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Low Sheet Resistance F-Doped SnO_2 Thin Films Deposited by Novel Spray Pyrolysis Technique

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Abstract: Transparent conductive glass (Fluorine-doped tin oxide (SnO_2: F or FTO)) thin films were deposited on glass substrates by pulsed spray pyrolysis (PSP) technique at substrate temperature of 500^{o}C and different fluorine concentrations. Tin metal dissolved in hydrochloric acid used as a precursor of tin and ammonium fluoride (NH_4F) as a fluorine precursor. X-ray diffraction (XRD) shows that the pure SnO_2 and fluoride doped films are polycrystalline with a tetragonal crystalline structure. The pure SnO_2 and fluoride doped films showed 60- 80% of transparency in the visible region depending on the F ratio. FTO deposited films have the lowest sheet resistance for spray technique that is 2 Ω /cm^2 and highest figure of merit of 4.7x10^{-3} cm. Ω^{-1} at 800 nm. The obtained results indicated that the structures, optical and electrical properties of the films were greatly affected by the fluorine (F) concentration ratio.
Keywords: F doped SnO_2; Thin films; Transparent Conductive Oxides (TCOs); Pulsed Spray Pyrolysis (PSP) technique.

Introduction

Transparent conducting oxides (TCOs) are the most important materials for application into the large scenario of renewable energy and energy savings technologies. The TCOs- oxides as well as non-oxides- can indeed play an important role for both energy generation and energy saving. A basic reason why TCOs are in the focal point of interesting, is that they can show highly transparency to the visible region and highly conductivity too[1].

Tin oxide (SnO_2) is one of the most metal oxides widely used for a commercial transparent conductive glass manufacturing because of its easy to prepare and fabricate, besides its properties as thermal and chemical stability. SnO_2 has the rutile crystal structure with a tetragonal unit cell (space group P42/mnm) and lattice parameters (a=b = 4.738 Å and c= 3.188 Å)**.** Tin oxide is an n-type semiconductor material with a wide band gap (E_g) 3.5 eV, with up to 95% optical transparency in the visible range and resistivity of 10^{-4} - 10^6 Ω cm. SnO_2 have a high conductivity that is due to the intrinsic defects, i.e. oxygen deficiencies. It was shown that the formation energy of oxygen vacancies and tin interstitials in SnO_2 is very low and thus these defects form readily, explaining the often observed high conductivity of pure, but nonstoichiometric, SnO_2. The conductivity is further increased by extrinsic dopants such as Antimoine (Sb) as a cation dopant and fluorine (F) as an anion dopant. The pure tin oxide is a highly resistance material that will be transformed into an electrical conductor due to the doping process besides it's highly transparency. So that tin oxide material is one of the most important materials in the transparent conductive oxides family[3-5]. Tin oxide (SnO_2) properties; let it be easy to use in a number of different applications such as electrode materials in solar cells, smart windows, gas sensor,

flat panel displays, light emitting diodes and other optoelectronic devices[6-9]. Tin oxide thin films can be prepared by different techniques such as sputtering, molecular beam Epitaxy, electro deposition, sol-gel, spray and pulsed spray pyrolysis…etc[10-15]. Since the spray pyrolysis technique is very simple with low cost, need no vacuum and allow a large area.

The main aim of this study is to produce transparent conductive oxides (TCOs) films using a simple and easy technique of preparation- pulsed spray pyrolysis (PSP). Study the effect of different fluorine concentrations on structural, optical and electrical properties of SnO_2 thin films.

Experimental Work

The precursor sprayed solution of pure tin oxide is prepared by dissolving tin metal powder (BDH limited Poole England) in suitable amount of hydrochloric acid (HCl) 37% (Polskie Odczynniki Chemiczn), isopropanol (99.9%) is added to have a solution of 0.2 M. Ammonium fluoride (NH_4F) is dissolved in water and then added to dissolved tin solution in molecular ratio of 10, 15, 20, and 25 at. %. Then the solution stirred for 30 min. to get a clear and homogeneous solution.

$$Sn\ (s) + 2\ HCl\ (aq) \rightarrow Sn(2+)\ (aq) + 2Cl\ (1-)\ (aq) + H_2\ (g) \uparrow$$

$$NH_4F\ (s) + H_2O \rightarrow NH_3\ (g) + HF\ (aq)$$

All solutions of undoped and fluorine doped tin oxide were sprayed by pulsed spray pyrolysis (PSP) technique [16] at substrate temperature of 500^{o}C with a fixed pulse frequency equals one pulse (On/ Off mode) per two seconds for total deposition time of 10 minutes onto glass substrates with a nozzle-substrate distance of 30 cm. The substrates were cleaned ultrasonically to improve the adhesion between the deposited films and substrate surface. All of the deposition parameters all over the experimental work were optimized. Since, the pulsed spray technique has the same advantageous of the conventional spray pyrolysis methods of low cost, no vacuum needed and large area mass production but it distinguished over these common spray systems by: carrier gas is depend and related to the automatic control of the hydraulic pressure (like in a cosmetics perfume atomizer), the droplet size is very fine in a form of mist or fog which makes the distribution of the deposited droplets are more homogenous and enhance the wettability factor between the different deposited layers and with substrate too. Besides, the pulse duration (On/ Off mode) keeps the substrate temperature constant during the whole deposition process and gives enough time for the deposited film to grow up relax on the surface of the substrate.

X-ray diffraction (XRD) using a Diano corroboration-USA equipment with *Cu* K_α radiation (λ= 1.514 Å) with a scanning speed of 1deg/min and angular range of 2θ= 20^o to 80^o. Film thickness was measured by 3D surface profilmeter Dektak 150. Film surface topography was carried out using the Atomic Force Microscopy (AFM) (Coated Sharpened Microlever – Model MSCT-AUNM). Optical properties of the prepared films were measured using the UV- VIS- NIR spectrophotometer (JASCO- 670) within the wavelengths range from 200 nm to 2500 nm. All electrical properties of the prepared films were measured by Hall Effect measurement Lake Shore model -7700A in Van der Pauw configuration at room temperature.

Results and Discussion

Structure

The XRD patterns for the pure SnO_2 and F- doped sample with different Fluorine concentrations (10, 15, 20 & 25 at. %) prepared at constant substrate temperature 500^{o}C and spray time of 10 min. are shown in Fig.1. The XRD patterns show a polycrystalline single phase of tetragonal structure tin oxide which is corresponds with the JCPDS- card. The pure SnO_2 thin films have a preferred orientation along (200) peak. The low intensity of (101) & (211) peaks in XRD- spectra of pure SnO_2 prove the presence of oxygen vacancies[17,18]. This observation means that the investigated pure sample is nonstiochiometric tin oxide with predominant (Sn) interstitial atoms accompanied with oxygen vacancies.

The preferred orientation becomes (110) instead of (200) with Fluorine dopant samples. SnO_2 doped 20% F shows the most highly intensive peaks of (110) and (200) and this could be considered as a good

evidence for the nearly complete substitution of fluorine atoms in oxygen vacancies and bonded oxygen and some of fluorine atoms are in interstitial position.

With increasing the fluorine concentration up to 20%, the peak intensity of (110) peak decreases. This decreasing is relating to the destroying of the equilibrium of SnO_2 lattice which will be retained by generation of oxygen vacancies. Since at high concentration of fluorine, atoms start to occupy the interstitial points instead of oxygen vacancies and this leads to the coulomb forces bind the lattice together tends to reduce and more oxygen vacancies becomes free from fluorine atoms[19].

The mean crystallite size *D* was calculated using the Williamson-Hall equation:

$$\beta_{hkl} \cdot \cos(\theta_{hkl}) = \eta \sin(\theta_{hkl}) + \frac{K.\lambda}{D}$$

Where *D* is the crystallite size, *k* is a constant ~ 0.94, λ is the X-ray wavelength, θ is the Bragg's angle, β_{hkl} is the instrumental broadening and η is the slope of β_{hkl} Cosθ and Sinθ[20].

From the width of the (200) peak the average crystallite size is $D_{200} \approx 40.9$ nm for the pure SnO_2 and the average crystallite size is $D_{110} \approx 40.7$ nm from the width of (110) peak for F-doped SnO_2. Fig.2 shows the effect of the fluorine concentration on the crystallite size which decreases with increasing the fluorine concentration. This reflects that the fluorine atoms start to replace all of the oxygen vacancies and bonded oxygen and occupy most of the interstitial position at high concentration. The film thickness measured with the 3D profilometer for the pure sample is 124 nm and 156 nm for the 20% doped fluorine one.

Atomic force microscopy (AFM) image for the SnO_2 20% F- doped is shown in Fig. 3. AFM-image represents that an average crystallite size is 29 nm and surface roughness is 16 nm which is compatible with XRD- calculated values. The different between the average crystallite size that calculated from XRD and that obtained from AFM is due to the basic point that the XRD is sensitive to the crystallite thickness while the AFM show the surface topography of the film. Therefore, the size of the grains at the inner regions is smaller than that at the film surface.

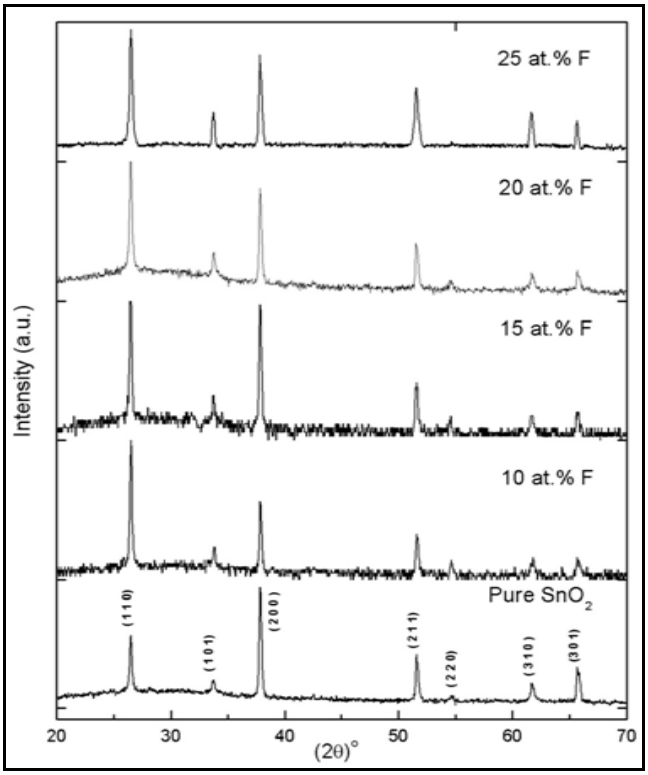

Fig. 1 x-ray diffraction (XRD) patterns of pure and doped SnO_2 with different concentrations of fluorine (a): pure, (b):10%, (c): 15%, (d): 20% and (e): 25%.

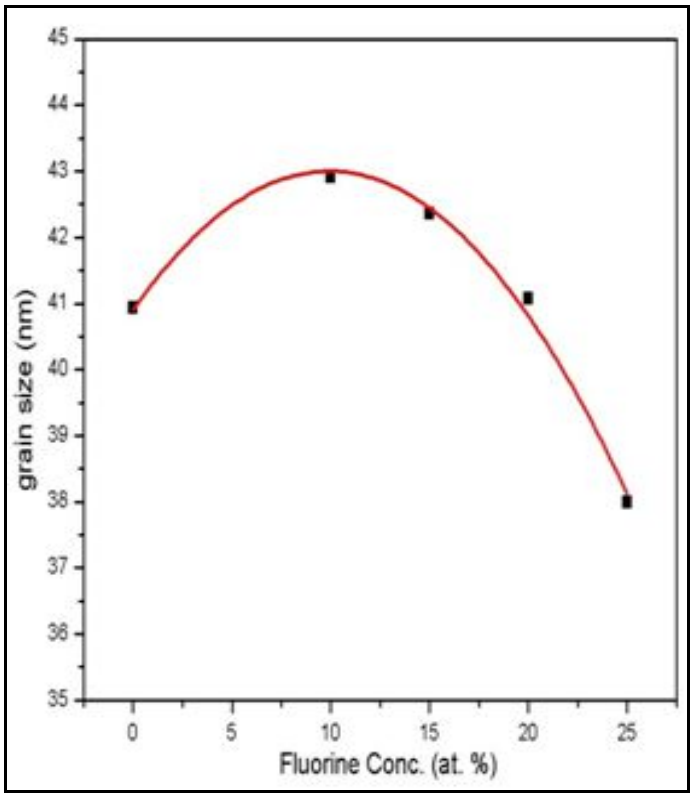

Fig. 2 the effect of fluorine concentration on the crystallite size.

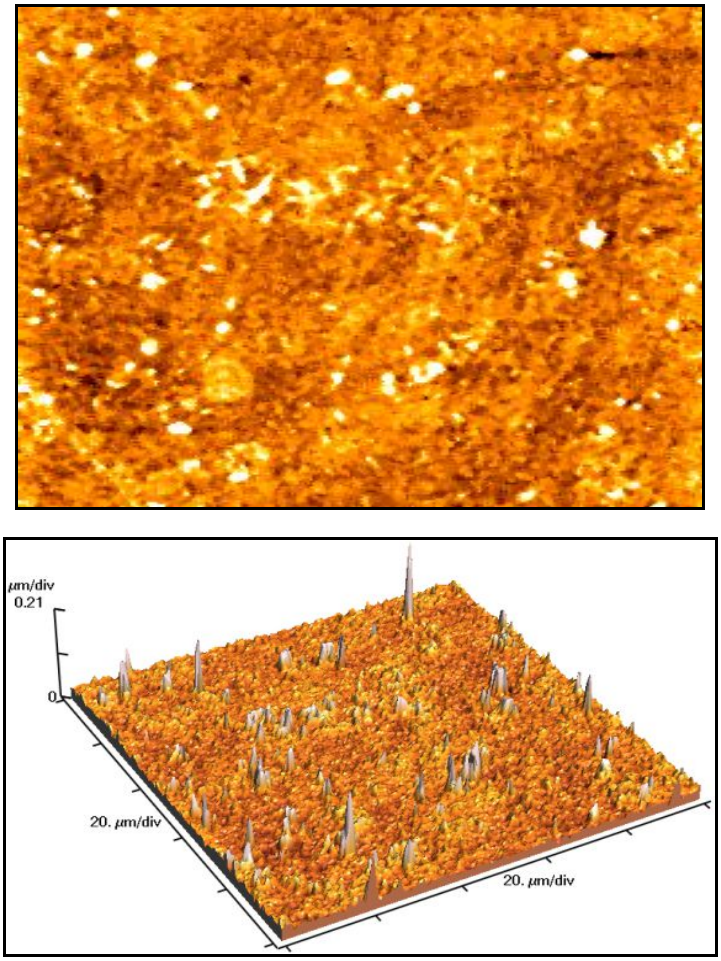

Fig. 3 Atomic force microscopy (AFM) images for SnO_2 20% F-doped.

Optical properties

Optical transmission and reflection for the pure SnO_2 and 20% F-doped thin films were measured in a wavelength ranged from 0.3 to 2.5 μm are show in Fig. 4. It was observed that the pure SnO_2 has a highest transmission of ~ 80% which decreases with increasing the fluorine concentration to ~ 60% in visible region. This significant reduction could be related to the optical scattering by surface morphology and grain boundaries of the prepared TCO films. The optical reflection of pure SnO_2 slightly increases in near infrared region (NIR) while the optical reflection of 20% F: SnO_2 thin film is increase in NIR region and intersected with the transmission at wavelength 1.73 μm. This intersection is due to the increase in the charge carrier concentration (n) up to 10^{21} cm^{-3} in the doped SnO_2 thin films as measured by Hall Effect which confirmed by the reasonable decrease in the film sheet resistance. The optical transmittance is high except at the very highest magnitude of n, where plasma effects tend to NIR region. The absorption coefficient (α) is determined from the transmittance measurements using this formula of $T = \exp(-\alpha d)$, where d is the film thickness and T is the transmittance. The calculated α value is ranging from ≈ 1 to 4.02×10^4 cm^{-1} at wavelength 500 nm. Data such as this in Fig.4 makes it possible to optimize FTO films for different applications.

Many literatures reported that SnO_2 has a direct band gap[21]. For a direct transition, the absorption coefficient (α) value as a function of photon energy of the transition from valence band to conduction band can be calculated by following equation[22]:

$$(\alpha h \upsilon)^2 = A(h \upsilon - E_g)$$

Where, A is constant, hν is the energy of the incident light and E_g is the SnO_2: F film energy gap. Fig. 5 shows that the band gap E_g is determined by extrapolating the linear portion of $(\alpha h\nu)^2$ vs. hν plot to hν axis and shows 3.75 eV for pure and 3.54 eV for 20 at.% F thin films, which reflects the effect of the fluorine doping on SnO_2 band gap.

Electrical properties

Fig. 6 (a & b) shows the change of sheet resistance, resistivity, carrier concentration and Hall-mobility of the SnO_2: F thin films deposition temperature of 500 °C, spraying time of 10 min. Fig. 6a shows that the sheet resistance decreases with the increasing Fluorine concentration initially reaching the minimum and increases beyond this particular concentration. When fluorine concentration is 20%, the sheet resistance (R_s) reached the minimum value of 2 Ω /cm^2 with a highly carrier concentration of 7.2 x 10^{21} cm^{-3} and at the point of fluorine concentration is 25%, R_s start to increase to the high value of 5 Ω /cm^2 with low amount of carrier concentration. Fig. 6b shows also that SnO_2:20% F ˉ doped sample has the highest Hall-mobility value μ = 39 cm^2/ V.s with lowest resistivity ρ = 2.19 x 10^{-5} Ω. cm. with this small sheet resistance for SnO_2:20% F – doped samples one can sees in Fig. 7 that the sample of shows the highest figure of merit (Φ) with value of 4.7x10^{-3} cm. Ω^{-1} of all the prepared samples at wavelength 800nm.

These sheet resistance values agree with the reported films deposited by $SnCl_2.2H_2O$ or $SnCl_4.5H_2O$ starting solution[23,24]. Thangaraju has reported[25] that sheet resistance decreases with the Fluorine concentration initially reaching the minimum and increases beyond this particular concentration. In the fluorine doped tin oxide films, the F anion substitutes for O^{2-} anion in the lattice, creates more free electrons and decreases the value of sheet resistance. The minimum value is obtained at fluorine concentration is 20%. Increasing the value of sheet resistance after a specific level of F content probably represents doping limit of F in the tin oxide lattice.

The excess F atoms do not occupy the proper lattice positions to contribute to the free carrier concentration and at the same time the increasing disorder leads to the increase of the sheet resistance[25]. This excess doping is not able produce more free electrons and the films have greatly increased the scattering centers, so that the degree of free electron scattering is enhanced, resulting in SnO_2: F thin film resistance at room temperature to gradually increase. Table 1 concludes our experimental work for the pure and F-doped thin films as follows:

Our sheet resistance is the lowest value obtained by spray pyrolysis technique till now.

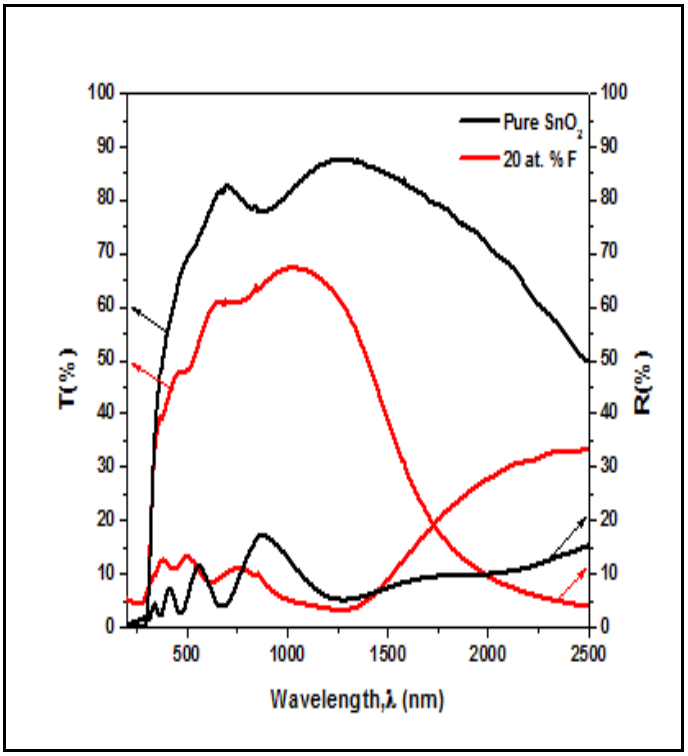

Fig. 4 optical transmittance & reflectance spectra of pure and 20at. % F-doped SnO_2 thin films

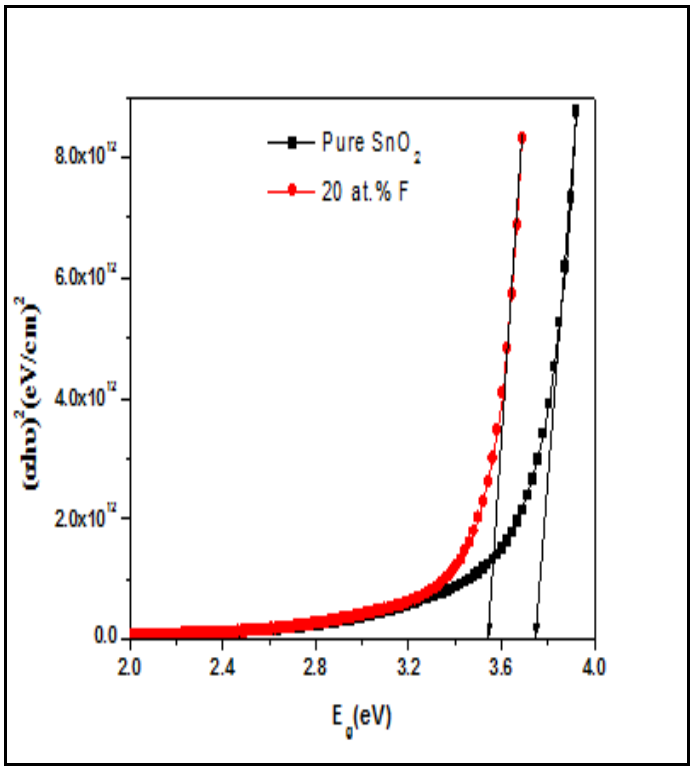

Fig. 5 change of band gap position for SnO_2 thin films doped with 20at. % F.

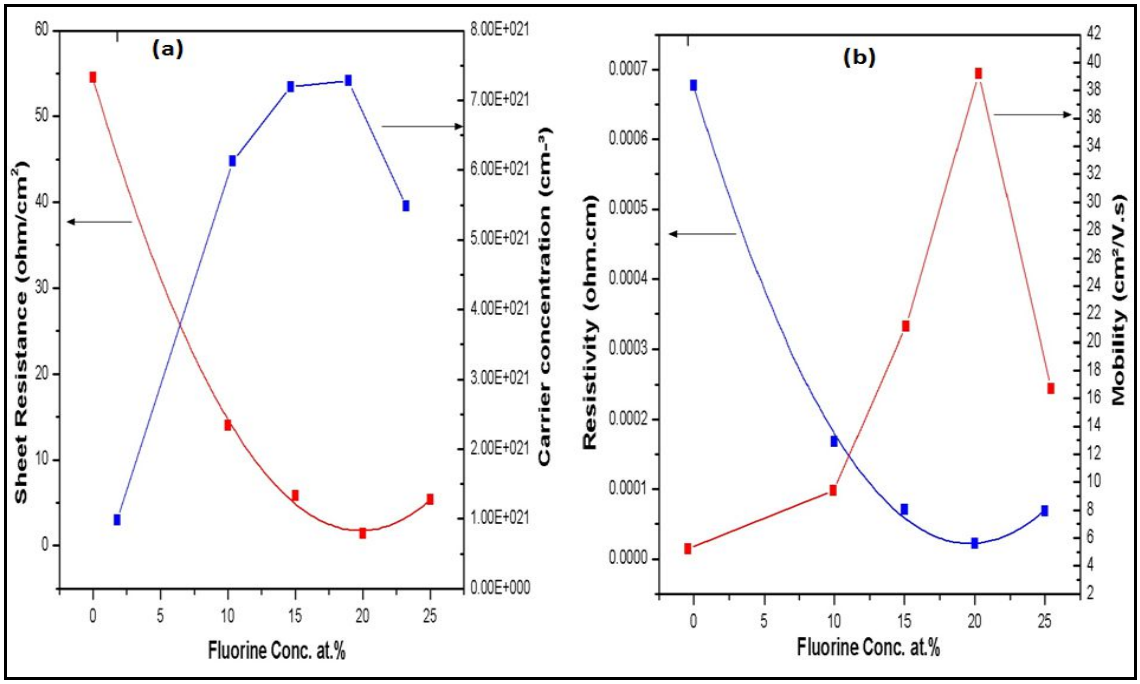

Fig. 6 sheet resistance, carrier concentration, resistivity and Hall-mobility of sprayed SnO_2: F versus the Fluorine concentration.

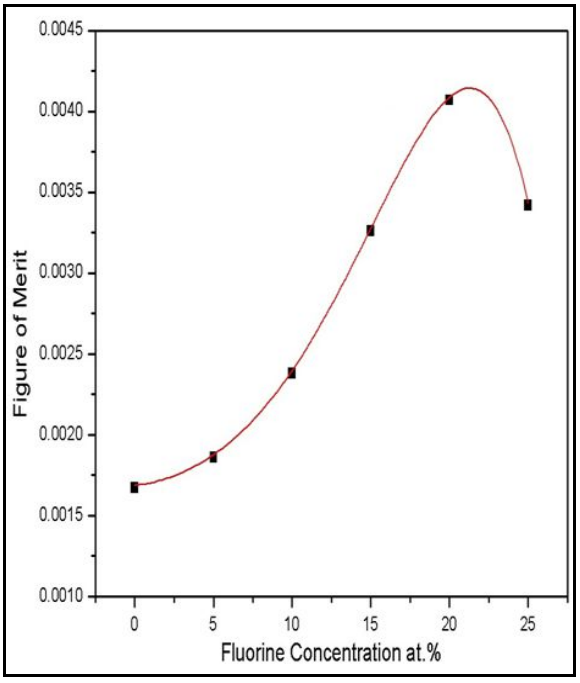

Fig. 7 figure of merit for pure and F-doped samples at different concentrations

Table. 1 variation of sheet resistance, carrier concentration, resistivity, Hall-mobility and film thickness of sprayed SnO_2: F

F (%)	Resistivity (Ω. cm)	Carrier Concentration (cm^{-3})	Mobility ($cm^2/V.s$)	Sheet Resistance (Ω. Cm^{-2}) (Previous work)	Sheet Resistance (our work) (Ω. Cm^{-2})	Film Thickness (nm)
0	**6.77E-04**	**9.81E+20**	**9.42E+00**	21 Ω/cm^2 (6wt%)[26]	**5.45E+01**	**124.22**
10	**1.68E-04**	**7.13E+21**	**5.20E+00**	9.03 Ω/cm^2()[27]	**1.40E+01**	**120.43**
15	**7.07E-05**	**7.19E+21**	**2.11E+01**	(42·59 Ω sq^{-1})(40at%)[28]	**5.80E+00**	**121.89**
20	**2.19E-05**	**7.28E+21**	**3.92E+01**	3.71 Ω.cm^{-1}()[29]	**1.40E+00**	**156.42**
25	**6.83E-05**	**5.48E+21**	**1.67E+01**	-	**5.35E+00**	**127.66**

3. Conclusion

In this work, thin films of tin oxide with different fluorine concentration were prepared on glass substrates at 500 °C by pulsed spray pyrolysis (PSP) technique. The physical properties of pure and doped SnO_2 thin films were characterized by different methods. The film with 20% F shows the best crystalline structure and has the high mobility, highest carrier concentration and lowest sheet resistance, highest figure of merit and optical transparence ~ 60%. This means that 20% Fluorine is the best concentration to improve the conductivity and optical transparence of sprayed SnO_2 thin film. Thus, fluorine doped tin oxide (FTO) or commonly transparent conductive oxide (TCO) as known could be promised for renewable energy and energy savings applications and also for meta-material applications and helping to unravel the interesting physical phenomena in a new generation of meta-material and transformation-optics devices.

References

1. K. L. Chopra, S. Major and D. K. Pandya, "Transparent conductors—A status review", Thin Solid Films. 102, 1 (1983).
2. S. Ahmed, H. H. Afify and H. A. Zayed, "Nanostructure Transparent Conducting Oxide Thin Film", (Lambert Academic Publishing (LAP) – Germane (2011)), pp.25-30.
3. J.F. Wagner, Transparent Electronics, Science, 300, 1245-1246 (2003).
4. R.E. Presley, C.L. Munsee, C.-H. Park, D. Hong, J.F. Wager, D.A. Keszler, "Transparent Tin Oxide Thin-Film Transistors," J. Phys. D37, 2810 (2004).
5. M. Batzill, U. Diebold, "The surface and materials science of tin oxide", Progress in Surface Science, 79, 47 (2005).
6. R.L. Hoffman, B.J. Norris, J.F. Wagner, "ZnO-based transparent thin-film transistors", Appl. Phys. Lett. 82, 733 (2003) .
7. S. Masuda, K. Kitamura, Y. Okumura, S. Miyatake, H. Tabata, T. Kawai, "Transparent thin film transistors using ZnO as an active channel layer and their electrical properties", J. Appl. Phys. 93, 1624 (2003) .
8. C.G. Granqvist, A. Hultåker, "Transparent and conducting ITO films: new developments and applications, Transparent, Thin Solid Films, 411, 1 (2002**).**
9. M. Boshta, F. A. Mahmoud, M. H. Sayed, "Characterization of sprayed SnO_2: Pd thin films for gas sensing applications", Journal of Ovonic Research,6, 93 (2010) .
10. S.H. Hahn, N. Barsan, U. Weimar, "Investigation of CO/CH_4 mixture measured with differently doped SnO_2 sensors", Sensors Actuators, B78, 64 (2001).
11. C. Cobianu, C. Savaniu, P. Ciciliano, S. Caponoe, M. Utrianien, L. Niinisto, "SnO_2 sol gel derived thin films for integrated gas sensors, Sens. Actuators B77, 496-502 (2001).

12. S. Harbeck, A. Szatvanyi, N. Barsan, U. Weimar, V. Hoffmann, "DRIFT studies of thick film un-doped and Pd-doped SnO_2sensors: temperature changes effect and CO detection mechanism in the presence of water vapour", Thin Solid Films, 436, 76-83 (2003).
13. J. Liu, X. Huang, G. Ye, W. Liu, Z. Jiao, W. Chao, Z. Zhou, Z. Yu, "H_2S Detection Sensing Characteristic of CuO/SnO_2", Sensors 3, 110- 118 (2003).
14. G. Gordillo, L.C. Moreno, W. de la Cruz, P. Teheran, "Preparation and characterization of SnO_2 thin films deposited by spray pyrolysis from SnCl2 and SnCl4 precursors", Thin Solid Films, 252, 61- 66 (1994).
15. S.H. Hahn, N. Barsan, U. Weimar, S.G. Ejakov, J.H. Vissar, R.E. Soltis, "CO sensing with. SnO_2 thick film sensors: role of oxygen and water vapour", Thin Solid Films,436,17(2003).
16. K. Ravichandran, B. Sakthivel, P. Philominathan, "Nanocrystalline transparent SnO_2- ZnO films fabricated at lower substrate temperature using a low-cost and simplified spray technique", Cryst. Res. Technol., 45, 292- 298 (2010).
17. C.Agashe, S. S. Major, "Effect of heavy doping in SnO_2:F films", Journal of Materials Science, 31, 2965- 2969 (1996).
18. C. D. Canestraro, M. M. Oliveira, R. Valaski, M. VS. da Silva, D. GF. David, I. Pepe, A. F. da Silva, L. S. Roman, C. Persso, "Strong inter-conduction-band absorption in heavily fluorine doped tin oxide", Applied Surface Science, 255(5), 1874-1879 (2008).
19. M. Fantini, I. Torriani, "The compositional and structural properties of sprayed SnO_2:F thin films", Thin Solid Films, 138, 255 (1986).
20. G.K.Williamson and W.H.Hall, "X-ray Line Broadening from Filed Aluminium and Wolfram," Acta Metall. 1, 22-31 (1951).
21. Leite E.R., Bernardi M.I.B., Longo E., Varela J.A. and Paskocimas C.A., "Enhanced electrical property of nanostructured Sb-doped SnO_2 thin film processed by soft chemical method", Thin Solid Films, Vol. 449, pp. 67-72 (2004).
22. Uplane, M.D., Kshirsagar, P.N., Lokhande, B.J., Bhosale, "Characteristic analysis of spray deposited Cadmium oxide thin films", C.H., Mater.Chem. Phys. 64, 75-78 (2000).
23. L. Chinnappa. K. Ravichandran. K. Saravanakumar. G. Muruganantham B. Sakthivel, "The combined effects of molar concentration of the precursor solution and fluorine doping on the structural and electrical properties of tin oxide films", J Mater Sci: Mater Electron 22, 1827-1834 (2011).
24. Yang Ren, Gaoyang Zhao, Yuanqing Chen," Fabrication of textured SnO_2:F thin films by spray pyrolysis", Applied Surface Science 258, 914- 918 (2011).
25. B. Thangaraju, "Structural and electrical studies on highly conducting spray deposited fluorine and antimony doped SnO2 thin films from $SnCl_2$ precursor", Thin Solid Films, 402, 71-78 (2002)
26. Benhaoua, A. Rahal, A., Benhaoua, B., Jalaci, M.," Effect of fluorine doping on the structural, optical and electrical properties of SnO_2 thin films prepared by spray ultrasonic", Superlattices and Microstructures 70, 6169(2014).
27. Tatar D., Turgut G., Düzgün B.," Effect of substrate temperature on the crystal growth orientation and some physical properties of SnO_2: F thin films deposited by spray pyrolysis technique", Romanian Reports of Physics 58,(1-2),143(2013).
28. Chinnappa L., Ravichandran K. , Saravanakumar K., Jabenabegum N., Sakthivel B., "Analysis of critical doping level of sprayed SnO_2 :F films", Surface Engineering 27 (10), 770-774 (2011).
29. Moholkar A.V., Pawar S.M., Rajpure K.Y., Almari S.N., Patil P.S., Bhosale C.H.," Solvent-dependent growth of sprayed FTO thin films with mat-like morphology", Solar Energy Materials and Solar Cells 92 (11),1439-1444(2008).

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