THE EFFECT OF BIAS AND TEMPERATURE ON THE DEPOSITION OF Au-CONTAINING PLASMA POLYMERIZED FLUOROETHANE

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ABSTRACT

The effect of a D.C. self-induced bias and of the substrate temperature are studied for the deposition of Au-containing plasma polymerized fluoroethane in a R.F. discharge. It is shown how it is possible to control discharge conditions, polymer cross-linking degree and aging effects on the composite film.

1. INTRODUCTION

An increasing interest has been devoted in last years to metal-containing polymer films due to their unique chemical and physical characteristics. In fact, the variation of the metal content in the polymer matrix allows the electrical properties and the optical transmission characteristics of the composite material to be changed in a very broad range. In particular, Au-containing plasma polymerized fluoroethane (Au-PPFE) exhibits attractive properties, eventhough a significative aging effect due to the mobility of gold clusters prevents its utilization for many applications.

In the present study we have deposited Au-PPFE films from a C_2F_6-20%H_2 mixture feeding a RF-triode reactor equipped with a gold target operated at a pressure of 140 mtorr [1,2,3]. This architecture allowed to obtain gold particles in plasma phase (through sputtering of Au target) and in the deposited material.

The reactor contains a second R.F. electrode, at controlled temperature, of lower dimensions with respect to the principal one, connected to this by means of a capacitive partitor: with this electrical system it was possible to study the effects of self-induced negative bias (U_S) and temperature (T_S) on the physical characteristics of the deposited films.

Actinometric Optical Emission Spectroscopy (AOES) was utilized as diagnostic technique of the plasma phase showing that the variation of the substrate bias does not affect significantly the electrical plasma parameters.

IR Spectroscopy, X-rays Photoelectron Spectroscopy and Visible Transmission Spectrometry have been utilized to study the modification of films characteristics as a function of U_S and T_S. It will be shown that both U_S and T_S induce the same type of modification in the films, leading to a more cross-linked film with a lower fluorine and a higher gold content. It has been also demonstrated that the aging effect due to gold particles coalescence can be definitely eliminated.

The reported phenomena can be justified by considering that a higher substrate bias increases the energy of the particles impinging on the growing polymer surface, while a higher temperature reduces the polymerization rate. This leaves the growing layer exposed to the impinging particle flux for a longer time. In both cases it can be concluded that the increase of the energy flux associated to the particle bombardment has the principal responsibility of the composite polymer chemical structure and of its improved physical properties.

2. EXPERIMENTAL APPARATUS

The schematic of the experimental apparatus and of the triode reactor is shown in Fig.1: the larger powered electrode (7 cm) can be covered by either gold or PTFE targets. The smaller powered electrode (3.6 cm) is the substrate holder. Its smaller dimensions ensure a minimal influence of the plasma electrical parameters when the bias is varied.

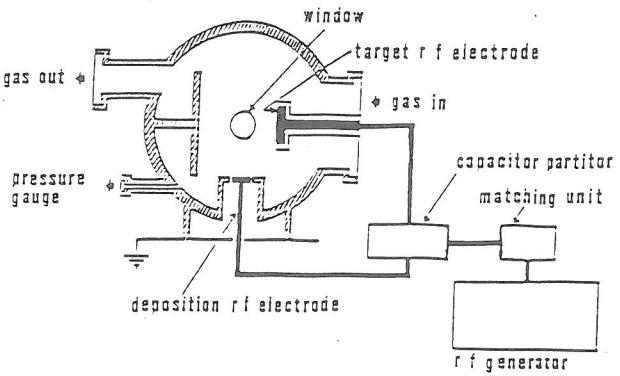

FIG.1: Schematic of the experimental apparatus.

A capacitive partitor connects, via a matching units, the R.F. generator (13.56 MHz) to the powered electrodes, delivering 200 Watts with the bias on the main R.F. electrode of about -500 Volts.

A small and constant flux of Ar-N_2-He as actinometers[2] is added to the main feed.

The visible spectrum emitted from the discharge is analyzed by a multiarray PAR-OMA III system.

The films were analyzed by Visible Transmission Spectroscopy, IR Spectrometry and X-rays Photoelectron Spectroscopy.

3. RESULTS AND DISCUSSION

AOES has been utilized to perform the diagnostic of the gas phase during all the experiments: in particular, the spectral features of Au (242.8 nm), CF_2 (254.13 nm), N_2 (400.1 nm), and Ar (415.86 nm) were followed.

From Fig.2 it can be seen that the emission intensities of the two actinometers (Ar and N_2, since He has an excitation threshold too high to be detected) are not influenced by the variation of the bias, U_S, up to -200 Volts. This allows a direct correlation of the emission intensity of the various species to their density in the ground state. Under this conditions CF_2 and Au emission intensities represent the gas phase densities of CF_2 produced by the decomposition of fluoroethane and of atomic gold produced by sputtering, respectively.

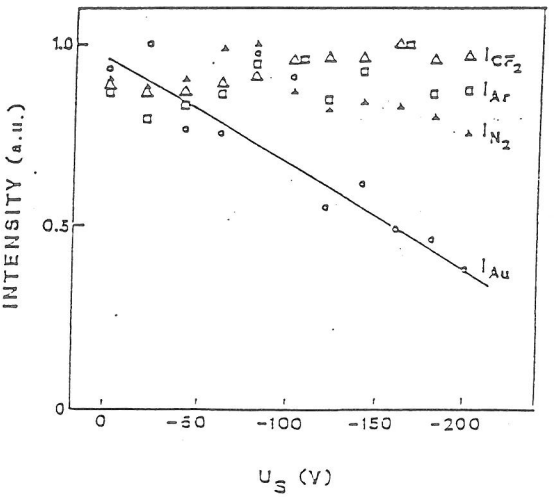

FIG.2: Trends of N_2 (▲), Ar (□), CF_2 (△), and Au (○) emission intensities when varying the substrate bias U_S.

On the other hand it appears from the data of Fig.2 that varying U_S the emission intensity of CF_2 radicals remains fairly constant while that of Au-atoms decreases. The concentration variations of sputtered gold atoms in the gas-phase has been shown to be due[1,2] to a decrease of

the product (positive ions flux) x (bias) at the target electrode when more power is delivered to the substrate electrode in order to increase its bias.

The chemical structure of Au-PPFE films, analyzed by XPS and IR spectroscopies, is markedly affected by experimental conditions of substrate electrode: in Fig.3 and 4 it can be seen that both U_S and T_S produce the same effect in the film, namely an increase in Au/C and a decrease in F/C atomic ratios.

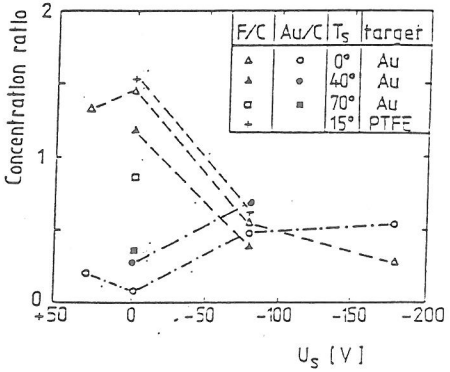

FIG.3: Effect of substrate bias U_S on the F/C and Au/C concentration ratios of films deposited at different temperature.

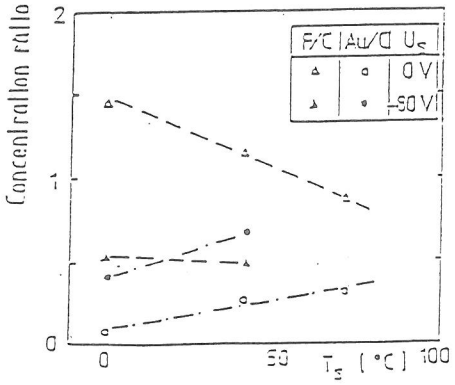

FIG.4: Effect of substrate temperature T_S on the F/C and Au/C concentration ratios of films deposited at different substrate bias.

These findings lead to think that T_S and U_S act in a similar way on the deposition process of the composite material. It is known that an increase in T_S decreases the deposition rate of fluoropolymer films deposited from C_2F_6/H_2 gas mixture (4): considering the same true for the Au-composite materials, an increase in T_S leaves the growing surface exposed to ion bombardment for a longer time; on the other hand, an increase in the negative value of U_S increases the energy of ions impinging on the growing film. As a consequence, higher values of T_S and/or U_S induce the same effect on the deposited material in that it increases the energy flux (EF) delivered by species bombarding the film surface. On the other hand, enhancing EF both a decrease of the more volatile organic matrix of the composite film and an higher cross-linking degree have to be expected. In fact, a more pronounced signal associated to the tetra-bonded C atom (284.6 eV) develops in our XPS spectra of C1s.

XPS spectra allow also an interpretation of IR spectra,

reported in Fig.5. It can be seen that, besides to a series of convoluted well known absorption peaks, corrisponding to CF_x groups, falling in the 1100-1250 cm^{-1} range, there is a peak, centered at 740 cm^{-1}, known as "amorphous band". We have shown that the ratio between the intensity of the IR bands centered at 740 and 1220 cm^{-1} is representative of the cross-linking extent of the material as determined by XPS.

This analysis allowed to find experimental conditions (high value of T_S and U_S) suitable for the preparation of stable Au-PPFE films which show no tendency to coalescence of the gold clusters contained in the organic matrix [1,2,3]. Polymer cross-linking leads, in fact, to a more rigid structure where "aging" can be reduced or fully eliminated, as it has been shown by visible spectrophotometry and wettability tests of our samples performed at various times after preparation [3].

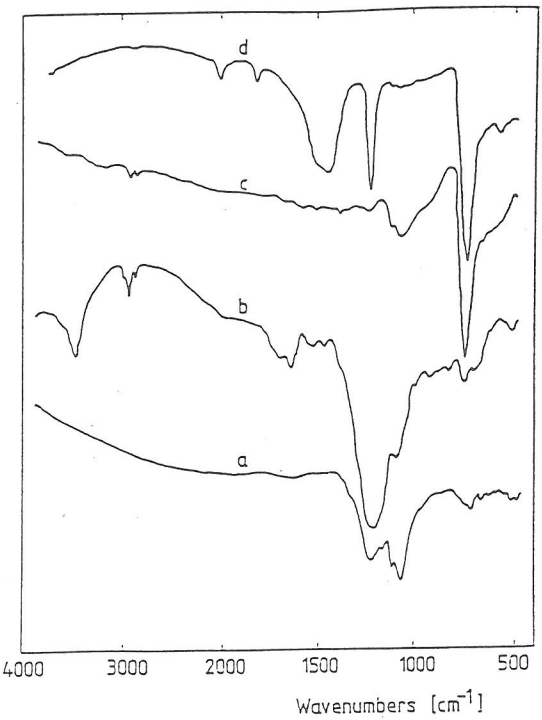

FIG.5: Effect of substrate bias U_S on the IR transmission spectra of films deposited at T_S= 20 °C. and a) U_S= +30 Volts b) U_S= 0 Volts c) U_S= -80 Volts d) U_S= -170 Volts.

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