Effect of Fluorine Concentration on Structural, Electrical and Optical Properties of SnO_2:F Thin Films Orepared by Spray Pyrolysis Technique

Mushtak Abdulmohsin Jabber **Muhsin Attia Kudhier**
Al-Mustansiriyah University, College of Education, Department of Physics, Baghdad, Iraq

Abstract

Fluorine doped tin oxide, SnO_2: F (FTO) thin films deposited on glass substrates at 405±2˚C have been prepared using Spray Pyrolysis Technique. Structural, electrical and optical properties of FTO thin films under different doping concentration (5, 15, 20, 25 and 30) wt% are investigated using XRD patterns, Hall effect measurement and UV–Vis spectrophotometry. X-ray diffraction studies of FTO films indicate that all films are polycrystalline with tetragonal structure. The lattice constants *a* and *c* vary from (4.7269 to 4.7557)Å and (3.2548 to3.2103) Å respectively. While the crystallite size D varies from 8.07 to 7.85 nm. Electrical measurements showed that all the films are of n-type conductivity. Carriers mobility (μ), concentration of carrier (n) and resistivity (ρ) reached 6.05 cm^2/Vs, $5.62x10^{19}cm^{-3}$ and $8.79x10^{-2}$ Ω cm, respectively. The energy gap decrease from 3.9 to 3.78 eV with increase fluorine concentration from (5-30) wt% respectively. FTO films can be used as conducting layers(Electrodes) in photovoltaic devices.

***Keywords*:** SnO_2:F; spray pyrolysis; thin films

Introduction

Transparent conducting oxide (TCO) thin films such as tin oxide, indium tin oxide zinc oxide, indium oxide, and cadmium oxide have attracted significant attention because of their low electrical resistivity and high transmittance [1]. Because of these properties, the transparent conductive oxides materials have been used in a large number of applications in science and technology, including solar cells [2], heat reflecting mirrors [3], antireflection coatings [4] and a group of electro-optical devices such as flat panel display devices [5,6].Currently, Sn doped In_2O_3 (ITO) is the majority of used electrodes because of its excellent properties such as high optical transmittance (80-90%T) and low resistivity (~ 10^{-4} Ω cm) [7]. However, the abundant use of ITO as TCO thin films has numerous disadvantages such as scarcity, extremely toxic, and expensive source of indium itself. Many efforts to improve alternative electrode materials are in progress [8]. SnO_2:F(FTO) is a conceivable alternative to ITO due to FTO is low-cost as well as chemically and thermally stable . Fluorine doped tin oxide was described to behave as n-type semiconductor with wide band gap within (3.0 - 3.6) eV [9]. The fluorine doping to the SnO_2, can encourage more numbers of charge carriers and therefore improved the electrical conductivity [10]. SnO_2 thin films are manufactured by different techniques such as thermal evaporation, spray pyrolysis, sputtering, hydrothermal and sol-gel [11-18]. Among these, spray pyrolysis is well suitable for the preparation of doped tin oxide thin films due to its simple and low-cost experimental procedure, simplicity of adding various doping materials, high growth rate and mass production capability for homogenously large area coatings [1, 19].

Experimental

The FTO films were grown on the Macroscopic glass slides (2.5 × 2.5 cm^2) substrates by spray pyrolysis method. Films of ~ 400 nm thickness were grown. 0.1M of an aqueous solution of high purity tin chloride ($SnCl_4 \cdot 5H_2O$) was used as starting solution. Small quantity (few drops) of hydrochloric acid (HCl) was added to avoid hydrolysis. To prepare fluorine doping, ammonium fluoride (NH_4F) (99% purity, BHD) was dissolved in deionized water and added to the starting

solution. The doping concentrations were varied from (5 , 10, 15, 20 , 25 , 30) wt%. The carrier gas flow rate was maintained at a pressure of 10^5 N/m^2. The distance between the spray nozzle and the substrate is 30 cm. The spray time is 10 s and the spray interval at ~3 min. The substrate temperature was maintained at (405 ± 2 ^{o}C). The spray process is not continuous to keep constant temperature of substrates. The structural characterization of the films is carried out by X-ray diffraction (XRD) measurements using (SHIMADZU diffractometer system (XRD - 6000)) with CuKα radiation (λ=1.54060 Å), at 40KV, 30 mA. The thicknesses of the films are measured by using a gravimetric method. The optical measurements of the SnO_2: F thin films are calculated from the transmittance spectrum over the range (300 – 900 nm) using UV-VIS spectrophotometer (SHIMADZU) (UV-1600/1700 series). The electrical measurements of SnO_2:F films are carried out by Hall effect measurement (HMS3000, Ecopia).

3. Results and Discussion

3.1 Structural Properties

XRD patterns for SnO_2:F thin films deposited on glass substrate at a temperature equal to (405±2^{o}C) by the spray pyrolysis method as a function of fluorine doped concentrations are shown in figure (1) in the (2θ) range of (20 – 60°). All films are polycrystalline, tetragonal structure with preferred orientation along (110) plane. Other orientations like (101), (200) and (211) are also observed, with relatively lower intensities. The presence of other phases such as (tin oxide, Sn and tin fluoride) are not observed, indicating the (O) atoms were replaced by (F) atoms in the (SnO2: F) films [20]. In addition, there is no significant shift in the peak positions of all the prepared thin films, which perhaps means that fluorine dopant did not occur any considerable stress in the films. It is therefore concluded that the fluorine (F) does not impact the structural characteristics of the films, In spite of the increase in the intensities of the main peaks with increasing concentrations of fluorine. The observed d-values, lattice constants *a* and *c* and the size of the crystallite are presented in table (1) and compare with the standard values of JCPDS – PDF data (No. 41 – 1445) for SnO2 powder specimen. [21].

Table 1. the miller indices (*hkl*), lattice constants *a* and *c* and crystallite size (*D*) of FTO thin films.

concentration	(hkl)	d(A°)(JCPDS)	d(A°)observe	*a* (A°)	*c* (A°)	D (nm)
5%	110	3.347	3.34246	4.7269	3.2548	8.07
	101	2.6427	2.68078			
	200	2.369	2.40812			
	211	1.7641	2.40812			
15%	110	3.347	3.35918	4.7505	3.1778	6.5
	101	2.6427	2.64136			
	200	2.369	2.37467			
	211	1.7641	1.76759			
20%	110	3.347	3.34966	4.7371	3.1898	6.13
	101	2.6427	2.64588			
	200	2.369	2.37291			
	211	1.7641	1.76422			
25%	110	3.347	3.35378	4.7429	3.1980	6.82
	101	2.6427	2.65157			
	200	2.369	2.37291			
	211	1.7641	1.76978			
30%	110	3.347	3.3628	4.7557	3.2103	7.85
	101	2.6427	2.66081			
	200	2.369	2.3753			
	211	1.7641	1.76699			
Standard JCPDS Card No: 41–1445; *a* = 4.738, *c* = 3.187						

The size of the crystallite *D* of SnO2:F films deposited with different fluorine concentrations were estimated by using Scherrer's formula [22]: $D = 0.9\lambda/(\beta \cos \theta)$, where β is the full width at half maximum (FWHM) of the peak , θ is Bragg's angle (in degree) and λ is the wavelength of X-rays (λ = 1.5418 Å). The crystallite size changes very slowly, At first decrease from 8.07nm at 5 wt% to 6.13nm at 20 wt%, then increase up to 20 wt%, then rapidly increase to 6.82nm with increase fluorine concentration to 25 wt%. This shows that D values of the film depend on the concentration of the dopant. The obtained results are in good agreement with the reference [23]. The crystallite size values for different fluorine levels are shown in Figure (2) . The lattice constant (*a*) and (*c*) for the films of different fluorine concentrations are calculated using the relation: $(1/d^2) = \{[(h^2 + k^2)/a^2] + (l^2/c^2)\}$, where d is the interplaner distance and (h k l) are Miller indices, respectively. Table (1) gives the values of the lattice constants *a* and *c*. It was found that the lattice parameters differ from (4.7269 to 4.7557) Å and (3.2548 to 3.2103) Å respectively. The

change in lattice constant refers , that the film grains are strained, Which is probably Because of the change in the nature and concentration of the original imperfections [24].Figures (3) and (4) show the lattice constants change with the change of the concentration of fluorine.

Table 2. Electrical parameters (resistivity (ρ), mobility (μ),carrier concentration(n)) of FTO thin films with different doping concentrations.

Concentration %	Carrier concentration (n) x 10^{19} cm^{-3}	Resistivity (ρ) X 10^{-2} Ω cm	Mobility (μ) cm^2/Vs	Conductivity (σ) $\Omega^{-1}cm^{-1}$
5	1.24	186	0.26	0.53
15	2.66	8.97	2.61	11.1
20	0.95	10.9	6.05	9.18
25	1.28	29.1	1.66	3.42
30	5.62	59.7	1.85	16.75

3.2 Electrical properties

The electrical properties were performed by using Hall measurements. Negative sign of the Hall coefficient indicate that all the films prepared with n-type conductivity. Mobility, electrical resistivity and carriers concentration vary with fluorine concentration to the SnO2: F films are shown in table (2) and figure (5). From both figure and table, It can be seen that resistivity decreases at the beginning heavily with increase the concentration of fluorine from 5% to 15%, but as we kept on increasing the fluorine concentration, the resistivity increases with increase doping concentration, this can be attributed to the fact that at high concentrations, the fluorine atoms incorporated in the interstitial sites and crystal structure films, leading to the film begins to deteriorate, therefore the free mobility of electrons decreases and increases resistivity [25]. In regards to the carriers mobility is increasing with increasing fluorine concentration until 20 wt % of fluorine doping , then decreases for higher doping concentrations. On the other hand, the carriers concentration is increasing with increase in fluorine doping at the beginning and reaches a maximum value at 15 wt % , but then decreases with further increase in the fluorine doping till 25wt.% , then return to the increase with increasing doping concentration. The primary increase in carrier

concentration (n) indicates that the fluorine dopant substitutes oxygen atoms [26]. This replacement determined by the size of the ion and charge of the dopant. In this work, fluorine shows to be most favored replaced due to many reasons of which: the ionic size for F^- (0.133 nm) so close with that of O_2^- (0.132 nm) and the energy bond of the Sn-F (~26.75 D˚/kJ mol^{-1}) comparable to that of the Sn-O (~31.05 D˚/kJ mol^{-1})[27].

3.3 Optical properties

Figure (6) shows variation of the transmittance spectra of FTO thin films as a function of wavelength with different doping concentration. It was noted that the transmittance for all films increases with increasing fluorine concentration along the visible range. It has been found that the highest transmittance obtained (85.645%) was at 30 wt.% of fluorine doping concentration at a wavelength (630 nm).The good transmittance value of the SnO2:F film may be attributed to the decline in the intrinsic defects, like oxygen interstitials[28]. The energy gap of FTO films were calculated using the formula [29]: $\alpha h\upsilon = A(h\upsilon - Eg)^n$: where A constant, α : absorption coefficient, hν: the photon energy , Eg : energy gap and n constant. Take value n = ½ for direct allowed transition. Figure (7) shows plots of $(\alpha h\upsilon)^2$ versus photo energy (hν), Extrapolation of the curve to hν = 0 gave the direct band gap of SnO2:F films in the range 3.9 eV – 3.78 eV, and was found to slightly decrease for increase fluorine concentration. This result can be attributed to the small grain size effect of the films [30].

4. Conclusions

In the this work, SnO2:F thin films were deposited using the pyrolysis technique at various fluorine concentrations deposited onto glass substrates. XRD diffraction studies indicate that all thin films are polycrystalline with tetragonal structure. Hall measurements exhibited that the conductivity of all films is of n-type conductivity. The resistivity for the FTO films significantly decreases at first and then begin to increase with the increase doping concentration. The doping of SnO2 films with fluorine leads to decreases in energy gap. While increases in transmittance in the visible wavelengths, the higher transmittance of the doping films found to be 85.6%.

References

[1] E. Elangovan, K. Ramamurthi," A study on low cost-high conducting fluorine and antimony-doped tin oxide thin films" Appl. Surf. Sci.,249 (2005)183.

[2] C. S. Ferekides, R. Mamazza, U. Balasubramanian, and D. L. Morel," $Cd_{1-X}Zn_XTe$ thin films and junctions",Thin Solid Films, 480-481, (2005) 471.

[3] K. L. Chopra, S.R. Dass, "Thin film solar cells", Plenun Press, New York,1983.

[4] H. L. Hartnagel, A. L. Dawar, A. K. Jain, and C. Jagadish,"Semi-conducting transparent thin films", Institute of Physics, Philadelfia, 1995.

[5] J. E. Costellamo,"Hadbook of display Technology", Academic Press, New York,1992.

[6] S. Ishibashi, Y. Higuchi, Y. Ota, and K. Nakamuva,"Low resistivity indium–tin oxide transparent conductive films. I. Effect of introducing H_2O gas or H_2 gas during direct current magnetron sputtering"J.Vac. Sci.Technol.A, 8(1990)1399.

[7] Li, D., Haneda, H., Hishita, S., Ohashi, N. & Labhsetwar, N.K.," Fluorine-doped TiO_2 powders prepared by spray pyrolysis and their improved photocatalytic activity for decomposition of gas-phase acetaldehyde",Journal of Fluorine Chemistry ,126 (2005) 67-77.

[8] Kim, H., Kushto, G.P., Auyeung, R.C.Y., & Pique, A.," Optimization Of F-doped SnO_2 electrodes for organic photovoltaic devices"Appl. Phys. A 93(2008)521-526.

[9] Han, C.H., Han, S.D., Gwak, J. & Khatkar, S.P. ," Synthesis of Indium tin oxide (ITO) and fluorine-doped tin oxide (FTO) nano-powder by sol–gel combustion hybrid method",Materials Letters, 62 (2007)1701-1703.

[10] Russo, B. & Cao, G.Z.," Fabrication and characterization of Fluorine-doped thin oxide thin films and Nano rod arrays via spray Pyrolysis",Applied Physics A, 90(2008)311-315.

[11] D.R. Acosta, E.P. Zironi, E. Montoya, W. Estrada,"About the Structural, optical and electrical properties of SnO_2films produced By spray pyrolysis from solutions with low and high contents of Fluorine",Thin Solid Films 288 (1996) 1.

[12] T. Schuler, M.A. Aegerter," Optical, electrical and structural properties of sol gel ZnO:Al coatings",Thin Solid Films 351 (1999) 125.

[13] K. Kim,T.G. Finstad, W.K. Chu, X.B. Cox, R,W. Linton,"Ann- ealing effect of SnO_2 films prepared by chemical vapor deposition: Evidence of chlorine removal by auger electron spectroscopy and Rutherford back-scattering spectrometry studies", Solar Cells 13 (1984) 301.

[14] S. Ghosh, H. Kim, K. Hang, C. Lee," Microstructure of indium tin Oxide films deposited on porous silicon by rf-sputtering",Mater Sci. Eng., B, Solid-State Mater. Adv.Technol. 95 (2002) 171.

[15] M. Okuya, S. Kaneko, K. Hiroshima, I. Yagi, K. Murakami," Low temperature deposition of SnO_2 thin films as transparent electrodes by spray pyrolysis of tetra-*n*-butyltin(IV)",J. Eur. Ceram. Soc. 21 (2001) 2099.

[16] J.R. Brown, P.W. Haycock, L.M. Smith, A.C. Jones, E.W. Williams, " Response behaviour of tin oxide thin film gas sensors grown by MOCVD",Sens. Actuators B, Chem. 63 (2000) 109.

[17] O.K. Varghese, L.K. Malhotra," Studies of ambient dependent Electrical behavior of nanocrystalline SnO2SnO2 thin films using Impedance spectroscopy",J. Appl. Phys. 87 (2000) 7457.

[18] Q. Chen, Y. Qian, Z. Chen, G. Zhou, Y. Zhang," Fabrication of Ultrafine SnO_2 thin films by the hydrothermal method",Thin Solid Films 264 (1995) 25.

[19] I. Taniguchi, D. Song, M. Wakihara," Electrochemical properties of $LiM_{1/6}Mn_{11/6}O_4$ (M = Mn, Co, Al and Ni) as cathode materials for Li-ion batteries prepared by ultrasonic spray pyrolysis method",J. Power Sources 109 (2002)333.

[20] Ren, Y.; Zhao, G.; Chen, Y." Fabrication of textured SnO_2:F thin Films by spray pyrolysis", Appl. Surf. Sci. 258(2011)914–918.

[21] Powder Diffraction File Alphabetic PDF-2 Data Base,file41-1445, International center of Diffraction Data, Newtown Square, PA, USA, 1994.

[22] B. D. Cullity and S.R. Stock, "Elements of X-Ray Diffraction" 3th Edition, Prentice-Hall, United States of America, 2001.

[23] S.A.Yousif, J. M. Abass," Structural, Morphological and Optical Characterization of SnO2:F thin films prepared by Chemical spray Pyrolysis", International Letters of Chemistry,Physics And Astro-nomy,13 (2013) 90-102.

[24] C M Shen, X G Zhang and H L Li," Influence of different deposition Potentials on morphology and structure of CdSe films",Appl. Surf. Sci.,240 (2005) 34.

[25] H. Kim, R. C. Y. Auyeung and A. Pique," Transparent conducting F-doped SnO_2 thin films grown by pulsed laser deposition",Thin Solid Films,516(2008)5052.

[26] C. Agashe, S.S. Major ," Effect of heavy doping in SnO_2:F films" J. Mater. Sci. 31 (1996) 2965-2969.

[27] E. Elangovan, K. Ramamurthi," Studies on micro-structural and Electrical properties of spray-deposited fluorine-doped tin oxide thin Films from low-cost precursor",Thin Solid Films 476 (2005)231-236.

[28] G. Muruganantham, K. Ravichandran, K Saravanakumar," Effect of Solvent volume on the physical properties of undoped and fluorine Doped tin oxide films deposited using a low-cost spray Technique " Superlattices and Microstructures 50(2011) 722.

[29] S. Ray , P. S. Gupta and G. Singh," Electricaland optical properties of sol-gel prepared Pd-doped SnO_2 thin films : effect of multiple layers and its use as room temperature methane gas sensor", J.Ovonic Res. 6(2010) 23.

[30] Zhu,H.;Yang, D.; Yu, G.; Zhang, H.; Yao, K ," A simple hydrothermal route for synthesizing SnO_2 quantum dots", Nanotechnology 17(2006) 2386.

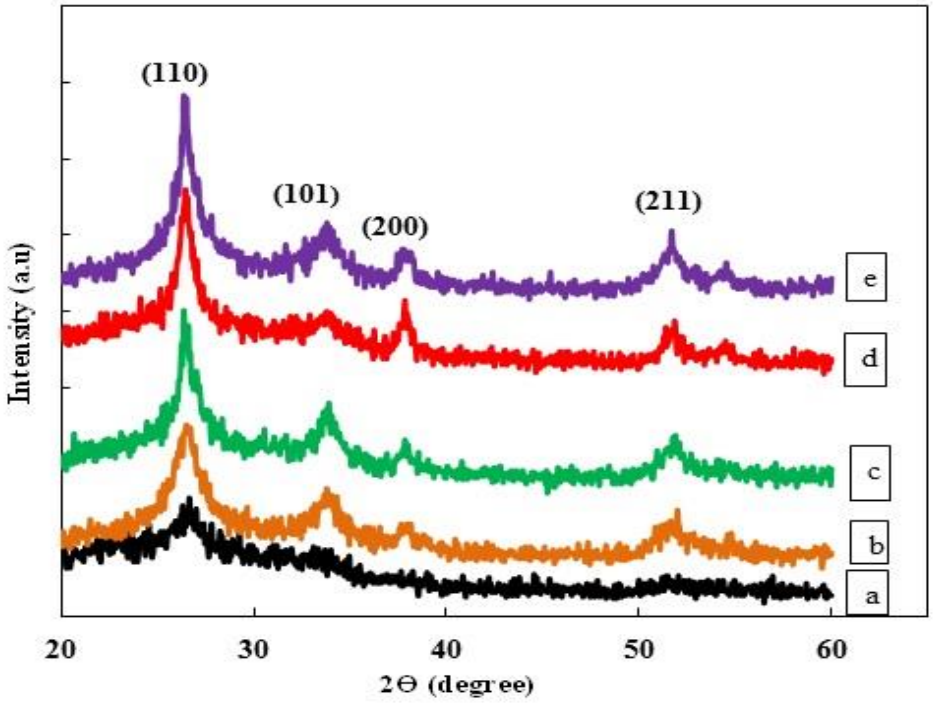

Figure 1. X-ray diffraction patterns of FTO thin films for different fluorine doping (a.5%,b.15%,c.20%,d.25%and e.30%).

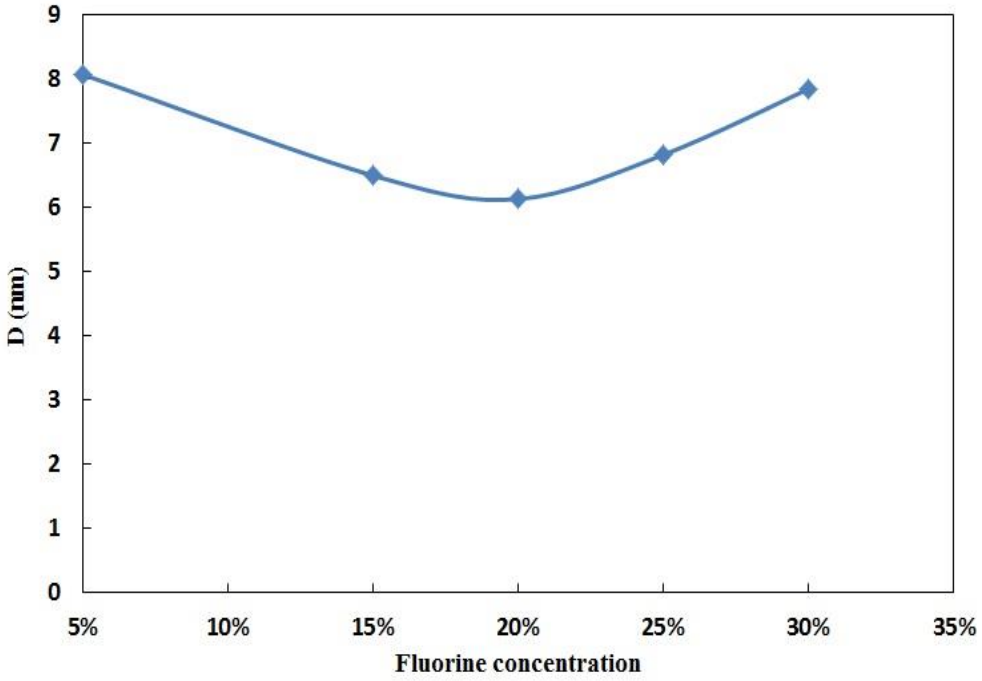

Figure 2. crystallite size vs. fluorine concentration

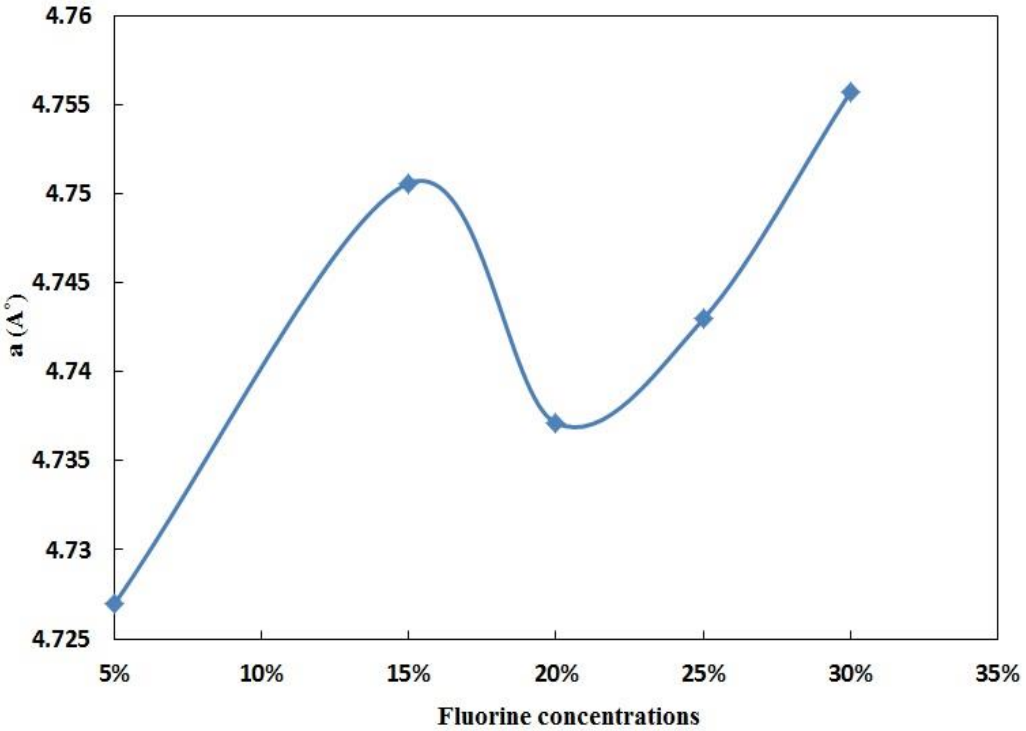

Figure 3. Lattice constant (a) as function of fluorine concentration of FTO films

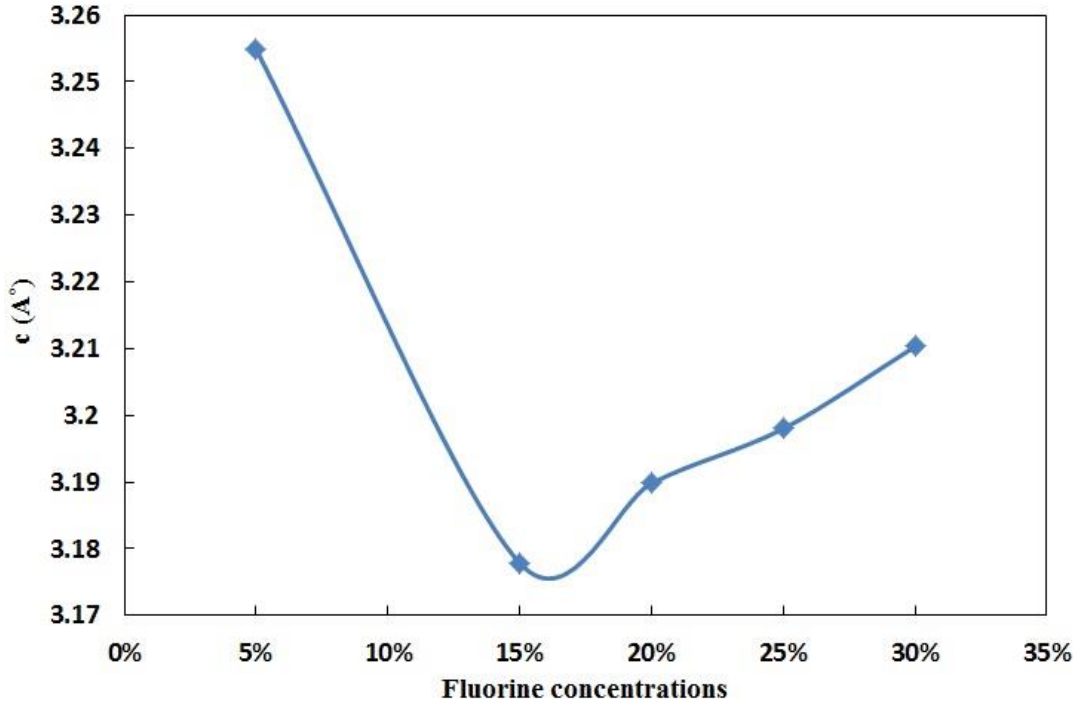

Figure 4. Lattice constant (a) as function of fluorine concentration of FTO films

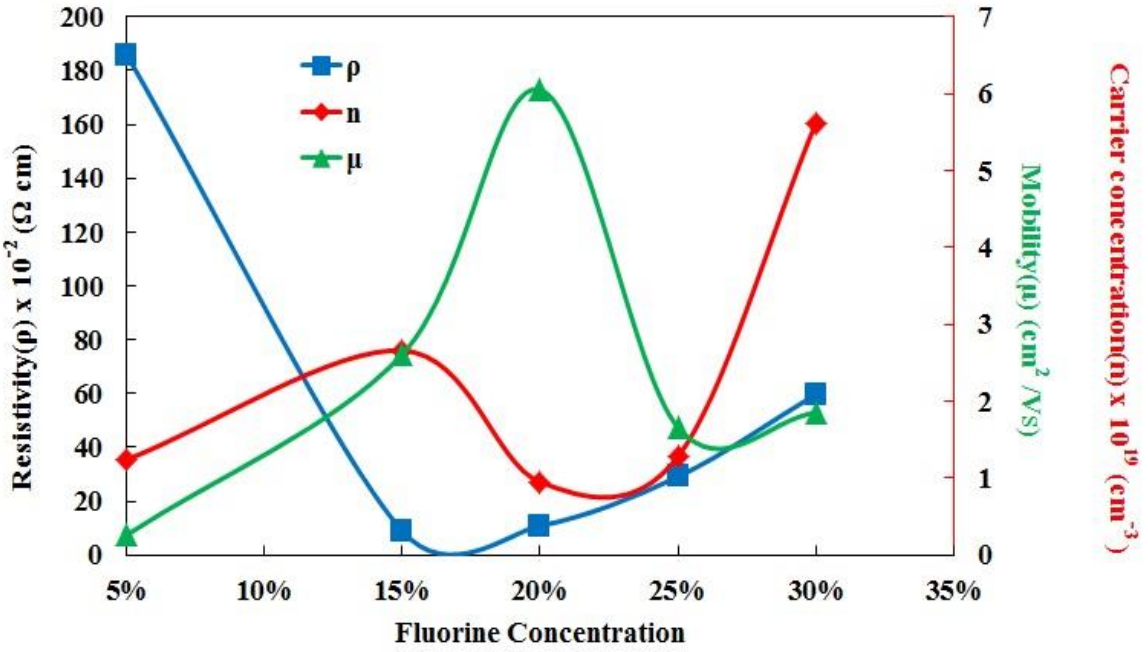

Figure 5. Resistivity, mobility and carrier concentration of FTO films as a function of fluorine concentration.

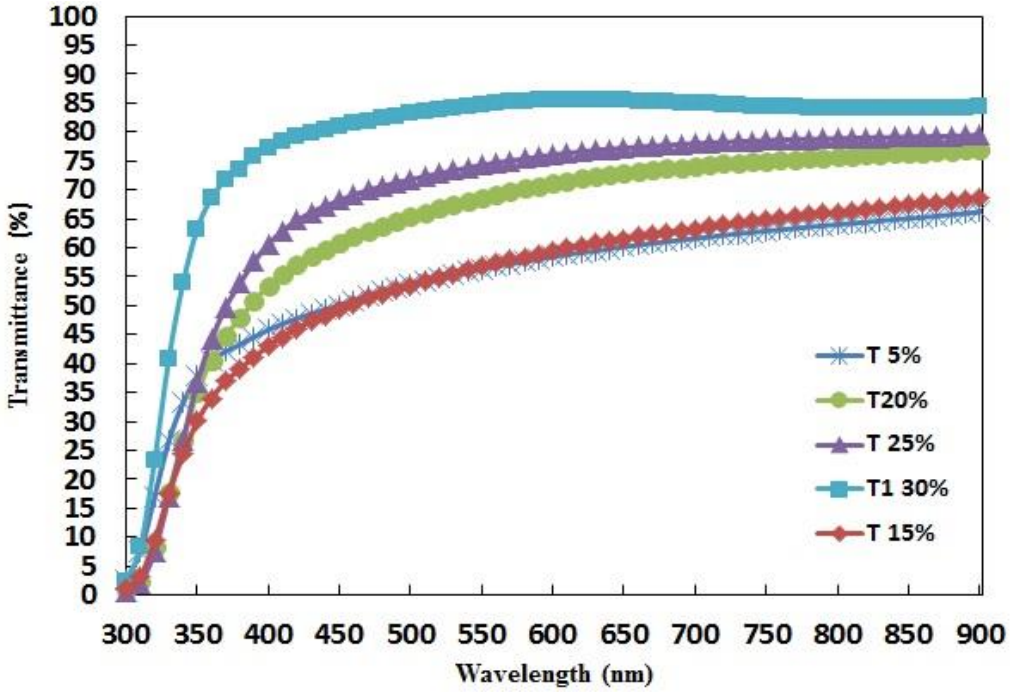

Figure 6. Transmittance spectra of SnO_2:F thin films as a function of wavelength for different fluorine concentration

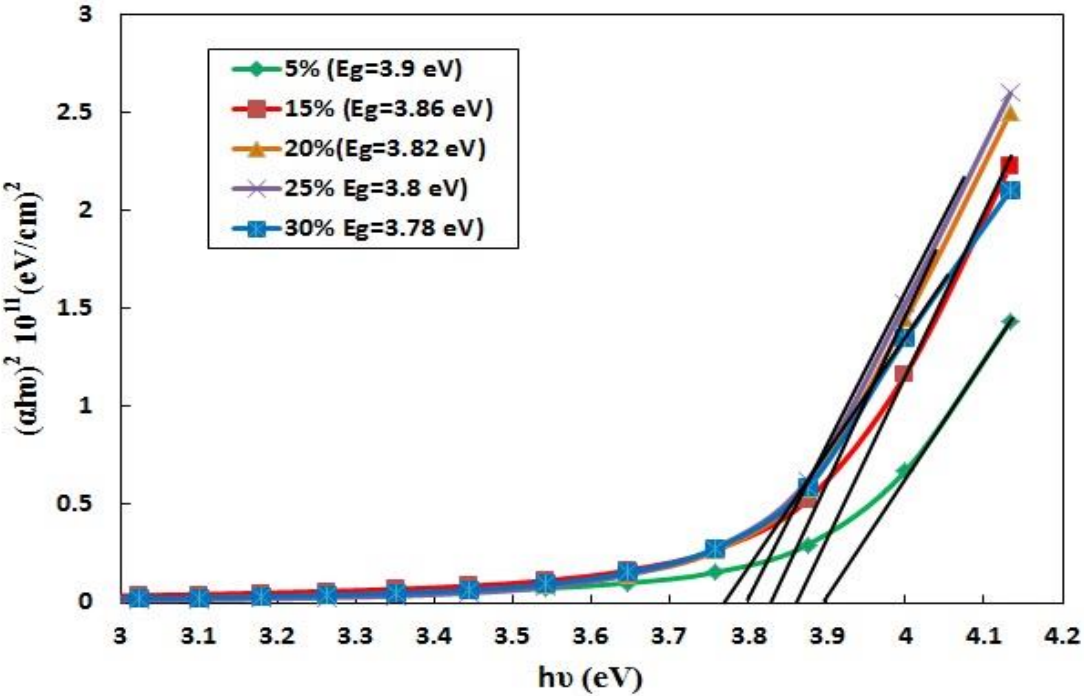

Figure 7. $(\alpha h\upsilon)^2$ versus (hν) of SnO_2:F films for different fluorine concentration.