PLASMA-SURFACE INTERACTIONS EFFECTS IN THE GROWTH OF METAL-FILLED PLASMA POLYMERS

L. Martinu[1], V. Pische[2], and R. d'Agostino[2]
[1]"Groupe des Couches Minces (GCM) and Department of Engineering Physics,
Ecole Polytechnique, Box 6079, Station"A",
Montreal, Quebec, H3C 3A7, Canada
[2]Dipartimento di Chimica, Universita di Bari,
Via Amendola 173, 701 26 Bari, Italia

ABSTRACT

Composite thin films were deposited by simultaneous plasma polymerization of a C_2F_6 monomer and sputtering of gold in a radio frequency glow discharge. Variations in the substrate bias voltage and/or the substrate temperature were shown to strongly influence the plasma-surface interactions in terms of the energy fluxes delivered to the growing films. As a result, important changes in the film structure, composition and surface wettability were observed.

1. INTRODUCTION

A negative bias potential U_B develops at the target in a radio frequency (RF) glow discharge where the powered electrode is capacitively coupled to the RF power supply. When introducing an active gas into such a type of reactor thin films may be deposited under low energy fluxes of charged particles (e.g. on the grounded or floating walls or substrate holders) or under high energy fluxes on the biased electrode. When a threshold bias value U_B is exceeded, the target material can be sputter-etched and incorporated into the films growing on less biased surfaces. These processes, occuring simulataneously in one reaction system, were used for the deposition of plasma polymers or hydrogenated amorphous carbon films containing metal clusters and the recent advances have been reviewed /1-3/.

It has been generally accepted that the properties of metal-filled plasma polymers depend strictly on the film microstructure, particularly on the metal volume fraction and cluster morphology /4-6/ which controls e.g. the anomalous optical absorption or percolation thereshold. In this respect, the gold-containing plasma polymerized fluorocarbons (PPFC) were predominantly investigated.

In usual cases, the desired amount of metal embedded in the dielectric matrix was achieved by regulating the rate at which the components are generated, i.e. by varying the feed gas composition (different monomer/argon mixtures), sputtering rate of the metal from the target electrode etc. Our present contribution is devoted to the study of plasma interactions with the growing composite films when different substrate biases or substrate temperatures are applied at constant parameters of the bulk plasma so that the effects at the plasma-wall interfaces leading to pronounced modification of the film microstructure can be observed.

2. EXPERIMENTAL DETAILS

The composite films were prepared in a "triode" deposition system consisting of a powered electrode capacitively coupled to an RF power supply (13,56 MHz), a large paralell grounded electrode, and a third temperature-controlled small electrode (substrate holder) placed perpendicularly in the gap between the larger ones at the edge of the plasma zone (for more details see ref. 7). The delivered RF power was divided using a variable capacitor assembly to provide development of negative bias voltage at the main target electrode (U_T) and at the substrate electrode (U_S).

In the first series of experiments the substrates (quartz, aluminum, glass) were mounted onto the third small electrode and the discharge was performed at 200 W of the total incident power (corresponding U_T was -480V) and a total pressure of 130 mTorr of the feed gas mixture - 83% C_2F_6/17%H_2 - at the total flow rate of 20 sccm. A sheet of gold or of teflon were used as targets at the main powered electrode. In the second series of depositions the substrates were placed on the grounded electrode and the RF powered electrode was covered by a stainless-steel target. Total power of 120W, pressure of 130 mTorr and a total flow rate 20 sccm of the C_2F_6/H_2 feed gas mixture were adjusted.

The film chemical structure was analyzed by X-ray photoelectron spectroscopy (XPS) in a Perkin Elmer PHI 548 system. Surface wettability was determined by measurements of the advancing (α_a) and receding contact (α_r) angles for water drops by a telescopic goniometer. Optical transmission was measured by a Cary-4 spectrophotometer.

3. RESULTS AND DISCUSSION

Increasing the negative substrate bias U_S (up to -170V) or the substrate temperature T_s (from 0°C to 90°C) showed qualitatively the same effects on the film composition. Namely, the gold component in the films was increasing whereas the concentration of fluorine was decreasing. As an example, the effect of T_s on the C(1s) core level spectra for films deposited at $U_S = 0$ V (ground potential) is illustrated in Fig. 1. The spectra were deconvoluted using a superposition of five peaks due to different chemical suroundings of carbon in agreement with previous XPS studies of PPFC/3,8,9/.

It can be seen, that the highest fluorine concentration in the films is reached at low T_s, and, compared with the dependences on U_S, substrate bias values near the ground potential. When U_s or T_s is increased, the peak due to CF_2 group (291.3 eV) diminishes, and the peak around 284.5 eV coinciding with quaternery carbon but also C-H photoemission signals becomes dominant. Similar effects on the composition were observed when comparing films grown with a teflon target at otherwise identical conditions. Nevertheless, the F/C ratio was always lower when the layers contained gold than in gold-free films.

The observed trends in the composition can be explained in terms of energy fluxes delivered to the growing films. When the negative bias U_S, is increased the enhanced ion bombardment of the surface leads to preferential losses in fluorine, and to a decrease in the deposition rate of the polymer component causing relatively larger amount of incorporated gold. Similarly, the increased substrate temperature causes a decrease in the deposition rate, particularly of the polymer. In average the actual surfaces are subjected to energy fluxes from the plasma region for a longer period of time.

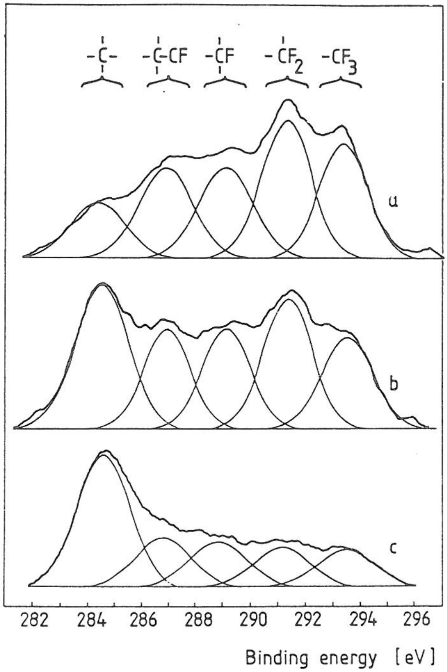

Fig. 1: C(1s) core level spectra of Au-PPFC films deposited at U_s = 0V and different substrate temperatures: a) T_s = 0°C, b) T_s = 40°C, c) T_s = 70°C.

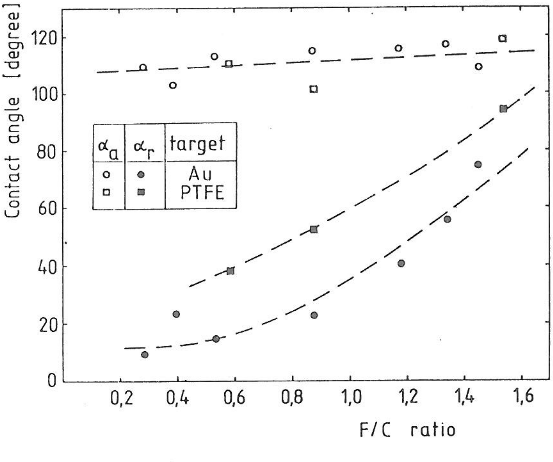

Fig. 2: Advancing (α_a) and receding (α_r) contact angles of Au-PPFC and PPFC films as a function of the XPS stoichiometric F/C ratio.

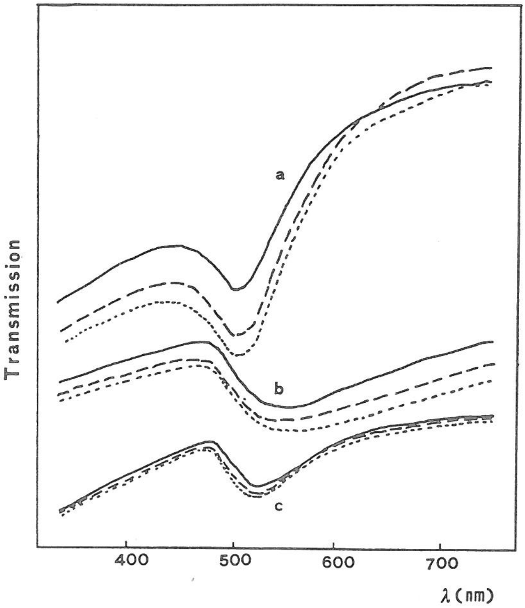

Fig. 3: Optical transmission spectra of Au-PPFC films deposited at different substrate conditions: a) $T_s = 0°C$, $U_s = 0V$, b) $T_s = 70°C$, $U_s = 0V$, c) $T_s = 70°C$, $U_s = -80V$, and measured as deposited (full line), after 22 days (dashed line) and after 42 days (dotted line).

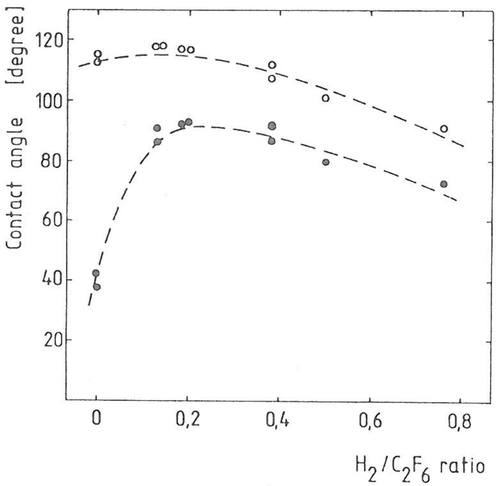

Fig. 4: Advancing and receding contact angles of PPFC films as a function of hydrogen concentration admixed to a C_2F_6 feed. Depositions were performed on the grounded electrode at the total power of 120 W.

The relation between the film composition and the advancing and receding contact angles is illustrated in Fig. 2. The F/C ratio appears to be the key parameter in FC systems controlling the wettability properties. It can be seen that the contact angle hysteresis, defined as the difference between α_a and α_r /10,11/, decreases when F/C is increased, and it always remains smaller for metal-free PPFC. The observed behaviour is in agreement with the model of a heterogeneous surface composed of distinguishable hydrophilic and hydrophobic regions linked with α_r and α_a, respectively /10/. In our films the high energy (hydrophilic) surface component, causing the decay of α_r, is represented by a direct presence of gold clusters and by accompanying higher degree of crosslinking and fluorine deficiency when elevated U_s or T_s are applied. It is interesting that the relatively simple measurement of surface contact angles can provide a good information about the surface composition, measured e.g. by XPS.

The increased energy fluxes supplied to the growing film surfaces at higher U_s or T_s cause higher surface migration of adsorbed surface species before the reactions termination. These effects give rise to a crosslinked and more rigid polymeric matrix and a completed nucleation of the metal component so that the films show improved temporal stability in their properties. Such situation is illustrated in Fig. 3 comparing optical transmission of films deposited at different U_s and T_s. The spectra are characterized by an anomalous optical absorption around 500 nm due to the optical resonance on gold clusters /4,6/. When T_s = 70°C and U_s = -80V were used no more pronounced time changes in the position and intensity of the absorption maximum were observed.

The surface properties of metal free plasma polymer were observed to be modified by the variation of H_2 concentration mixed with the C_2F_6 monomer for films deposited on the grounded electrode in the second series of experiments (Fig. 4). The large contact angle hysteresis for films resulting from 100% C_2F_6 is believed to be the consequence of the simultaneously competing etching process due to F atoms and highly fluorinated radicals in the gas phase. When about 20% H_2 is added to C_2F_6 optimum conditions are reached when a higher deposition rate and contact angles nearest to teflon are observed. In this case the reactions leading to scavenging fluorine in the form of volatile HF and, simultaneously, enhanced CF_2 radical concentration /9/ are most efficient. When still more H_2 is mixed in the C_2F_6 feed, both α_a and α_r decrease mostly due to the formation of hydrogenated fluoropolymer.

4. CONCLUSIONS

It has been shown in this work that both the increasing substrate bias and substrate temperature lead to a substantial decrease in fluorine concentration and an increase in gold concentration in Au-PPFC films. U_s as well as T_s may be considered as interchangeable parameters affecting the energy fluxes delivered to the growing surface from the plasma region. In this respect the higher energy fluxes result in a more crosslinked and relaxed microstructure giving rise to a better time stability of the composite films. A straightforward correlation between the contact angle hysteresis and the film composition (F/C ratio in the case of Au-PPFC) has been demonstrated. It has been also shown that the closest "teflon-like" film wettability for water can be reached when 20% of hydrogen is mixed to the C_2F_6 feed gas.

ACKNOWLEDGEMENTS

The authors are indebted to Drs F. Garbassi, M. Morra and E. Occhiello (Istituto Guido Donegani, Novara, Italy) for a vast assistance with the XPS and wettability measurements and for helpful discussions.

REFERENCES

1. H. Biederman and L. Martinu, in "Plasma Deposition of Polymers" (R. d'Agostino ed.), Academic Press, 1989.
2. H. Biederman, L. Martinu, D. Slavinska and I. Chudacek, Pure Appl. Chem. 60, 607 (1988).
3. E. Kay, Z. Phys. D - Atoms, Molecules and Clusters 3, 251 (1986).
4. L. Martinu, Solar Energy Materials 15, 21 (1987) and 15, 135 (1987).
5. J. Perrin, B. Despax, and E. Kay, Phys. Rev. B 32, 719 (1985).
6. J. Perrin, B. Despax, V. Hanchett, and E. Kay, J. Vac. Sci. Technol. A 4, 46 (1986).
7. L. Martinu, V. Pische, and R. d'Agostino, Plasma Chem. Plasma Process., submitted.
8. D.W. Rice and D.F. O'Kane, J. Electrochem. Soc. 123, 1308 (1976).
9. R. d'Agostino, F. Cramarossa, F. Fracassi, E. Desimoni, L. Sabbatini, P.G. Zambonin and G. Caporiccio, Thin Solid Films 143, 163 (1986); R. d'Agostino, F. Cramarossa, and F. Illuzzi, J. Appl. Phys. 61 (8), (1987).
10. R.E. Johnson and R.H. Dettre, J. Phys. Chem. 68, 1744 (1964).
11. J.D. Andrade, L.M. Smith and D.E. Gregonis in "Surfaces and Interfacial Aspects of Biomedical Polymers", (J.D. Andrade, ed.) Plenum Press, New York, 1985.