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# Incorporation of Metals into Fluoropolymer Films Synthesized by Plasma Techniques

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## ABSTRACT

A method is described to incorporate metals into fluorocarbon polymer films produced in a plasma environment by a simultaneous etching and polymerization process. The emphasis of this work is on a molybdenum-perfluoropropane system, and films produced in this manner were found to contain as much as 20% molybdenum by weight. Some aspects of their structure are discussed.

## INTRODUCTION

The glow discharge synthesis of polymers has been a particularly active area of interest over the past few years, in both industrial and academic laboratories [1-4]. Films produced in this way are generally uniform and pore-free, have superior physical, chemical, electrical and mechanical properties [1], and therefore lend themselves to many interesting technological applications. The incorporation of metals into these polymers is an attractive prospect, since it can be envisaged that careful choice of the metal and organic monomer (the term "monomer" is used here in its loosest sense, referring to the organic molecule in which the plasma is initiated, rather than the specific precursor to polymerization), as well as close control of the overall composition of the product, would greatly extend the scope of these plasma polymerized materials in, for example, electrical, magnetic and optical applications.

There are several possible routes to the incorporation of metals into plasma polymers and they include: polymerization of volatile organometallic compounds or copolymerization with other organic monomers [5, 6]; evaporation of the metal directly into the discharge region of a polymer-forming plasma excited in a suitable manner; and, combination of plasma etching with polymerization simultaneously. It is with the last of these that the present study is concerned.

The plasma chemistry of highly fluorinated organic molecules is of considerable importance in the field of plasma etching, and the selective nature of this process with regard to, for example, silicon and its compounds has in recent years received a great deal of attention in the microelectronics industry [7-10]. The generally accepted mechanism for plasma etching is via the formation of volatile species at the surface of the material to be etched which subsequently desorb and enter the gas phase. The volatile nature of $MoF_6$ makes molybdenum an excellent choice for this initial investigation.

## EXPERIMENTAL

A schematic of the diode reactor configuration employed in this work is given in Fig. 1, in which molybdenum is used as the cathode material (cathode in this context, referring to the electrode which attains an overall negative potential under plasma conditions). In this arrangement sputtering will play only a relatively minor role, although this competitive physical etching process will be expected to dominate for metals which do not form volatile molecular species.

The cathode is 4 in. in diameter and is positioned 4 cm above the anode maintained at ground potential. The etch rate is monitored by weight loss of the active part of the cathode. Previous work in these laboratories [10] has amply demonstrated that the relative rates of etching and polymerization, for a given fluorocarbon depends strongly on the fluorine/carbon ratio of the monomer injected into the plasma as well as the residence time [2], which is directly related to flow rate and pressure. Thus, while $CF_4$ is an efficient etching gas, $C_2F_4$ shows no etching but a high degree of polymerization. The choice of $C_3F_8$ for this preliminary investigation, therefore, has proved to give convenient rates of both etching and polymerization. The polymer films are collected for analysis on either gold or quartz substrates, mounted in the anode plane, which were weighed before and after deposition. The temperature of the substrates is variable,

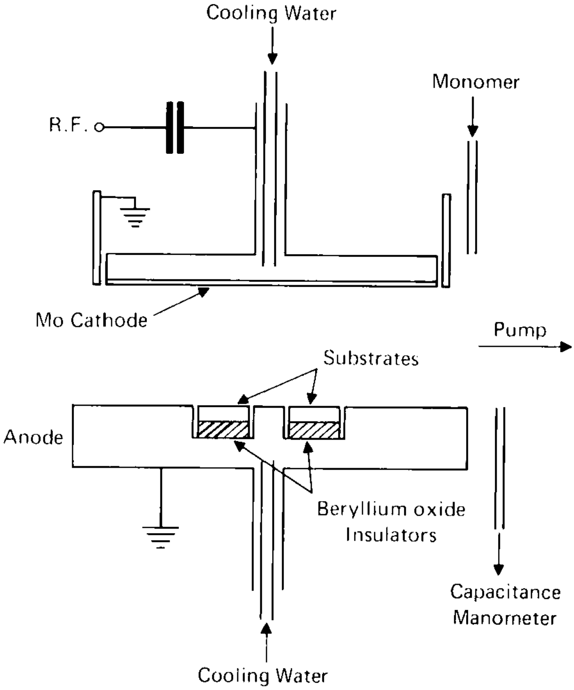


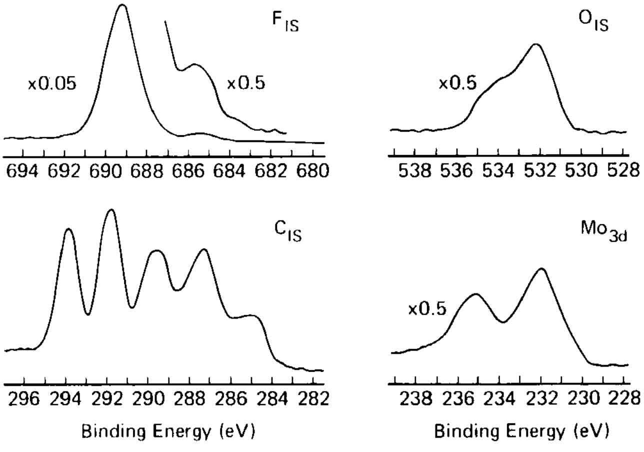
FIG. 1. Schematic diagram of reactor configuration.

as is the potential of the gold with respect to the anode. For the example presented in this study, the temperature was fixed at ~ 16°C and the gold substrates were electrically isolated from the anode.

The monomer flow rate was ~30 cm$^3$/min (at STP), the pressure in the reactor ~0.015 Torr, and the radio frequency power 100 W at 13.56 MHz. Under these conditions the molybdenum cathode etched at a rate of $1.6 \times 10^{-7}$ g/cm$^2$-sec, and the corresponding polymer deposition rate was $2.5 \times 10^{-7}$ g/cm$^2$-sec. The polymer films were studied by x-ray fluorescence and x-ray photoelectron spectroscopy.

## RESULTS AND DISCUSSION

Figure 2 shows typical $C_{1s}$, $F_{1s}$, $Mo_{3d}$, and $O_{1s}$ core level spectra of the polymer produced in the diode system. The $C_{1s}$ spectrum



(a) (b)

FIG. 2. $C_{1s}$, $F_{1s}$, $Mo_{3d}$, and $O_{1s}$ core level spectra obtained by using a Hewlett-Packard 5950B ESCA spectrometer.

clearly exhibits several carbon environments which may be assigned as $\underline{C}F_3$ (293.9 eV), $\underline{C}F_2$ (291.7 eV), $\underline{C}F$ (289.6 eV), $-\overset{|}{\underset{|}{C}}-$ (287.3 eV), and a small amount of CH contaminant at 285.0 eV. This spectrum is not unlike that of plasma polymerized tetrafluoroethylene [11], and it would seem likely that the precursors to polymerization are the same in these systems. This aspect will be discussed in more detail in a forthcoming publication. Now focusing on the $F_{1s}$ spectrum in Fig. 2, it is clear that in addition to the large full width at half maximum of the $F_{1s}$ signal centered at 689.2 eV, as is expected since this peak is a convolution of fluorine signals arising from several types of carbon-fluorine environment, the spectrum reveals a less intense signal to lower binding energy (685.7 eV) which may be assigned to the fluorine attached directly to molybdenum. The $Mo_{3d}$ signal is centered at a binding energy consistent with it being present in a high oxidation state [12]; however, the large full width at half maximum suggests that molybdenum is not present in a unique environment. It is not possible at this stage to postulate a mechanism based on the available data; however, further work in this direction is currently in progress and will appear in the literature in due course.

The ESCA spectrum also shows a significant amount of oxygen present in the polymer. This is characteristic of plasma polymers after exposure to the atmosphere and detailed discussions of this phenomenon can be found elsewhere [1, 13, 14]. It will suffice to say here that the presence of oxygen functionalities in these polymers is largely due to the reaction of free radical sites with molecular oxygen although the lower binding energy components are most likely to be associated with structural features involving oxygen bonded to the metal.

With a knowledge of the relative sensitivity of the ESCA spectrometer to the various core level signals, it is possible to estimate an empirical formula of $(C_3F_4O_{0.6}Mo_{0.3})_n$ for the surface regions of the polymer film. Estimation of the bulk molybdenum content by x-ray fluorescence gives a value of ~20% by weight. These estimates are in good agreement, demonstrating that, at least as far as the molybdenum content is concerned, the composition of the polymer on the ESCA sampling depth scale (~50 Å) is the same as that of the bulk.

The evidence presented here clearly demonstrates that the technique of combining plasma etching and polymerization is a convenient means to incorporate molybdenum into plasma polymers. The same principles can be applied directly to tungsten and other metals with sufficiently volatile fluorides, while the competitive physical sputtering process is expected to extend the scope to many more metals, and their compounds.

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