DEPOSITION OF TRANSPARENT CONDUCTIVE TIN OXIDE THIN FILMS DOPED WITH FLUORINE BY PACVD.

N. Bandoun, F. Alii, Khousni, A. Nouamoun
Laboratoire de Génie des Procédés Plasmas et Traitement de Surfaces
CNRS-INP, 14 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

ABSTRACT

The conductivity of plasma-deposited tin oxide films from a mixture of Tetrachloroethylen (TCE) and fluorine (F2) can be enhanced from 0.01 to 100 Ω-1 cm-1 by using the substrate by means of a second RF generator. In this work, an attempt was made to coat the films by a one-step process by introducing a fluorine source which was SF6, with the plasma mixture used for the deposition of SnO2. Optical emission spectroscopy and mass spectrometry were used to study the plasma phase and the characteristics of the film were carried out by different surface characterization techniques such as SEM, AES, and TSC. A rise of the electrical conductivity was obtained for very short times of SF6 introduced in the discharge from 0.1 to 1000 s. A rise was observed for higher flow rates, and a sharp decrease of the conductivity was obtained. For higher flow rates of SF6, competitive anion and fluorination processes involved by the uncharged anion in the discharge took place. Without this, the conductivity dropped below the theoretical transmission of the deposited films remained higher than 90%.

1. INTRODUCTION:

The conductivity of plasma-deposited tin oxide film, which is typically used in solar cells by doping them with elements possessing a different valence such as tellurium or antimony, is very sensitive to the nature of the substrates. Several studies have used CVD techniques for the deposition of tin oxide films. The precursor mixtures composed of SnCl4, and SF6, and where a very high concentration of the doping precursor has been used, in this paper, the tin oxide films deposited by PACVD from a mixture of C2H4 and TCE, were doped with fluorine atoms by introducing SF6 as the fluorine containing precursor in a triple configuration: the substrate was biased by a second RF generator.

The aim of this study was to introduce a very small quantity of fluorine in the structure of the films so as 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 on the physical chemical properties of the deposited films by different surface analyses.

2. EXPERIMENTAL:

The tin oxide films were deposited in a capacitively coupled RF reactor at a pressure of 10 Pa. The gas mixture was introduced through the high voltage shower electrode. The substrate electrode was biased by a second RF generator.
Silicon as the depositing precursor was introduced in the gas mixture in very small quantities with a maximum flow rate of 0.5% of the total gas flow. In order to control such very small flow rates, a MKS MKS flow controller of a maximum flow rate and range of 0.02 sccm of SF6 was used. The mass spectrometer used was a Balston FFT 500 which was able to detect neutral species, positive and negative ions in a mass range of 1-500 atomic mass units total. The optical emission spectroscopic studies were carried out on a Perkin-Elmer SpectraPro 500 spectrometer equipped with a grating in 250, 300, and 400 grating and a charge coupled device (CCD) camera.

3. RESULTS AND DISCUSSION:

3.1. Variation of the electrical conductivity.

The electrical conductivity of the oxide films deposited with various amounts of SF6 as the gas mixture was determined by four probe resistivity meter. As shown in Figure 1, the electrical conductivity increased with an increase of SF6 flow rates but only for a very small range of flow rates. Beyond the maximum of conductivity was obtained for a flow rate of SF6, the conductivity of the thin film rapidly increased. For higher values the conductivity slowly decreased.

\[ \text{Conductivity} = \frac{1}{\text{Resistivity}} \]

Figure 1: Variation of the electrical conductivity with SF6 flow rates.

To better understand how the presence of SF6 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.

3.2. Characteristics of the discharge.

Energy properties

The energy properties of the discharge was determined by measuring the rotational temperature of N2 and rotational temperature of OH which were carried out through OES studies. The rotational temperature remains constant at 150 K, whereas the rotational temperature slightly increases for values to 3500 K.
Figure 2: Variation of the vibrational temperature of N₂ and Rotational temperature of OH with SF₆ flow rate.

Figure 3: Variation of the dissociation rates of N₂ and SF₆ versus percentage of SF₆ present in the gas mixture.

These modifications in the plasma phase were able to modify the recombination processes and alter the properties of the films.


XPS analysis were carried out on the deposited films in order to determine the amount of chlorine present in the films. No chlorine was detected for SF₆ flow rates lower than 0.05 sccm. We have calculated the atomic chlorine ratios of the different elements present as a function of the flow rate of SF₆ introduced in the gas mixture. As shown in Figure 4, the increase of the flow rate of SF₆ increased the apparent chlorine ratio of the films in terms of atomic ratio.
By the co-occurrence of the photoplates of SnO and AES studies, we observed that there were characteristic peaks of SnO at 434.4 eV and 455 eV with a shoulder at 433.6 eV. Furthermore, the AES photoemission showed a peak at 485 eV which was attributed to Sb-Sb bonding. The latter was detected only when the SnO concentration was higher than 10%. With an increase in the SnO flow rate, an increase in the Sn-O bond was detected as well as a decrease in the Sn-O bond resulting from the decomposition of Sb species. A slow decrease of the Sn-O bond and an increase of the Sn-S bond, probably in the form of SnO bonded to SnO species as well as a formation of Sb-O bonds, was also observed. Therefore, the separation of SnO from Sn could be due to the contamination level observed on the surface.

FTIR studies showed by deposition of the evolved films on CsI pellets from SnO preserves the IR spectrum of the pure SnO, SnO deposited with 0.18% SnO with a decrease in the OII and OIII relative. We noticed the presence of two bands characteristic of SnO at 530 and 475 cm⁻¹ with and without SnO. The presence of SnO in the discharge resulted in a modification of the spectrum with two new bands which could correspond to OI and OIII bands. The bands at 530 and 475 cm⁻¹. But the modifications that could be pointed out by FTIR analysis occurred only when the amount of SnO in the discharge was higher than 10%. Flow rates of 0.1 sccm for lower flow rates, no modifications were observed by this technique.
SAXM studies

SAXM micrographs were done in order to see if the chemical modifications observed previously were associated to morphological modifications. As shown by the micrographs of figure 6, the morphology of the surface of the films was strongly modified by increasing the SF6 flow rate with the appearance of clusters with a mean diameter between 200-300 nm whereas the undoped tin oxide films were composed of small grains diameter 50 nm 1). This important modification of the morphology of the films probably was responsible for the change of the electrical conductivities.

EDX analyses made on the 200 nm clusters have shown that there were no differences between the chemical composition between the clusters and the film.

Figure 6: SAXM Micrographs of tin oxide films doped by fluorine: role of SF6 flow rate.

Experimental conditions: Ar+O2+SF6, plasma pressure 15 Pa.
Gas flow: 9 sccm, power 190 watts, bias voltage -120 Volts

Optical transmission studies

Optical measurements were carried out in order to see if the incorporation of fluorine in the discharge and consequently in the films induced a modification of the optical properties such as maximum optical transmission. As shown in Figure 7, the optical transmission was not modified when a high percentage of fluorine was incorporated in the films except optical transmission was higher than 90%.
4. CONCLUSION:

In this paper, the doping effect of tin with carbon on the electrical properties of the tin oxide films deposited by the reactive sputtering of a tin target in an atmosphere of oxygen and carbon dioxide was studied. It was found that an increase in the oxygen and carbon dioxide concentrations in the discharge chamber led to an increase in the electrical resistivity of the films. This effect was more pronounced at higher flow rates of the reactive gases. The results showed that the electrical resistivity of the films deposited at lower oxygen and carbon dioxide concentrations was lower than that of the films deposited at higher concentrations. The optical transmission of the films was also affected, with a decrease in the transmission observed for films deposited at higher concentrations of the reactive gases.

5. REFERENCES: