# ADHESION OF COPPER TO PLASMA-TREATED FLUOROPOLYMERS

M.K. Shi, J.E. Klemberg-Sapieha, G. Czeremuszkin,
L. Martinu and E. Sacher

Groupe des Couches Minces (GCM)
and Engineering Physics Department
École Polytechnique, Montreal, Quebec H3C 3A7, Canada

## Abstract

Low pressure plasma treatment can substantially enhance adhesion of metals to fluoropolymers. In the present work, we study the effects of $O_2$, $N_2$ and $H_2$ plasma treatments on different fluorocarbons: Teflon PFA, Teflon AF and plasma-polymerized trifluoroethylene. Using X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectrometry (SSIMS), we relate the improved Cu adhesion to the formation of Cu-N and Cu-O bonds at the interface, while moderately improved adhesion in the case of $H_2$ plasma is linked with the presence of a weak boundary layer containing C-H groups.

## 1. Introduction

Fluoropolymers possess many desirable characteristics which make them ideal for microelectronic and optical applications [1]. Our present interest in fluoropolymers is motivated by the fact that future ultrafast microelectronic devices demand minimal interconnection delay times (=RC), far lower than those presently achievable [2]. This may be accomplished in multilevel interconnects by using novel materials of lower dielectric constant, such as fluoropolymers, and lower resistivity metals, such as copper. However, the fluoropolymer/copper combination presents several manufacturing problems in the areas of processability, adhesion and etching.

Low pressure plasma treatment of polymer surfaces is one of the most efficient activation techniques for the enhancement of adhesion (for a recent critical review, see [3]). The interaction of a plasma with a polymer surface includes physical bombardment by energetic ions, UV irradiation and chemical reactions at the surface: These result in surface cleaning (etching), crosslinking and the incorporation of new functional groups. Plasma-introduced groups serve as surface active sites [4,5], and promote formation of chemical linkages at the interface [4,6].

Fluoropolymers are resistant to oxygen attack. Both surface degradation and oxygen incorporation were found to be small for $O_2$-plasma-treated PTFE (polytetrafluoroethylene) [7]. In contrast, $H_2$ plasma was reported to be very efficient in eliminating fluorine atoms from the surface, probably due to the formation of volatile HF gas [8]. The work in our laboratory has shown [9-12] that the adhesion of evaporated Cu to Teflon PFA (a copolymer of tetrafluoroethylene, TFE, and 2.5% perfluorovinyl propyl ether [13]), upon plasma treatment using several gases, decreased in the following order: $N_2 > O_2 > (N_2 + H_2) > (O_2 + H_2) > H_2$. Among these gases, $H_2$ was found to be the most efficient for fluorine elimination and $N_2$+$H_2$ for surface functionalization. Based on an X-ray photoelectron spectroscopy (XPS) study, it was proposed that strong Cu-N and Cu-O bonds formed at the interface are responsible for the substantially improved adhesion, while the lower efficiency of $H_2$ plasma could not be explained.

In the present work, we apply static secondary mass spectroscopy (SSIMS) for the study of Teflon PFA. XPS investigation is then focused on the interaction of Cu with the plasma-treated surfaces of Teflon AF 1600 (copolymer of TFE and 65% 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole [13]), and of plasma-polymerized fluorocarbon (PPFC): trifluoroethylene ($C_2F_3H$). The latter two types of fluoropolymers appear very attractive in the context of multilevel interconnects since thin uniform coatings can be produced from a vapor or a liquid phase.

## 2. Experimental Methodology

DuPont Teflon PFA films (50.8 µm thick) were used as received. DuPont Teflon AF 1600 was dissolved in Sigma Fluorinert FC-77, spun (~3 µm thick) onto a freshly cleaned Si wafer, and dried and annealed at 170°C in air for 3 hours. The PPFC films, about 1 µm thick, were deposited by plasma polymerization [14] in an RF (13.56 MHz) parallel plate electrode system onto Si wafers placed on a grounded electrode. The deposition conditions were: RF power density 0.8 $W/cm^2$, pressure 40 mTorr, monomer flow rate 10 sccm.

Films of Teflon PFA and AF were exposed to a microwave (MW, 2.45 GHz) discharge in $O_2$, $N_2$ and $H_2$, using a 30 cm long MW slow wave applicator. The treatment conditions were those leading to a strong copper adhesion determined earlier for PFA [9-11]. They are: pressure 200 mTorr, MW power 100 W, gas flow rate 50 sccm, treatment time 60 s.

After plasma deposition and treatment, the samples for XPS analysis were momentarily exposed to laboratory atmosphere while being transferred to the preparation chamber of a VG ESCALAB MKII system. Submonolayers of Cu were deposited by e-beam evaporation at a pressure of $2 \times 10^{-8}$ Torr at a rate of about 0.07 Å/s, determined by a quartz crystal microbalance. The XPS measurements were performed using a Mg anode (1253.6 eV), operated at 12 kV and 20 mA. Charging shifts were compensated for by setting the position of Cu and F peaks. Selected samples were analyzed by SSIMS [15] in a Charles Evans Time-of-Flight spectrometer with a pulsed Ga ion beam. For positive SIMS the parameters were: primary energy 10.5 keV; 600 pA d.c. current with a 4 ns width, pulsed at 5 kHz, resulting in 15 ions/pulse; the 1 µm diameter beam was rastered over a $97 \times 97$ $\mu m^2$ area.

## 3. Results and Discussion

In the first series of experiments, we attempted to explain a lower Cu adhesion to Teflon PFA when $H_2$ was used in the plasma treatment, as compared with other gases [9-11]. Results of the SSIMS measurements are summarized in Fig. 1. We present the fragments for which the most important variations have been observed upon plasma modification. The species at 12, 31, 50, 69 and 169 a.m.u. are constituents of the

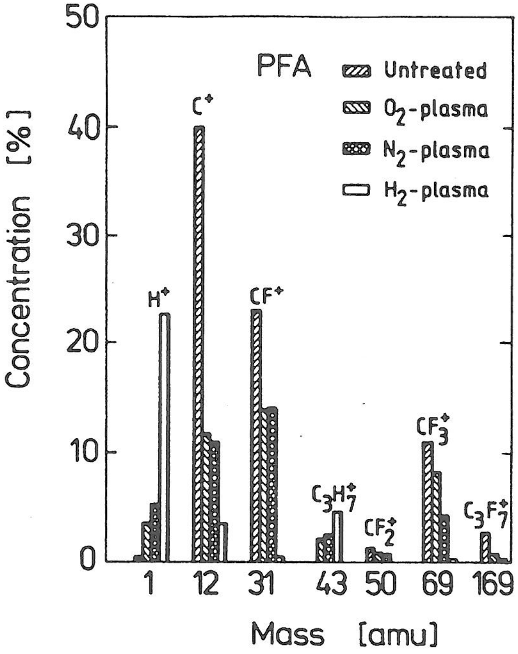

Figure 1: SSIMS relative concentrations of positive ions on the untreated and plasma-treated surfaces of Teflon PFA.

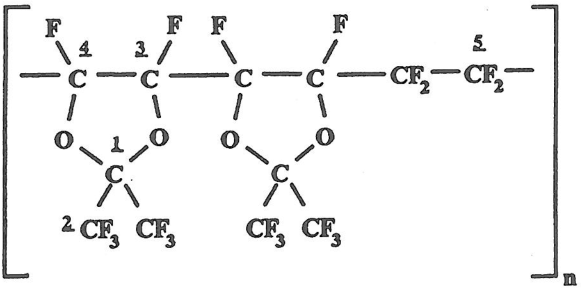

Figure 2: Chemical structure of Teflon AF 1600.

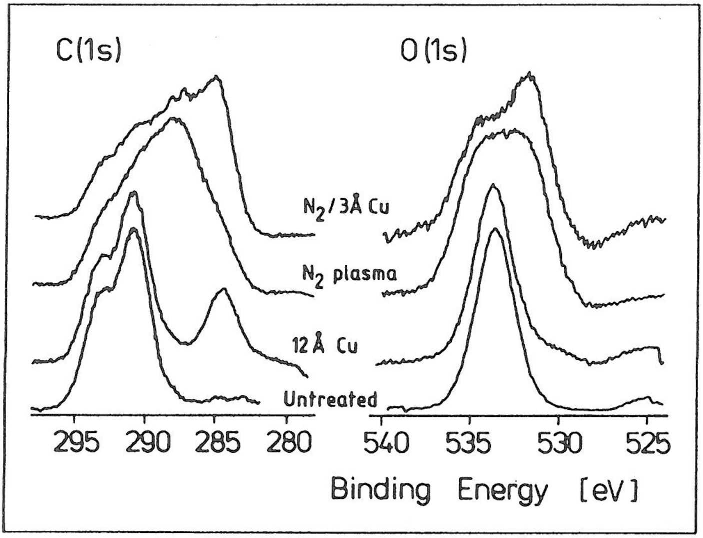

Figure 3: XPS C(1s) and O(1s) spectra of Teflon AF.

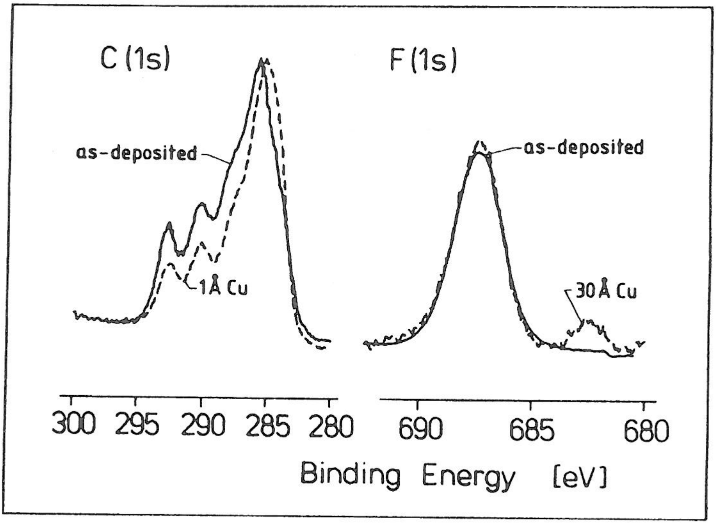

Figure 4: XPS C(1s) and F(1s) spectra of PPFC before and after Cu deposition.

untreated surface. These peaks are seen to markedly diminish upon plasma treatment due to the appearance of new groups, in particular at 1 and 43 a.m.u. One can see that the surface restructuring effects become more pronounced in the following sequence of discharge gases: $O_2<N_2<H_2$. This is in agreement with our earlier results using XPS and with the concept of plasma-surface interaction involving chemical reactions (e.g. HF formation) and vacuum ultraviolet (VUV) radiation (for example, the hydrogen Lyman $\alpha$ line at 121.5 nm) [3].

This suggests formation of $C_xH_y$-containing groups at the surface (the peak at 13 a.m.u., due to C-H, not shown here, is also substantially increased). These species are most probably constituents of a weak boundary layer, which can explain the systematically lower adhesion of Cu when $H_2$-containing plasma is involved. This rules out the possibility that intense VUV radiation alone in the $H_2$ plasma is sufficient to mechanically stabilize the metal/polymer interface by crosslinking, eventually leading to a higher adhesion. In this respect, He and He+$N_2$ discharges may be more efficient [12]. It should be noted that the peak at 43 a.m.u., following the $O_2$ and $N_2$ plasma treatments, represents a CNOH complex. In general, behavior similar to that for PFA has been observed for Teflon AF.

In the second series of experiments we studied the interaction of Cu with untreated and $N_2$-plasma-treated surface of Teflon AF (Fig. 2). The corresponding C(1s) and O(1s) XPS peaks are shown in Fig. 3. In the Teflon AF repeat unit, carbon can be found in five different environments (Fig. 2), and the C(1s) spectrum has recently been successfully analyzed (see ref. 16, where, however, the energy of the spectrum was not corrected): Carbon in position 2 contributes to the most intense feature centered around 291 eV, while carbons from positions 4 and 5 contribute to the lower peak around 293 eV. When Cu is evaporated, the C(1s) peak shape remains qualitatively unchanged, but a new feature appears around 285 eV, which contains components from the formation of C-C and Cu-O-C bonds [4,9]. The O(1s) peak preserves its form after the Cu evaporation; however, a new feature around 531 eV, due to a Cu-O bond, appears.

$N_2$ plasma treatment of Teflon AF resulted into incorporation 18 at.% of nitrogen, and it imparts a pronounced change to the surface chemical structure, including opening of the dioxolane ring and creation of linear fluorocarbon fragments. Substantial broadening of the C(1s) peak between 286 and 290 eV (Fig.3) suggests formation of new N- and O-containing groups. Upon evaporation, Cu reacts with these groups, as documented by the dominating feature around 285.5 eV due to Cu-O-C- and Cu-N-C- structures.

Surface restructuring is further exhibited by changes in the O(1s) peak (Fig. 3). After $N_2$ plasma treatment, the peak broadens, possibly to accomodate the contributions of C-O bonds (533.5 eV) and of the newly formed C=O bonds (532 eV). The more pronounced component, around 532 eV after Cu evaporation, confirms the formation of Cu-O-C bonds.

XPS data for the PPFC film are shown in Fig. 4. Even without deconvolution, the C(1s) envelope reveals the presence of C-C (C-H), CF, $CF_2$, and $CF_3$ groups, in general agreement with previously published results [14]. Upon Cu evaporation, the shape of the C(1s) peak remains basically unchanged, but the peak at 286 eV shifts to a lower binding energy, near 285.5 eV. This may be explained by the formation of Cu-O-C bonds. Copper appears to modify the fluorine chemical environment, as revealed by the F(1s) spectrum in Fig. 4, documented by a new feature at 682.5 eV, possibly due to metal oxyfluoride [17]. In all our studies, we observed a substantially higher sticking coefficient of Cu on the PPFC and the plasma-activated Teflon compared to the untreated surfaces, as judged by comparison with the nominal thickness measured by the microbalance.

## Conclusions

The complementary combination of XPS and SSIMS has been used to assess the interaction of Cu with three types of fluoropolymers. We have interpreted a moderately improved adhesion of Cu to the Teflon PFA surface, following $H_2$-containing plasma treatment, by the presence of a weak boundary layer containing C-H groups. On the other hand, we have observed creation of Cu-O-C and Cu-N-C bonds at the interface between Cu and $N_2$-plasma-treated Teflon AF and plasma-polymerized fluorocarbon. This we believe better explains the superior copper adhesion to fluropolymers.

## Acknowledgements

This work has been supported in part by the Natural Sciences and Engineering Research Council of Canada and by the Fonds Formation des Chercheurs et Aide à la Recherche of Quebec.

## References:

1. J.M. Park, L.J. Matienzo and D.F. Spencer, J. Adh. Sci. Technol., 5 (1991) 153.
2. S.P. Murarka, R.J. Gutmann, A.E. Kaloyeros and W.A. Lanford, Thin Solid Films, 236 (1993) 257.
3. E.M. Liston, L. Martinu and M.R. Wertheimer, J. Adh. Sci.Technol. 7 (1993) 1091.
4. L.J. Gerenser, J. Vac. Sci. Technol. A, 6 (1988) 2897.
5. S. Nowak, M. Colland, G. Dietler, O.M. Küttel and L. Schlapbach, J. Vac. Sci. Technol. A, 11 (1993) 481.
6. J. M. Burkstrand, Appl. Phys. Lett., 33 (1978) 387.
7. M.A. Golub, T. Wydeven and R.D. Cormia, Langmuir, 7 (1991) 1026.
8. D.T. Clark and D.R. Hutton, J. Polym. Sci., Polym. Chem. Ed., 25 (1987) 2643.
9. M.K. Shi, A. Selmani, L. Martinu, E. Sacher, M.R. Wertheimer and A. Yelon, J. Adhesion Sci. Technol., 8 (1994) 1129.
10. J.E. Klemberg-Sapieha, M.K. Shi, L. Martinu and M.R. Wertheimer, Proc. Ann. Tech. Conference - ANTEC '95, Society of Plastics Engineers, Boston, May 1995.
11. J.E. Klemberg-Sapieha, M.K. Shi, L. Martinu and M.R. Wertheimer, Proc. Int. Conf. on Plasmas - CIP'95, Société Française du Vide, Antibes, June 1995.
12. M.K. Shi, L. Martinu, E. Sacher, A. Selmani, M.R. Wertheimer and A. Yelon, Surf. Interface Anal., 23 (1995) 99.
13. DuPont Specialty Polymers, Technical Information Bulletins H-16577-1 and H-52454.
14. R. d'Agostino, ed., Plasma Deposition, Treatment and Etching of Polymers, Academic Press, New York, 1990.
15. P. Bertrand et al., to be published.
16. E. Sacher and J.E. Klemberg-Sapieha, Appl. Surf. Sci., submitted.
17. Y.-S. Chaug and R. Adams, J. Vac. Sci. Technol. A, 11 (1993) 2269.