Effect of Volume Spray Rate on Highly Conducting Spray Deposited Fluorine Doped SnO_2 Thin Films

Dr.R.N. ARLE[1], B.L.KHATIK[2]

[1]Department of Physics, Jijamata College of Science and Arts, Bhende Bk.India
[2]Research scholar, JJT University, Rajasthan. India
Email- arleramdasmrp@gmail.com

Abstract

Tin oxide thin films doped with fluorine have been prepared by spray pyrolysis from $SnCl_2$ Precursor at the substrate temperature of 600^0C. The Fluorine doped tin oxide thin films belong to special class oxides that combine high electrical conductivity with high optical transparency. Such transparent Conducting Oxide (TCO) thin films thus an important component for optoelectronic applications. Spray pyrolysis deposition is a simple and relatively low cost technique for thin film preparation. This work consists the effects of volume of fluorine source on structural, optical and electrical properties of thin films. The characterization of samples was carried out by X-ray diffraction, scanning electron microscopy, UV-VIS spectrophotometer and the four probe method. The as-prepared films are polycrystalline with a tetragonal crystal structure. The films are preferentially oriented along the (200) direction. The films have moderate optical transmission of the deposited films is 75.6% for 25 wt. % fluorine-doped tin oxide films. The obtained results reveal that the structures and properties of the films are greatly affected by doping levels. These films are useful as conducting layers in optoelectronics and photovoltaic devices.

Keywords: Electrical properties and measurements; Pyrolysis; Tin oxide; X-Ray diffraction

Introduction

The highly transparent and conducting thin films and its high transmittance and conductivity, have wide applications [1, 2]. In recent years, there has been a growing interest in the use of transparent conducting oxide thin films as conducting solar window materials in thin film solar cells [3–6], as heat reflectors for advanced glazing in solar application[7,8] and as gas sensors [5–13]. Tin oxide is the first transparent conductor which is significantly commercialized [5, 9, 14]. Among the different transparent conductive oxides, SnO_2 films doped with fluorine are most appropriate for use in solar cells, owing to its low electrical resistivity and high optical transmittance. SnO_2 is chemically inert, mechanically hard, and can resist high temperatures [5]. Doped or undoped SnO_2 can be synthesized by numerous techniques such as thermal evaporation [3,9], sputtering [5,9–12,16,17], chemical vapour deposition [3,18–20], sol–gel coating [3,17,21], painting [3,17], spray pyrolysis [3,5,7,13],and hydrothermal method. Among the various deposition techniques, the spray pyrolysis is the most suitable method for the preparation of doped tin oxide thin films because of its simple and inexpensive experimental arrangement. It is easy of add to various doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings and is the essential characteristics of the simple spray pyrolysis technique [16]. Usually, the chemical spray pyrolysis method is used to deposit FTOs at optimized substrate temperatures of around 450-600^{0}C [20].

In the present work, SnO_2: F thin films were prepared by the spray pyrolysis technique at substrate temperature of 600^{0}C using dehydrate stannous chloride ($SnCl_2 \cdot 2H_2O$) and ammonium Bifluoride ($NH_4 HF_2$) as precursors. The aim of this work is to study the relationship between the doping levels and some physical properties of SnO_2: F thin films such as the electrical, structural and optical properties.

Experimental details

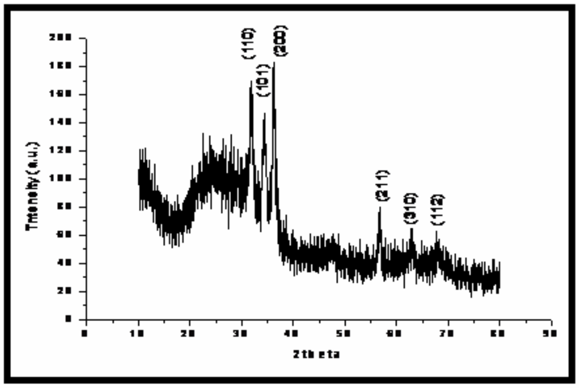
The fluorine-doped tin oxide thin films in the present study were prepared using a spray pyrolysis apparatus. Thin films of SnO: F (FTO) was deposited on an optical glass substrate. Dehydrate stannous chloride ($Sncl_2$:$2H_2O$) was used for making the precursor solution. This precursor was dissolved in 4 mL concentrated hydrochloric acid (HCl) and then added with methanol served as the starting solution. The solution molarities of 0.1 M were deposited and doping 0.1 M, ammonium Bifluoride ($NH_4 HF_2$) by ranging from 2 ml to 10 ml in step of 2 ml. Other preparative parameters like nozzle to substrate distance (45 cm), air flow rate (25 L/min) and substrate temperature (600^{0}C) were kept constant as the optimized values. The samples were analyzed with X-rays diffractometr using a monochromatic radiation Cu-Kα, λ=1.5406 Å in the range of scanning angle $20° < 2\theta < 79.99°$. Morphological analysis of the films was carried out by Scanning electron microscope (SEM). Optical transmittance spectra of the films were measured using a PC based UV-VIS Systronics spectrophotometer 119 model in the range 200 nm to 999 nm of wavelength with air as reference. Four probe set up was used for electrical measurements at room temperature.

Results and discussion

Structural and morphological properties

Fig.1 shows the typical X-ray micrograph for SnO_2: F (FTO) from 20ml solution and shows peaks along (110), (101), (200), (211), (310) and (112) planes. The crystallite size is 20 nm-100 nm. The crystallite Grain size decrease with increase fluorine doped films 2ml, 4ml, 6ml and for 8ml, 10ml solution grain size increase with increase fluorine doped.

Fig.2 shows a typical SEM micrograph of the SnO_2 thin film deposited at substrate temperature 600^{0}C and 20ml solution volume. The SEM microstructures reveal that all the films have a homogeneous surface morphology with nanocrystalline grains, also all the films are without any cracks and holes. Patterns indicate that films are polycrystalline in nature. The phase present in the deposited films belongs to pure tetragonal structure. The EDAX spectra of the same film reveal the elemental analysis, which shows that Sn and O were found to be 89.55: 11.45 in percent.



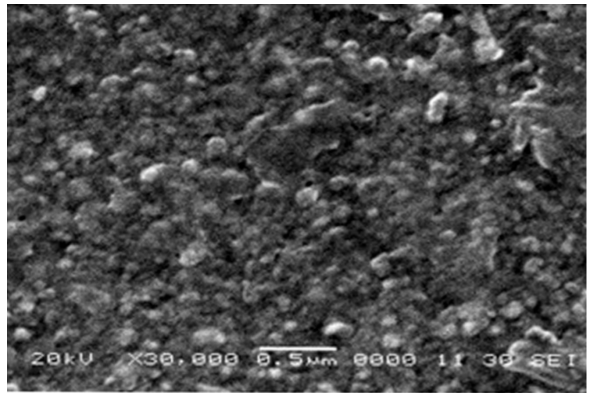


Fig. 1 XRD patterns of $SnO_{2:}$ F thin films. **Fig.2** SEM micrograph of SnO_2 thin films.

Fig.3 shows a typical SEM micrograph of the SnO_2: F film deposited at (Sn) 16 ml & (F) 4 ml solution flow rate. The SEM microstructures reveal that all the films have a homogeneous surface morphology with nanocrystalline grains, also all the films are without any cracks and holes. Patterns indicate that films are polycrystalline in nature and pure tetragonal structure. The Grain size ranges from 50 nm-250 nm.

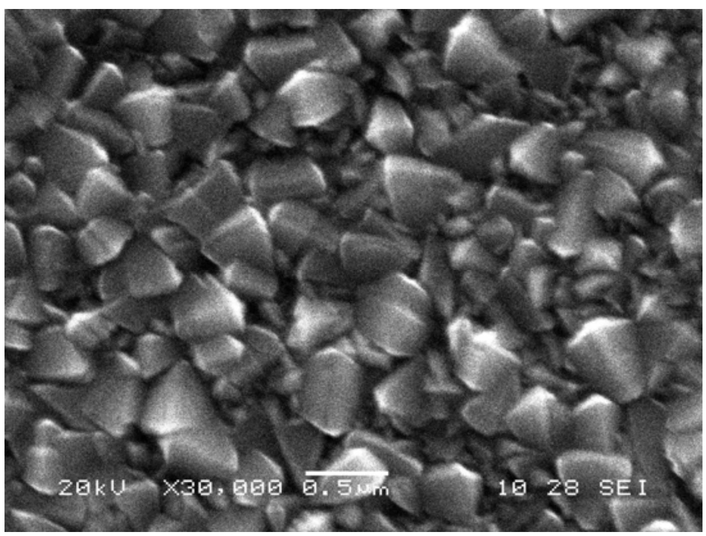


Fig.3. SEM micrograph of SnO: F thin films.

Optical properties

Fig.4 shows the variation of optical transmittance as a function of wavelength for the films prepared as SnO_2: F. the optical transmittance of the film deposited at low spray volume have high transmittance, those prepared at higher spray volume have low transmittance. It can be observed that in general an increase in the volume spray rate decreases the transmittance.

Analyzing the optical data with the expression for optical absorption coefficient 'α' and photon energy 'hυ' using the relation determined optical band gap 'Eg' Fig.5 shows the typical plot of $(\alpha h\upsilon)^2$ vs 'hυ' .Extrapolation of the linear portion of the plots to energy axis yielded the direct band gap values of 3.60 eV.

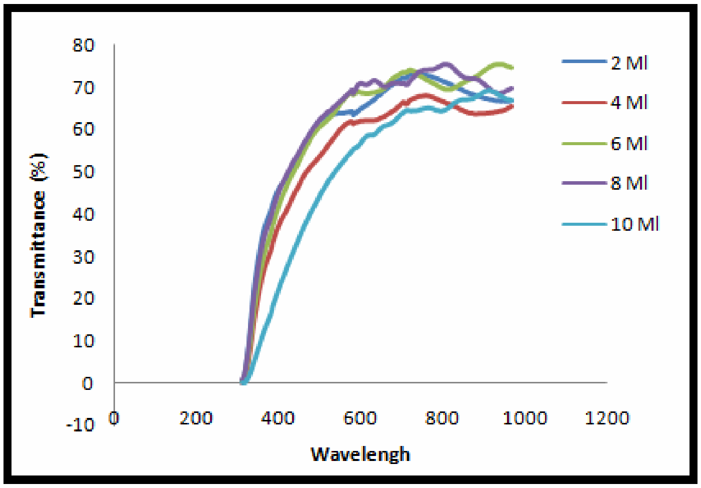


Fig. 4 Optical Transmittance of the SnO_2 thin films.

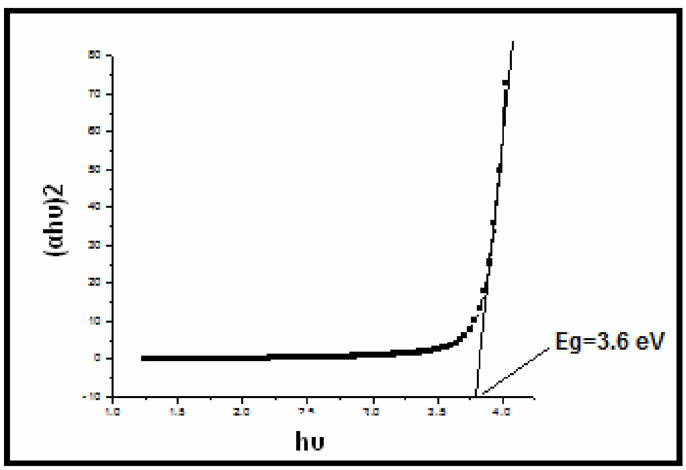


Fig.5 Typical plot of absorbance coefficient vs. Photon energy for SnO_2: F thin film.

Electrical properties

Fig .6 shows the typical plot of voltage vs current for SnO_2: F thin film at room temperature. From the analysis of the I-V curves, it is observed that resistivity decrease with increase of doping volume and after increases doping volume increase the resistivity. Values are 0.06 x 10^{-3}, 0.024 x 10^{-3}, 0.024 x 10^{-3} and 0.072x 10^{-3} Ω-cm for films deposited with doped Fluorine volume is 2ml, 4ml, 6ml and 8ml solution is respectively.

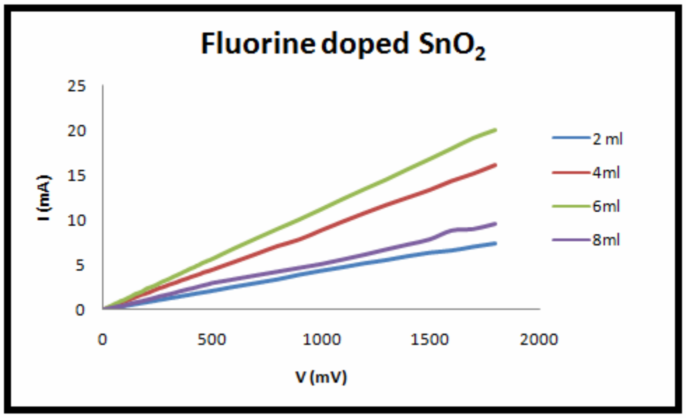


Fig. 6 I-V characteristics for SnO_2: F thin films.

Conclusions

Transparent conducting SnO_2: F thin films grown successfully by spray pyrolysis method. The structural investigation revealed that the films are crystalline in nature with (200) as a preferred orientation with a tetragonal crystal structure. As deposited films was uniform and strongly adherent to substrate. The average transmittance of the deposited thin films was about 75.6 % and optical band gap 3.60 eV. The resistivity decrease with increase of volume spray rate and films are found to be highly conducting and suggests it's used for the solar cell applications.

References:

[1] D. Miao, Q. Zhaoa, S. Wua, Z. Wange, X. Zihanga and X. Zhaoa, *J. Non-Cryst. Solids* 356,

[2] 2557 (2010)

[3] G. J. Exarhos and X. D. Zhou, *Thin Solid Films* 515, 7025 (2007)

[4] A. A. Yadav, E. U. Masumdar, A. V. Moholkar, M Neumann-Spallart, K. Y. Rajpure and C. H. Bhosale, *J. Alloys and Compounds* 448, 350 (2009)

[5] B. Thangaraju, *Thin Solid Films* 402, 71 (2002)

[6] A. Goetzberger and C. Hebling, *Sol. Energy Mater. Sol. Cells* 62, 1 (2000)

[7] G. Frank, E. Kaur and H. Kostlin, *Sol. Energy Mater.* 8, 387 (1983)

[8] S. Chen, *Thin Solid Films* 77, 127 (1981)

[9] W. Y. Chung, C. H. Shim, S. D. Choi and D. D. Lee, *Sens. Act.* B20, 139 (1994)

[10] J. R. Brown, P. W. Haycock, L. M .Smith, A. C. Jones and E. W. Williams, *Sens. Act.* B63,

[11] 109 (2000)

[12] P. Nelli, G. Faglia., G. Sberveglieri, E. Cerede, G. Gabetta, A. Dieguez and J. R. Morante, *Thin Solid Films* 371, 249 (2000)

[13] I. Stambolova, K. Konstantinov and T. Tsacheva, *Mater. Chem. Phys.* 63, 177 (2000)

[14] S. U. Lee, W. S. Choi and B. Hong, *Phys. Scr.* T129, 312 (2007)

[15] E. Elangovan, S. A. Shivashankar and K. Ramamurthi, *J. Crystal Growth* 276, 215 (2005)

[16] P. S. Patil, *Mater. Chem. Phys.* 59, 185 (1999)

[17] M. Ruske, G. Brauer and J. Szczrbowski, *Thin Solid Films* 351, 146 (1999)

[18] Q. Zhao, S. Wu and D. Miao, *Ad.Mater.Res.* 150–151, 1043 (2011)

[19] D. Belanger, J. P. Dotelet, B. A. Lombos and J. I. Dickson, *J. Electrochem. Soc.* 398, 1321 (1985)

[20] A. C. Arias, L. S. Roman, T. Kugler, R. Toniola, M. S. Meruvia and I. A. Hummelgen, *Thin Solid Films* 371, 201 (2000)

[21] P. S. Shewale, S. I. Patil and M. D. Uplane, *Semicond. Sci. Technol.* 25, 115008 (2010)

[22] O. K. Varghese and .L K. Malhotra, *J. Appl. Phys.* 87, 7457 (2000)

[23] M. K. Karanjai and D. D. Gupta, *J. Phys. D: Appl. Phys.* 21, 356 (1988)