DEPOSITION OF TRANSPARENT CONDUCTIVE TIN OXIDE FILMS BY PACVD FROM A MIXTURE OF TMT (TETRA METHYL TIN) + O_2 + AR

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Abstract : Non stoichometric transparent tin oxide films have been deposited by PACVD at low temperature (< 100°C). The experimental parameters were optimized by coupling plasma diagnostique techniques (OES, MS) with surface ones (XPS, 4 point probe technique, ellipsometry and profilometry). The ageing of the conductive properties of the films led to the conclusion that films prepared at higher power were more stable. Auger in-depth profiles were performed on tin oxide deposited on SiO_2/Si substrate which revealed that the interface was not sharp but a rather diffused one presenting a $SiO_xO_ySn_z$ type of stoichiometry. The refractive index measured by ellipsometry was around 1.87 ± 0.01 at a wave length of 632.8 nm. By applying a bias voltage to the electrode on which the substrate was deposited the conductivity was increased by more than 3 orders of magnitude up to 10^2 S.cm^{-1} for a deposition time as short as 10 minutes.

Introduction : Over the past decade there has been a growing interest in the study of thin conductive films of tin or tin oxides owing to their different electrical and optical properties which are suitable for different applications such as transparent conducting oxides, UV filters, protective (antistatic and antireflective) and barrier coatings, photovoltaïque applications, gas sensors etc....In previous works [1,5,10] we have shown that the tin oxide films deposited presented an excellent optical transmittance in the 400 - 900 nm range corresponding to an optical gap, varying between 3.5 and 4 eV. The important parameters such as the power and the flow rate of O_2/flow rate TMT were optimized in our 13.56 MHz diode glow discharge reactor. In the case of the latter an increase of conductivity of 5 orders of magnitude was obtained by vaying Q_{O2}/Q_{TMT} due either to the formation of an organometallic film or a carbon free non stoichiometric tin oxide deposit. The maximum conductivity obtained in this case was around 5 S.cm^{-1} before annealing in a non oxygen containing gas such as nitrogen which increased the conductivity by a factor of 4. In this work transparent tin oxide films were deposited in a diode RF plasma reactor and the experimental conditions were optimized by coupling plasma diagnostic techniques such as emission spectroscopy and mass spectrometry with surface diagnostic ones such as XPS, ellipsometry, Auger Electron Spectroscopy (AES) and four point probe measurement. The ageing of the conductive properties were studied in terms of the plasma power. Finally the role of applying a bias voltage by means of another rf generator to the substrate electrode was studied in terms of the physicochemical and electrical properties of the deposited films.

Experimental : The details of the experimental set-up used for the plasma deposition of tin oxide films is given elsewhere [1]. The diode reactor was composed of two symmetrical circular electrodes with a diameter of 6 cm. For the bias voltage studies the diameter of the

substrate electrode was reduced to 3 cm. The cylindrical stainless steel reactor was equipped with a quartz window in front of which was fixed the optical fiber. The axial radiation of the discharge was transmitted to this optical fiber and analyzed by a THR 1000 Jobin Yvon monochromator working in the UV-visible region with the help of a 2400 grooves/mm grating. The stable effluents of the plasma was pumped through a capillary tube, placed in the interelectrode distance up to a quadrupolaire mass spectrometer (Balzers QMG 420). The substrates used in this study were glass, or a 25 nm SiO_2 layer deposited on each side of silicon substrate (for ellipsometric and AES analysis).

Results and discussion

1. Plasma characterization by emission spectroscopy

The emission spectrum of the TMT + Ar + O_2 discharges at 25 Pa observed in the 250-750 nm range presents two different groups of species : on the one hand, species resulting from the TMT decomposition and reaction with oxygen, SnO lines ($D^1\Pi_1 \rightarrow X^1\Sigma^+$ at 384.4 nm, $B^3\Pi_1 \rightarrow X^1\Sigma^+$ at 408.0 and 426.2 nm) and CO ($B^1\Sigma \rightarrow A^1\Pi$ at 451.1, 483.5 and 519.8 nm), on the order hand those corresponding to pure carbon species, CH ($A^2\Delta \rightarrow X^2\Pi$ at 431.4 nm), and C_2 ($A^3\Pi g \rightarrow X^3\Pi u$ at 516.5 and 563.6 nm). Futhermore besides Ar and hydrogen lines corresponding to Balmer series i.e Hβ (n = 4 → n = 2 at 486.1), Hδ (n = 5 → n = 2 at 434.1) and Hγ (n = 6 → n = 2 at 410.1), the oxygen band ($3\,d^5\,D \rightarrow 3\,S^5P$ at 615.8) and traces of nitrogen were detected.

2. Mass spectrometric measurements of the effluents

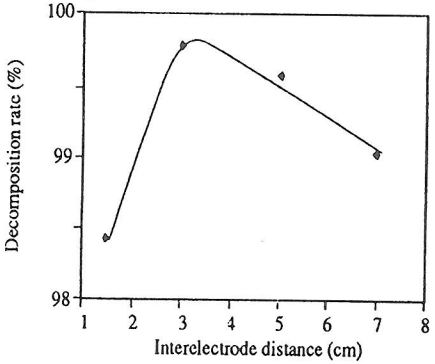

Figure 1 : Decomposition rate of TMT as a function of the interelectrode distance of diode reactor (Pi : 100 W, P : 30 Pa, Q_{O_2} : 5 sccm Q_{TMT} : 0. 25 sccm, Q_{Ar} : 1 sscm)

Mass spectrometry has been used to determine the dissociation rate of TMT and the evolution of the different fragments obtained from its decomposition in function of different parameters such as interelectrode distance, oxygen flowrate and power. The relative intensity of each peak expressed in arbitrary units has been determined by normalizing the intensity of each peak with respect to the sum of intensity of all of the peaks detected. The decomposition rate of TMT is calculated by the variation of the intensity of the parent peak that is Sn $(CH_3)_3^+$ (m/e = 165) [2,3] before and after putting the plasma on. The variation of the latter is shown in function of the interelectrode distance in Fig 1 which passes through a maximum (dissociation rate = 99.8 %) for d = 3 cm.

At the same time the intensity of the stannic fragments in Fig.2 ($SnOH^+$, SnO^+, Sn^+, SnH^+) as well as the carbon and hydrogen species formed by the TMT dissociation and their reaction with atomic and/or molecular oxygen i.e. CO, CO_2, H_2O represent the same maximum at an interelectrode distance equal to 3 (Fig.3). These species (Fig.3) can also result from the carbon or hydrogen elimination of the deposited films as will be observed in section 3.3. This phenomenon can be explained by the fact that for longer interelectrode distances for the same power injected in the plasma the electric field induced would be less therefore giving rise to a decrease of the energetic character of our discharge. This would therefore lead to a decrease of the excitation efficiency of the electrons needed to dissociate the TMT.

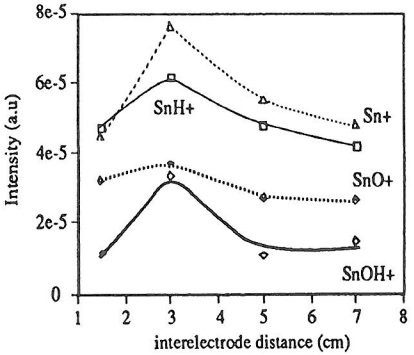

Figure 2 : Variation of the SnH^+, Sn^+, SnO^+, $SnOH^+$ peak intensities as a function of the interelectrode distance of diode reactor.

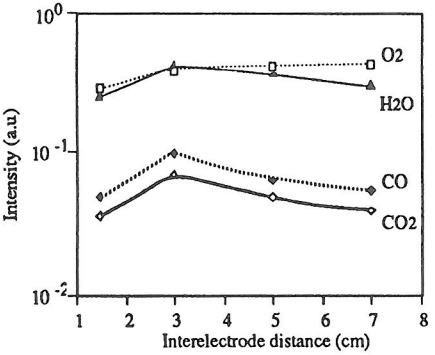

Figure 3 : Variation of the O_2, H_2O, CO , CO_2, peak intensities as a function of the interelectrode distance of diode reactor.

3 Surface characterization of the deposited films

3.a XPS

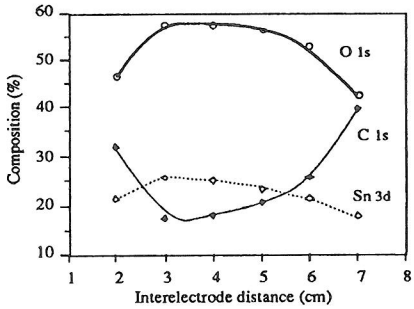

Figure 4 : Variation of the surface composition of the deposited films as function of the interelectrode gap
(t : 60 mn, Pi : 100W, P : 15 Pa, Q_{O_2} : 5 sccm
Q_{TMT} : 0. 15 sccm, Q_{Ar} : 1 sccm)

X-Ray photoelectron spectroscopy measurements were carried out on the deposited films obtained with different experimental conditions. Full details concerning the operating conditions have been given elsewhere [4]. Fig.4 represents the variation of the apparent stoichiometry of the deposited tin oxide films obtained by XPS in function of the same parameter i.e. the interelectrode distance. From this figure one can observe that the tin content of the deposited films is maximum whileas the carbon concentration is minimum for the same interelectrode distance i.e. 3 cm.

These results are in agreement with those obtained by mass spectrometry which pointed out that the concentration of the tin oxide precursors (SnO, SnOH) (Fig.2) and CO, CO_2 and H_2O (Fig.3) were maximum for the same interelectrode gap.

3.b Conductivity and deposition rate measurements

The macroscopic properties of the deposited films such as their conductivity and deposition rate are displayed in Fig.5 in function of the interelectrode gap which points out that in agreement with the results obtained above, the conductivity (measured by 4 point probe technique) was maximum for d=3 cm, but the deposition rate obtained by profilometry and ellipsometry decreased continuously with the electrode distance (Fig.5).

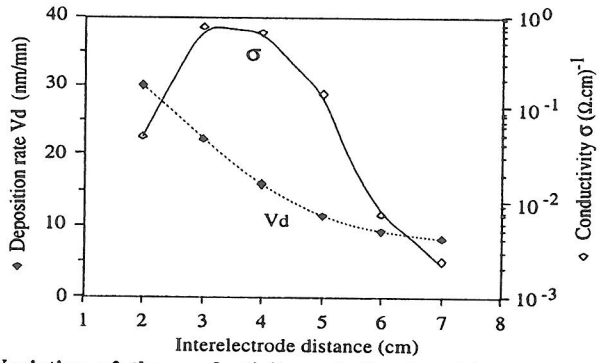

Figure 5 : Variation of the conductivity and the deposition rate as function of the interelectrode gap (same experimental conditions as in figure 4)

3.c Auger Electron Spectroscopy

In order to study the chemical composition of the deposited films and their interface with the substrate AES with in-depth profiling was done.

The experimental conditions concerning the Auger analysis and Ellipsometry have been given elsewhere [8,9]. The substrate used for AES and ellipsometry was a 25 nm SiO_2 film over each side of a silicon substrate. The Auger spectra are shown in Fig 6 in function of the sputter dose (corresponding to the thickness of the sputtered layer). One can observe that the carbon detected only constitutes a surface contamination and disappears at the beginning of the sputtering (Fig.6).

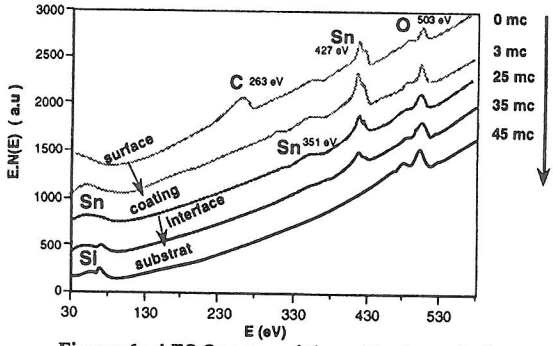

Figure 6 : AES Spectra of tin oxide deposited as a function of the sputter dose.

The Auger in-depth profiles of the deposited tin oxide layer on the SiO_2/Si substrate is represented in Figure 7.a. One can observe that the oxygen and tin profiles decrease up to the point where the silicon peak appears (SiLVV) at 74 eV, corresponding to silica. In fact oxygen is exclusively bonded to tin at the beginning and then is bonded at the same time to Sn as well as to Si which appears as we get close to the silica substrate.

The interface of the SnO_2/SiO_2 can be determined by using the relative intensity of the tin doublet in function of the sputter dose. This ratio gives some evidences on the chemical environment of tin and therefore determines the chemical nature of the deposited layer. This ratio changes right after a dose of 25 mC. This phenomenon does not seem to be related to a surface rearrangement after ion bombardment but to the appearance of the SiO_2 substrate. Therefore the interface reveals to be not a sharp one but rather a diffused one presenting a $Si_x O_y Sn_z$ structure (Fig7.b). The thickness of this diffused interface seems to be independant of the thickness of the deposited tin oxide layers. Besides for determining the thickness of the

deposit, the ellipsometry technique has been used to determine the refractive index of the tin oxide layers which gives a Ni = 1.85 ± 0.01 at a wave length of λ = 564.1nm and Ni = 1.87 ± 0.01 at a wave length of λ = 632.8 nm. These results are slightly lower than the one obtained for pure tin oxide equal to 1.9 and could be due to effect of the diffused interface on the ellipsometric measurements.

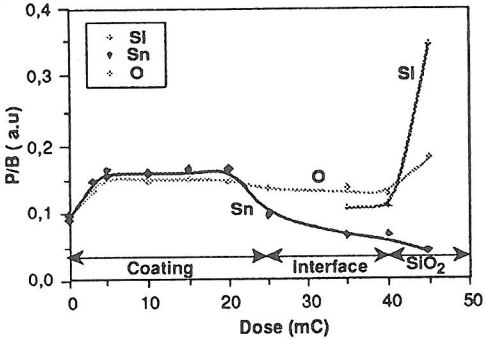

Fig. 7.a

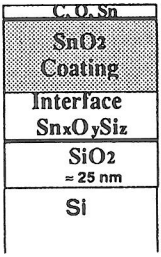

Fig. 7.b

Figure 7.a : Auger in depth-Profiles of tin oxide deposited on SiO_2/Si substrate
Figure 7.b : Estimated model proposed for tin oxide layer deposited on SiO_2/Si

4 Study of the ageing of the conductive tin oxides films

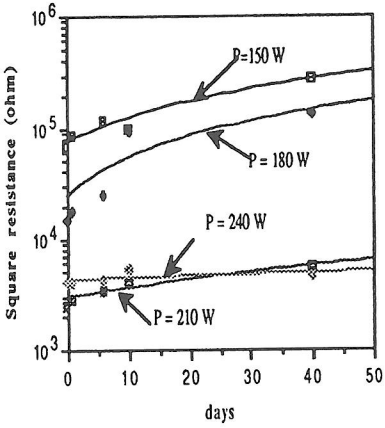

Fig. 8 : Ageing of the conductivity of the tin oxide films deposited as a function of power

The stability of the surface properties of conductive layers is an important issue. It has been observed that the conductivity of the deposited films decreased with time. In Figure 8 one can observe the ageing of the films expressed by an increase of the square resistance for different tin oxide films deposited at different plasma powers Since the results have been presented on a semi-log curve, a simple linear correlation has been calculated for the data of each curve in order to better represent the ageing kinetics by the slope of these correlations. This figure points out that the different films do not age in the same manner and that the films deposited at a high power age much slowlier than those prepared at a low power. Probably at higher powers the substrate temperature increases leading to a sort of annealing of the substrate which is known to increase the conductivity and to stabilize the properties of the deposited films [1,6].Therefore one can observe that the square resistance of the samples grown at 240 W is very slightly modified with time.

5 Role of bias voltage applied to the substrate electrode

The role of the substrate temperature and bias have been thoroughly investigated in the plasma deposition from Tetra Methyl Silane [7]. In order to study the role of the positive ion

bombardment on the structure of the deposited films, we have decreased the surface area of the substrate electrode by a factor of 4 and applied an RF power to this electrode for the same deposition time of 10 minutes.

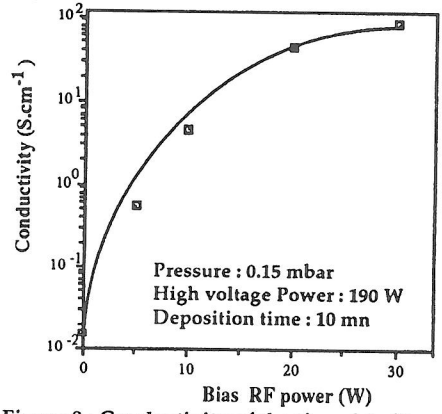

Figure 9 : Conductivity of the tin oxide films as function of the Bias RF Power

By applying a bias voltage to the substrate electrode one can clearly note that the conductivity of the films is increased by more than 3 orders of magnitude in function of the RF bias power or DC voltage (The bias voltage measured for a power ranging from 7 to 30 W varies between - 100 and - 350 V.) (Fig. 9). This is due to a modification of the chemical structure of the deposit i.e the tin content of the deposited films increases [11]. At the same time, the morphological aspect of the films changes with the applied bias voltage i.e. the deposit obtained without biasing presents a nodular structure (d≈ 0.2 mm) whileas with an applied bias voltage the surface presents a smooth dense structure [11].

Conclusion : In this work transparent conductive tin oxide films were deposited by a 13.56 MHz diode reactor from a mixture of Ar+ O_2 + TMT. Although the plasma mixture is a very complex one by coupling plasma diagnostic technique and surface spectroscopic ones interesting correlations have been obtained which allow to optimize the plasma reactor parameters such as the interelectrode distance. Since the study of the interfacial zone is crucial for the understanding of the junction losses in multilayer electronic devices, Auger analysis has been employed to determine the interface structure of our tin oxide layer deposited on a SiO_2/Si substrate. Finally applying a bias voltage to the substrate electrode seems to be a very promising route for the deposition of conductive thin films from organometallic precursors. Indeed in this case an increase of the conductivity of more than 3 orders of magnitude has been obtained for the tin oxide films deposited.

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