Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thin Solid Films 427 (2003) 208–214
thin solid films
www.elsevier.com/locate/tsf

Deposition of transparent conductive tin oxide thin films doped with fluorine by PACVD

F. Arefi-Khonsari*, N. Bauduin, F. Donsanti, J. Amouroux

Laboratoire de Génie des Procédés Plasmas, Université Pierre et Marie Curie, ENSCP, 11, rue Pierre et Marie Curie, 75231 Paris, France

Abstract

In this work an attempt has been made to dope the films by a one step process by introducing a fluorine precursor which was SF_6 with the plasma mixture used for the deposition of tin oxide films. Optical emission spectroscopy and mass spectrometry were used to study the plasma phase and the characterization of the films was carried out by different diagnostic techniques such as SEM, XPS and FTIR. An increase of the electrical conductivity was obtained for very small flow rates of SF_6 introduced in the discharge (from 95 to 130 S cm^{-1}). For higher flow rates, a sharp decrease of the conductivity was observed. For such flow rates, competitive etching and functionalization processes, assisted by fluorine atoms present in the discharge, take place. Although the conductivity dropped down, the optical transmission of the deposited films remained higher than 90%.

Keywords: TCO coatings; PACVD; Doping; Tin oxide

1. Introduction

Tin oxide films are n-type semiconductors. They present a high optical transmission in the visible, reflect IR and present a large range of electrical conductivity. That is why tin oxide thin films are used for several applications such as anodes for lithium rechargeable batteries [1,2], as anodes in electrochemical cells [3], transparent heating elements, protective (antistatic and antireflective) and barrier coatings, as well as gas sensors [4]. The conductivity of plasma deposited thin films, can be enhanced by doping them with elements possessing a different valence such as fluorine or antimony. In the case of the former, it substitutes oxygen atoms whereas the latter replaces tin atoms. Several studies have used CVD techniques for the deposition of fluorine doped SnO_2 using precursor mixtures composed of $SnCl_4$ and NH_4F [5,6] and where a very high concentration of the doping precursor has been used.

In a previous work the conductivity of plasma deposited tin oxide films from a mixture of O_2/Ar/Tetramethyltin (TMT) has been enhanced from 0.01 to 100 S cm^{-1} by biasing the substrate by means of a second RF generator in a triode configuration [7]. In this paper, an attempt has been made to dope the plasma deposited tin oxide films with fluorine atoms in a one step process by introducing SF_6 as the fluorine containing precursor in the plasma mixture in the same triode configuration.

The aim of this study was to introduce a very small quantity of fluorine in the structure of the films in order to create an excess of electrons leading to an increase of electrical conductivity as a consequence. The study was based on both characterization of the plasma phase (by optical emission spectroscopy and mass spectrometry) and of the physicochemical properties of the deposited films by different surface analyses.

2. Experimental set-up

Tin dioxide films were deposited in a capacitively coupled RF 13.56 MHz reactor at a pressure of 15 Pa. This pressure was regulated by a butterfly regulation valve and measured by a capacitive gauge. The gaseous mixture (O_2/Ar/TMT: 66%/33%/1%) was introduced through the RF-powered shower electrode. The substrate electrode was biased by a second RF 13.56 MHz generator [7]. SF_6 used as the doping precursor was introduced in the gas mixture in very small quantities with a maximum flow rate of 0.3 sccm (3% of the total gas flow). The mass spectrometer used was a Hiden

*Corresponding author.
E-mail address: coscia@na.infn.it (F. Arefi-Khonsari).

0040-6090/03/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0040-6090(02)01211-7

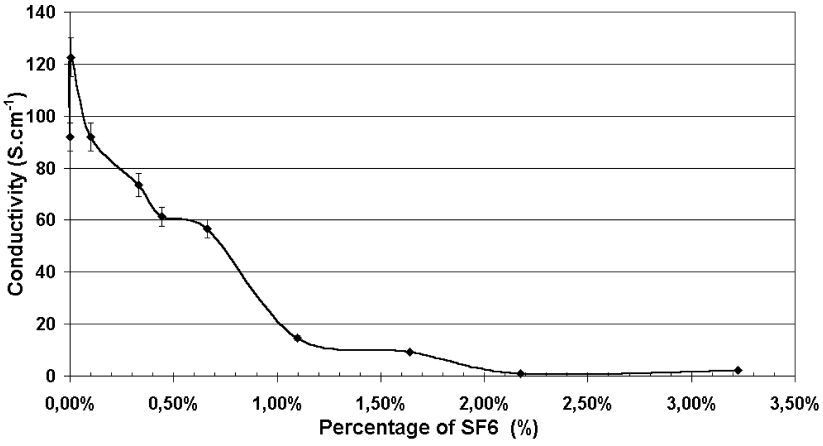

Fig. 1. Variation of the electrical conductivity with SF_6 flow rate. (Experimental conditions: Ar–O_2–TMT–SF_6 plasma; pressure: 15 Pa; Gas flow: 9 sccm; power: 190 W; bias voltage: −120 V.)

EPIC 500 which was able to detect neutral species, positive and negative ions in a mass range of 1–500 atomic mass units (amu). The optical emission spectroscopic studies were carried out with a Princeton Instrument SpectraPro 500i spectrometer equipped with three gratings (150, 1200 and 3600 g mm^{-1}) and an Acton CCD camera.

3. Results and discussion

3.1. Variation of the thickness

The deposition rate of undoped tin oxide films was approximately 30–50 nm min^{-1}.

The thickness of the deposited films were measured with a Dektar sloan 3030 profilometer.

The thickness of the deposited layer decreased when the SF_6 flow rate increased (550–100 nm for flow rate 0 sccm to 0.3 sccm for a treatment time of 10 min).

3.2. Variation of electrical conductivity

The electrical conductivity of tin oxide films deposited with various amounts of SF_6 in the gas mixture was measured using the 4-point probe method with a Keithley 617 electrometer.

The conductivity C was obtained with the equations:

$$C=\frac{1}{\rho} \text{ and } \rho=4.53\times e\times\frac{V}{I}$$

where *e*: thickness (cm); *V*: voltage (V); *I*: intensity (A).

As shown in Fig. 1 the electrical conductivity increased with the increase of SF_6 flow rate in the discharge but only for a very small flow rate. Typically, the maximum of conductivity was obtained for a flow rate of 5.10^{-3} sccm (0.05% of the total flow rate). For higher values, the conductivity sharply decreased.

In order to understand how the presence of SF_6 in the discharge influences the discharge and the properties of the films, we have determined by OES and mass spectrometry the characteristics of the plasma phase.

3.3. Characteristics of the discharge

3.3.1. Energetic properties

The energetic properties of the discharge were determined by measuring the vibrational temperature of $N_2(C)$ and the rotational temperature of OH which were carried out through OES studies. The background pressure was 10^{-3} Pa. The partial pressure of residual water was determined by mass spectrometry to be approximately 0.02 Pa which increased to 0.33 Pa where TMT is introduced in the discharge. A constant amount of nitrogen (1–2%) was introduced in the reactor in order to measure the vibrational temperature of $N_2(C)$.

In the case of the vibrational temperature, it was measured with the help of the second positive system of N_2, $(C^3\ \Pi_u,\ v'\rightarrow B^3\Pi_g,\ v'')(\Delta v=2)$ at 380.5, 375.5 and 371 nm, respectively, for transitions $0\rightarrow2$, $1\rightarrow3$ and $2\rightarrow4$ [8]. The rotational temperature was measured on OH radicals, the formation of which is due to the existence of water traces in the reactor. Several emission bands of the $A^2\Sigma^+$ excited state of this radical were detected by OES and the Q_2 rotational branch of the $A^2\Sigma^+(v'=0)\rightarrow A^2\Pi\ \ (v'=0)$ system (308–322 nm) was used to determine the rotational temperature on the low-lying rotational levels [9,10].

As shown in Fig. 2, the rotational temperature remained constant at 350 K. Considering the error bar of the measured values, the vibrational temperature also does not show a significant change by introducing SF_6 in the discharge.

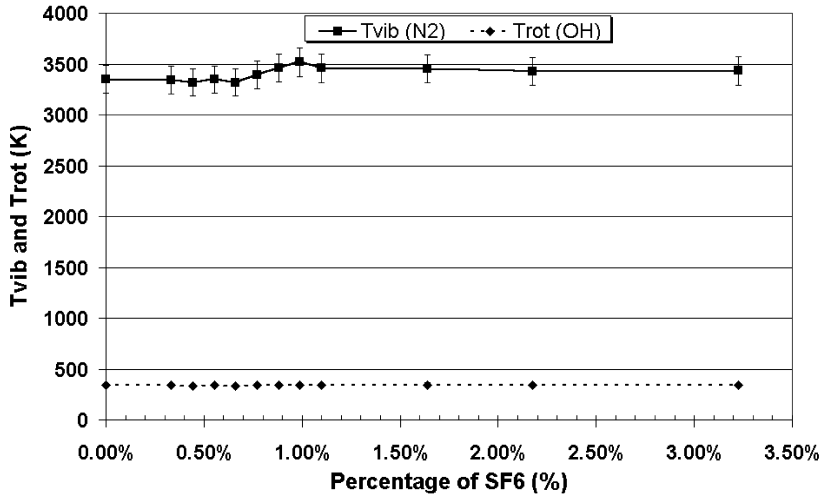

Fig. 2. Variation of the vibrational temperature of N_2 and Rotational temperature of OH with SF_6 flow rate. (Experimental conditions: Ar–O_2–TMT–SF_6 plasma; pressure: 15 Pa; Gas flow: 9 sccm; power: 190 W bias voltage: −120 V.)

3.3.2. Identification of the neutral species

Mass spectrometric studies were performed in order to understand the modifications of the species present in the plasma phase with an increase of the SF_6 flow rate. We made a calibration of the mass spectrometer using a calibration mixture composed of He–Ne–N_2–Ar–Kr–Xe supplied by Air Liquide. It enabled us to determine the density of the species produced in the plasma as well as the dissociation rate of the reactants i.e. TMT, SF_6 as well as O_2. The dissociation rate of TMT was measured on the major peak of dissociation of TMT i.e. the peak at 165 amu corresponding to $Sn(CH_3)_3^+$:

$$\text{Dissociation rate} = \frac{(I_{165})_{\text{plasma on}} - (I_{165})_{\text{plasma off}}}{(I_{165})_{\text{plasma off}}}$$

As shown in Fig. 3, the dissociation rate of TMT slightly increases in the presence of SF_6 from 90% up to 95% for small percentages of SF_6 (<1%) introduced in the discharge. On the other hand, the fluorine precursor was highly dissociated with dissociation rates higher than 90% for SF_6 flow rates lower than 0.1 sccm (1% SF_6) and then decreased to 80% for higher percentages of SF_6. The dissociation rate of the SF_6 was obtained by following the two major peaks i.e. SF_5^+ (parent peak 100%) and SF_3^+ (26% of the parent peak) [11].

Species resulting from the recombination of oxygen, hydrogen, fluorine and sulfur such as SOF_2, SO_2, SOF, HF were observed (Fig. 4). In this way, a large amount of oxygen was consumed to form these species instead of producing volatile species with carbon and hydrogen such as CO, CO_2 or H_2O (Fig. 4). Indeed Fig. 4 shows

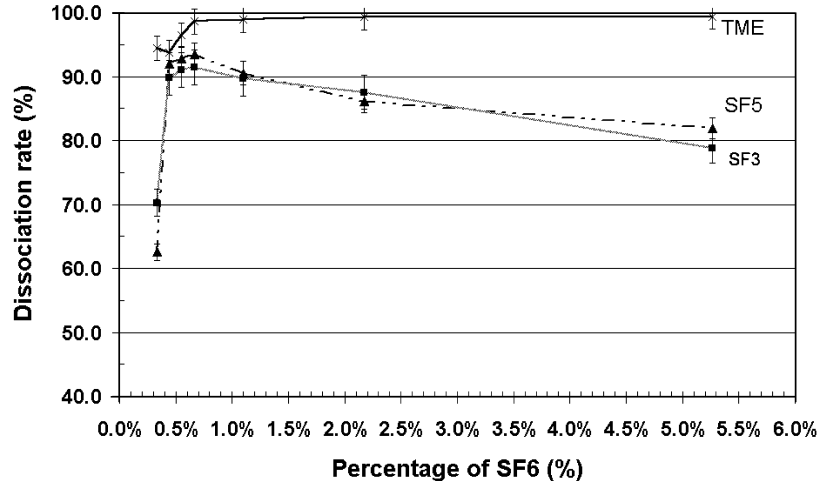

Fig. 3. Variation of the dissociation rates of TMT and SF_6 vs. percentage of SF_6 present in the gas mixture. (Experimental conditions: Ar–O_2–TMT–SF_6 plasma; pressure: 15 Pa; Gas flow: 9 sccm; power: 190 W bias voltage: −120 V.)

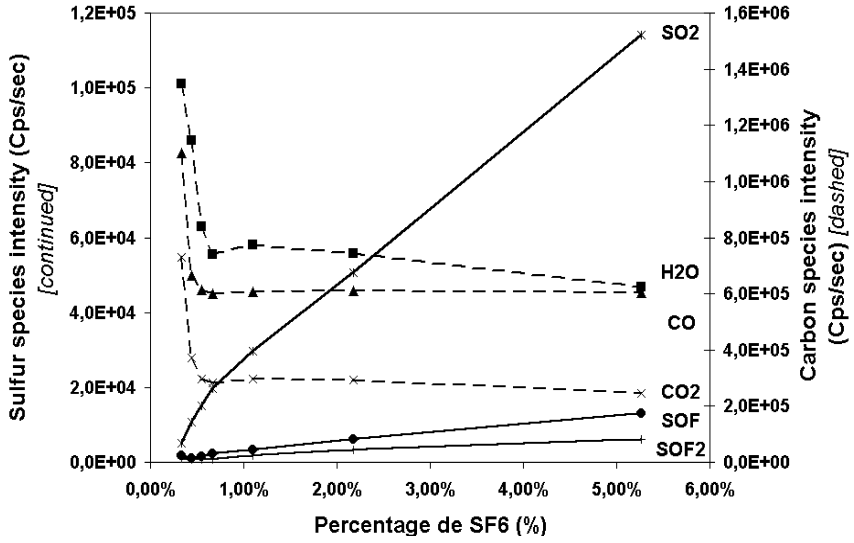

Fig. 4. Evolution of the intensities of identified species observed by MS as a function of SF_6 percentage introduced in the discharge. (Experimental conditions: Ar–O_2–TMT–SF_6 plasma; pressure: 15 Pa; Gas flow: 9 sccm; power: 190 W bias voltage: −120 V.)

a decrease of the production rate of such oxidized species resulting from the interaction of TMT with oxygen as soon as SF_6 is introduced in the discharge and despite the fact that TMT decomposition rate decreases. This decrease can be explained by the competitive mechanisms which exist between the production of such species (CO, CO_2 or H_2O) with those corresponding to sulfur containing species. The high production rate of SO_2, SOF and SOF_2 observed for discharges containing above 1% of SF_6 confirms what we postulated above (Fig. 4). The decrease of the production rate of hydrogen in the plasma with the introduction of SF_6 can be explained by the recombination of fluorine atoms, resulting from the decomposition of SF_6, with hydrogen giving rise to the stable HF species.

Therefore it can be postulated that a high concentration of SF_6 (>1%) could modify the recombination processes such as a sharp decrease of the elimination of the carbon species in the form of carbon monoxide and dioxide and therefore altering the properties of the deposited film.

3.4. Physicochemical properties of the deposited films

3.4.1. XPS studies

XPS analysis of the deposited films was carried out in order to determine the amount of fluorine present in the films (Fig. 5). No fluorine was detected for SF_6 flow rates lower than 0.03 sccm i.e. the concentration of the fluorine incorporated in the deposit in this case (through 50 nm which corresponds to the analytical depth of XPS) is less than a percent which is the sensitivity of the analytical method.

We have calculated the atomic relative ratios of the different elements present as a function of the flow rate of SF_6 introduced in the gas mixture. As shown in Fig. 5, the increase of the flow rate of SF_6 brought about a rise of the F/Sn ratio.

By the deconvolution of the peak of Sn $3d^{5/2}$, XPS studies have shown binding energies characteristic of the Sn–O (487 eV) bondings but not those corresponding to Sn–C bondings (485.5 eV). It is difficult to distinguish the Sn–F bonding on the deconvoluted Sn $3d^{5/2}$ photoelectron peak since it should appear approximately 487 eV which is very close to the binding energy of Sn–O in SnO_2 (486.8 eV) [13,14].

The Sn–F bond was detected only when the SF_6 flow rate was higher that 0.03 sccm, and its intensity increased with an increase of the SF_6 flow rate. For higher percentages of SF_6 introduced C–F bondings also could be identified on the F 1s photoelectron peak. These results confirm those obtained by MS showing that carbon resulting from the decomposition of TMT was not eliminated in the form of volatile species and was incorporated in the films (Fig. 4).

Fluorine atoms resulting from the decomposition of SF_6 seem to cause both etching of the tin oxide films (decrease of the thickness) probably in the form of Sn–O–F bondings as well as a functionalization of the surface forming either Sn–F and/or C–F bondings. Indeed for the same deposition time, by introducing 1.6% SF_6 in the discharge, the Sn photoelectron peak decreased 60%, that of oxygen decreased 45%.

These results confirm the fact that etching of the films took place, since the thickness of the films were half as much as the undoped films when 2% SF_6 was introduced in the discharge.

3.4.2. FTIR studies

FTIR studies were done by deposition of tin oxide films on CsBr pellets. Fig. 6 presents infrared spectra

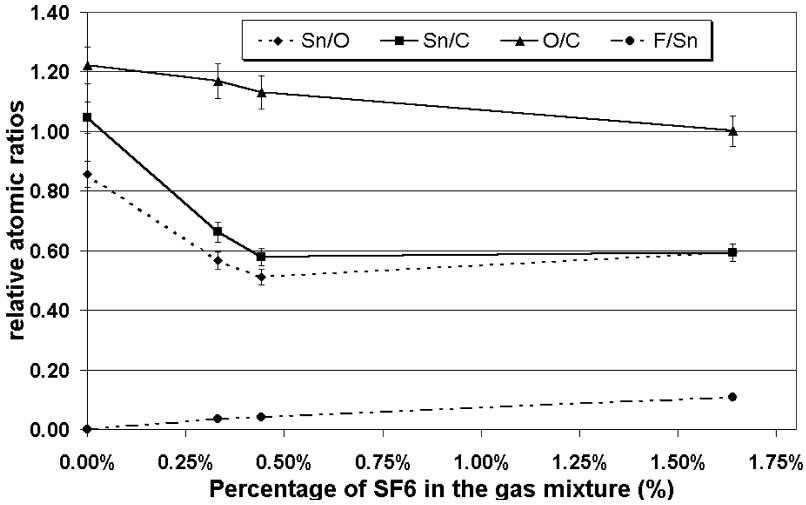

Fig. 5. Evolution of relative atomic ratios vs. percentage of SF_6 present in the gas mixture. (Experimental conditions: Ar–O_2–TMT–SF_6 plasma; pressure: 15 Pa; Gas flow: 9 sccm; power: 190 W bias voltage: −120 V.)

of undoped plasma deposited SnO_2, SnO_2 deposited with 0.05 sccm of SF_6 in the discharge and CsBr as reference. We notified the presence of two bands characteristic of SnO_2 at 550 and 328 cm^{-1} with and without SF_6. The presence of SF_6 in the discharge induced a modification of the spectra with two new bands which could correspond to C–F and Sn–F vibrational bands at 725 and 477 cm^{-1} confirming the results obtained by XPS [12]. But the modifications that could be observed by FTIR analysis occurred only when the amount of SF_6 in the discharge was higher than 1% (flow rate of 0.1 sccm). For lower flow rates, no modifications were observed by this technique.

3.4.3. SEM studies

SEM micrographs were carried out in order to see if the chemical modifications observed previously were associated to the morphological modifications. As shown by the micrographs in Fig. 7, the morphology of the surface of the films was strongly modified by increasing the SF_6 flow rate with the appearance of clusters with a mean diameter between 200 and 300 nm whereas the undoped tin dioxide films were composed of a homogeneous film characterized by small grains (diameter 50 nm [7]). Furthermore, the density of these large clusters increases as the SF_6 flow rate was increased. Apart from the change of the chemical structure of the films, the modification of the morphology of the films probably could also contribute to the change of the electrical conductivity. A higher magnification of the deposited film with a $Q_{SF_6}=0.2$ sccm showed that the 200 nm clusters were deposited in a regular manner on a matrix which was composed of 40 nm size grains. However,

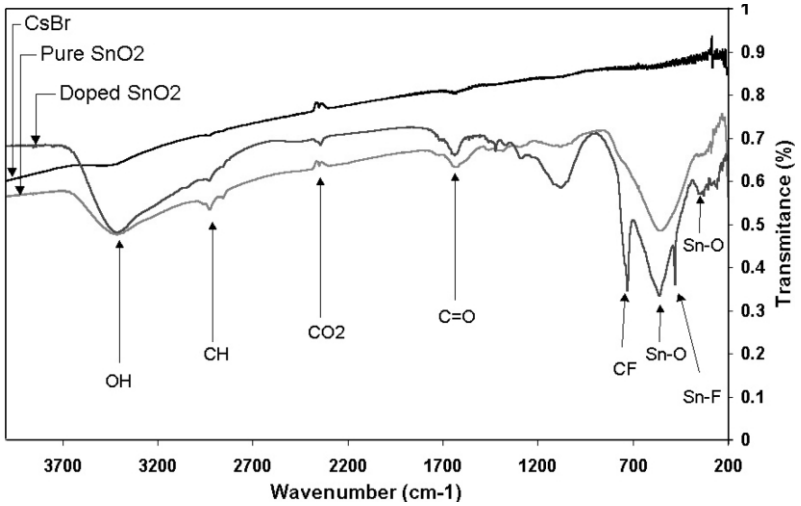

Fig. 6. FTIR spectra. (Experimental conditions: Ar–O_2–TMT–SF_6 plasma; pressure: 15 Pa; Gas flow: 9 sccm; power: 190 W bias voltage: −120 V.)

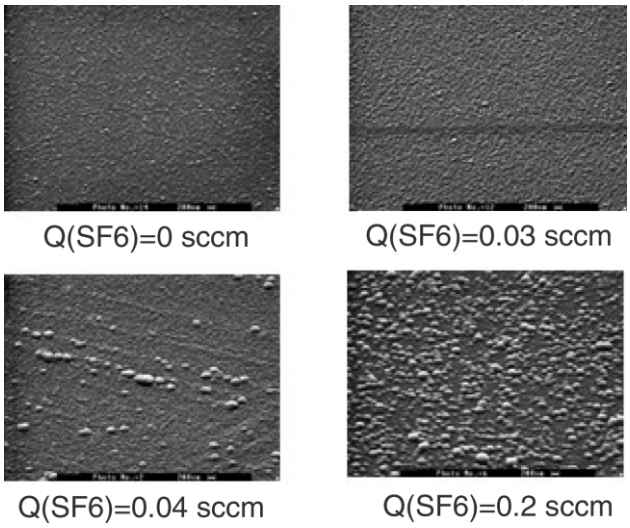

Fig. 7. SEM micrographs of tin oxide films doped by fluorine; role of SF_6 flow rate. (Experimental conditions: Ar–O_2–TMT–SF_6 plasma; pressure: 15 Pa; Gas flow: 9 sccm; power: 190 W bias voltage: −120 V.)

EDX analyses made on the 200 nm clusters have shown that there were no differences (besides from the carbon content which was not analyzed) in the chemical composition between the clusters and the surrounding matrix.

3.4.4. Optical transmission studies

Optical measurements were performed in order to verify if the introduction of fluorine in the discharge (and, consequently, incorporation in the films) induced a modification of the optical properties such as maximal optical transmission in the visible wavelength range.

Optical measurements were measured in the specular transmission mode using a Shimazu UV−vis spectrometer.

The refractive index was calculated with the equations below [11]:

$$n_c = \left[N + (N^2 - n_0^2 n_1^2)^{1/2}\right]^{1/2}$$

with

$$N = \frac{n_0^2 + n_1^2}{2} + 2n_0 n_1 \frac{T_{max} - T_{min}}{T_{max} T_{min}}$$

where n_0 and n_1: refractive indexes of substrate (glass) $n_0 = 1$ and $n_1 = 1.5$ at wavelength λ, n_c = refractive index of film, T_{max} and T_{min}: transmission at the same wavelength λ.

The thickness of the films was calculated using the interference fringes from two maxima of fringes using this equation [11]:

$$e = \frac{N\lambda_1\lambda_2}{2n(\lambda_2 - \lambda_1)}$$

where N: number of oscillations between the two extrema, λ_1 and λ_2: the corresponding wavelengths of the two extrema, n: refractive index of the film.

Our films are supposed to be homogeneous, parallel faced and smooth. Indeed, the deposited films show a very small roughness which has been determined by AFM to be approximately 2–3 nm rms [4]. The refractive indexes calculated are in fact mean values in the range of 400–900 nm. In this domain of wavelengths the imaginary part of the refractive index of tin oxide films is negligible $\eta = n - ik$ where k is supposed to be lower than 0.1 in the case of SnO_2 films deposited on a glass substrate [11]. The refractive indexes calculated by OT data is in the range of 1.91–1.93. The thickness of the films decreased with the increase of the SF_6 flow rate (600–250 nm). This is confirmed by the decrease of the interference fringes on the optical spectra (Fig. 8) and is in agreement with the profilometry results.

As shown in Fig. 8, the optical transmission was not modified when a high percentage of fluorine was incorporated in the films i.e. optical transmission was higher than 90%. This in agreement with what has been reported by other authors who have doped their tin oxide films by other processes [15].

Direct band Gap values have been estimated using $(h\nu \log(T))^2 = f(h\nu)$ curves from the OT data (Fig. 9) giving rise to values approximately 3.6 eV in all cases.

4. Conclusion

In this paper, the doping effect of fluorine (in one step process by using SF_6 in the discharge) was inves-

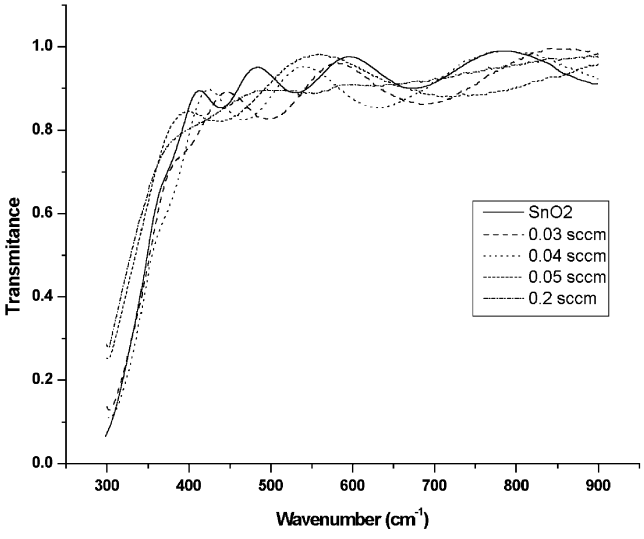

Fig. 8. Optical transmission curves. (Experimental conditions: Ar–O_2–TMT–SF_6 plasma; pressure: 15 Pa; Gas flow: 9 sccm; power: 190 W bias voltage: −120 V.)

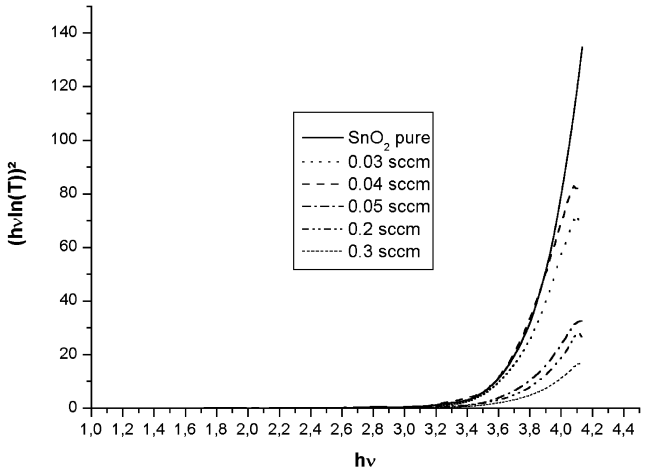

Fig. 9. $(h\nu \log(T))^2 = f(h\nu)$ curves. (Experimental conditions: Ar–O_2–TMT–SF_6 plasma; pressure: 15 Pa; Gas flow: 9 sccm; power: 190 W bias voltage: −120 V.)

tigated by studying the plasma and the material properties of the films. A very small introduction of SF_6 in the discharge induced an increase of the electrical conductivity from 95 to 130 S cm^{-1} for a flow rate of 0.005 sccm (0.05% of the global flow rate). In the case of the latter, the incorporation of fluorine atoms should take place by the substitution of O_2^- ions by F^- ones according to the following reaction: $O_2^- + F \rightarrow O + F^- + e$, giving rise to an increase of the conductivity of tin oxide film. However, for higher flow rates, a considerable decrease of the conductivity was obtained. This sharp decrease of the electrical properties was explained both by the chemical and morphological modifications of the deposited films. In fact, the incorporation of SF_6 in the discharge induced modifications of the neutral species created in the plasma. New species resulting from the decomposition of the fluorine precursor such as SO_2, SOF, SOF_2 or HF were formed. Oxygen being consumed to form such species, it was much less involved in forming CO, CO_2 and H_2O species, therefore leading to the incorporation of carbon species in the deposit.

High SF_6 flow rates in the plasma give rise to the appearance of Sn–F and C–F bonds in the films. Indeed these results are in agreement with those reported by Cachet et al. [16,17] who showed that for films presenting a high percentage of fluorine (>10% in their case for tin oxide films deposited by spray pyrolysis) the fluorine atoms can be either in an interstitial position and/or in the grain boundaries forming Sn–F bondings. The presence of the latter decreases the mobility of the charge carriers and therefore decreases the electrical conductivity. Furthermore, in the presence of a high SF_6 flow rate (>1%), an etching of the deposited tin oxide films takes place.

Moreover, the morphology of the films was modified by the presence of SF_6 with an increase of the grain size and the appearance of clusters on the surface of the films. However, the optical properties of the films were not modified with a maximum optical transmission higher than 90% for films deposited with an SF_6 discharge content varying from 0 to 3%.

References

[1] G. Goward, L. Nazar, W. Power, J. Mater. Chem. 10 (2000) 1241.
[2] K. Murali, T. Saravanan, T. Poovarasan, R. Karthikeyan, Proceeding of the 197th Meeting of the Electrochemical Society, Toronto, 2000.
[3] R. Kotz, S. Stucki, B. Carcer, J. Electrochem. 21 (1991) 14.
[4] F. Hellegouarc'h, F. Arefi-Khonsari, R. Planade, J. Amouroux, Sensors Actuat. B: Chem. 73 (1) (2001) 27–34.
[5] A. Rakhshani, Y. Makdisi, H. Ramazaniyan, J. Appl. Phys. 83 (2) (1998) 1049.
[6] C. Terrier, J.P. Chatelon, J.A. Roger, Thin Solid Films 295 (1997) 95.
[7] F. Arefi-Khonsari, F. Hellegouarc'h, J. Amouroux, J. Vac. Sci. Technol. A 16 (4) (1998) 2240.
[8] A. Ricard, Plasmas Réactifs, SFV Edition, Paris (1955).
[9] A. Bass, E. Broida, National Bureau of Standards Circular, (1953) 451.
[10] N. Sokabe, J. Phys. Soc. Jpn. 33 (2) (1972) 473.
[11] J.C. Manifacier, J. Gasiot, J.P. Fillard, J. Phys. E 9 (1976) 1002.
[12] Data base 'National Institute of Standards and Technology' NIST Chemistry WebBook. Available from http://www.webbook.nist.gov/chemistry/.
[13] Data base XPS du 'National Institute of Standards and Technology' NIST X-ray Photoelectron Spectroscopy Database. Available from http://www.srdata.nist.gov/xps/.
[14] P. Grutsch, M. Zeller, T. Fehlner, Inorg. Chem. 12 (1973) 1432.
[15] H. Afify, R. Momtaz, W. Badawy, S. Nasser, J. Mater. Sci. Mater. Electron. 2 (1991) 40.
[16] H. Cachet, G. Folcher, J. Bruneaux, Proceedings of the Tenth Workshop on Quantum Solar Energy Conversion, QUANTSOL'98, 1998.
[17] H. Cachet, A. Gamard, G. Campet, B. Jousseaume, T. Toupance, Thin Solid Films 388 (2001) 41.