and have preferential orientation (021) and (042) plane. X-ray diffraction results also confirmed that the various AFTO thin films consisted of nanoparticles with average grain size in the range of 222 -58 nm. SEM and AFM images depict that films are homogenous and uniform. The microstructure analysis of the AFTO thin films demonstrated that the layer deposition is a very important parameter. It affects crystalline microstructure and optical properties of the thin films. The highest transmittance of around 95% at 700 nm has been observed. The transmittance measurements indicated that present AFTO thin films can be used as a window material for solar cell devices due to their best transmittance is around 95 %. Various optical parameters such as optical band gap energy were calculated from the optical transmittance data recorded in the wavelength in the range of 300-1100 nm. We found that the optical band gap energy of AFTO thin films is the widest band gap values in the literature with this method. Wide optical band gap (4.45eV) and reasonable visible transmittance (95%) make these doubly doped films desirable candidates for low-cost solar cell materials. These findings revealed that doubly doped $SnO_2$ thin film layer deposition up to 6 is a good window material for solar cell devices. This point will be studied in the immediate future. Our experimental results indicated that $SnO_2$ thin films with the high optical quality could be synthesized by sol-gel spin coating techniques.

Although further research is necessary, the AFTO films show a promising potential for the improvement of AFTO thin film applications.

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## References

[1] A.P. Alivisatos, Science **271**, 933 (1996).
[2] C.B. Murray, D.J. Norris, M.G. Bawendi, J. Am. Chem. Soc. **115**, 8706 (1993).
[3] M. Nirmal, L. Brus, Acc. Chem. Res. **32**, 407 (1999).
[4] G. Turgut, D. Tatar and B. Düzgün, Asian Journal of Chemistry **25**, 245 (2013).
[5] D. Tatar, B. Düzgün, Pramana – J. Phys., **79**, 137 (2012).
[6] Y.S. He, J.C. Campbell, R.C. Murphy, M.F. Arendt, J.S. Swinnea, J. Mater. Res. **8**, 3131 (1993).
[7] J. Watson, Sens. Actuators **5**, 29 (1984).
[8] H. Pink, L. Treitinger, L. Vite, Jpn. J. Appl. Phys. **19**, 513 (1980).
[9] Z.M. Jarzebski, J.P. Marton, J. Electrochem. Soc. **123**, 199 (1976).
[10] D. Y. Torres Martınez, R. Castanedo Perez, G. Torres Delgado, O. Zelaya Angel, J Mater Sci: Mater Electron **22**, 684 (2011).
[11] D. Tatar, G. Turgut and B. Düzgün, Romanian journal of physics, accepted papers (in pres).
[12] H. Kim, R.C.Y. Auyeung, A. Pique, Thin Solid Films **516**, 5052 (2008).
[13] B. Thangaraju, Thin solid films **402**, 71 (2002).
[14] H.L. Ma, D.H. Zhang, S.Z. Win, S.Y. Li, Y.P. Chen, Sol. Energy Mater. Sol. Cells **40**, 371 (1996).
[15] H. Kim, A. Pique, Appl. Phys. Lett. **84**, 218 (2004).
[16] M.H. Madhusudhan Reddy, A.N. Chandorkar, Thin Solid Films **349**, 260 (1999).
[17] G. Turgut, D. Tatar, B. Düzgün, EÜFBED- Erzincan Üniversity Graduate School of Natural and Applied Sciences Journal **5**, 13 (2012).
[18] Srinvasa Murty N, Jawalekar SR. Thin Solid Films **108**, 277 (1983).
[19] Kim KS, Yoon SY, Lee WJ, Kim KH. Surf Coat Technol **138**, 229 (2001).
[20] K.O. Grosse-Holz, J.P.M. Cillessen, M.W.J. Prins, P.W.M. Blom, R.M. Wolf, R. Waser, Materials research society symposium proceedings, Physics of organic semiconductors **401**, 67 (1995).
[21] C. Terrier, J.P. Chatelon, R. Berjoan, J.A. Roger, Thin Solid Films **263**, 37 (1995).
[22] C. Terrier, J.P. Chatelon, J.A. Roger, Thin Solid Films **295**, 95 (1997).
[23] A.P. Rizzato, C.V. Santilli, S.H. Pulcinelli, A.F. Craievich, J Appl. Crystallogr **36**, 736 (2003).
[24] T.D. Senguttuvan, L.K. Malhotra, Thin Solid Films **289**, 22 (1996).
[25] K. Ravichandran, G. Muruganantham, B. Sakthivel, P. Philominathan, Journal Of Ovonıc Research, **5**, 63 (2009).
[26] K. Ravichandran, G. Muruganantham K Saravanakumar S Karnan B Kannan, R Chandramohan, B Sakthivel, Surface Eng **25**, 81 (2009).
[27] K. Ravichandran, G. Muruganantham, Sakthivel, B. Physica-B Con. Mater., **404**, 4299 (2009).
[28] T.D. Radheshyam Rai, S.T Senguttuvan,. Lakshmikumar, Computational Materials Science **37**, 15 (2006).
[29] L.N. Patro, K. Hariharan, Materials Letters **80**, 26 (2012).
[30] V. Arıvazhagan, S. Rajesh, Journal of Ovonic Research, **6**, 221 (2010).
[31] S. Bazargan, N. F. Heinig, D. Pradhan, and K. T. Leung, Crystal Growth & Design, **11**, 247 (2011).
[32] X. Zhong, B. Yang, X. Zhang, J. Jia, G. Yia, Particuology **10**, 365 (2012).
[33] V. Senthilkumar, P. Vickraman, J.J. Prince, M. Jayachandran, C. Sanjeeviraja, Philosophical Magazine Letters, **90**, 337 (2010).
[34] S. Das, S. Chaudhuri, S. Maji, J. Phys. Chem. C, **112**, 6213 (2008).
[35] E. Elangovan, K. Ramamurthi, Appl. Surf. Sci. **249**, 183 (2005).