THE DEPOSITION OF COPPER ONTO TEFLON AF1600: AN XPS COMPARISON OF VAPOR DEPOSITION AND SPUTTERING

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Electron beam evaporation and sputtering were used to deposit copper onto TeflonAF1600. Cu/polymer interfacial interactions were analyzed by X-ray photoelectron spectroscopy (XPS) and a scratch test was used to determine the so-called practical adhesion. Both evaporation and sputtering led to the loss of fluorine, as well as the formation of C-O• free radicals and Cu-C interfacial bonding. Additionally, the higher energies of sputter deposition led to the loss of oxygen and the formation of inorganic fluorides. The adhesion of copper was greater in the case of sputtering.

INTRODUCTION

The need of the semiconductor industry to increase the signal transmission speed beyond the present limit of 300 MHz requires faster transmission lines. This is because the overall speed of large, high-density chips is presently not limited by the transistor speed but, rather, by the on-chip circuits that connect them[1]. Specifically, the resistance (R) of the conductors and the capacitance (C) of the insulators cause what is known as an "RC" time delay, which limits the chip speed when it is larger than the inherent switching time of the transistor. The goal of the

microelectronics industry of reducing the RC time delay must be achieved for smaller dimensions and larger die sizes. This is a difficult challenge, for interconnects with smaller cross sections have higher resistances, as do the longer lines found in larger dies. Further, thinner dielectrics have higher capacitances. Thus, one is limited to any of three ways to reduce the RC delay time: (1) decrease R by using a higher conductivity metal, (2) decrease C by using dielectrics having lower dielectric constants and (3) decrease the length of the metal lines by using multilevel interconnect devices.

Copper, for example, having a resistivity 65% of the presently used aluminum[1], is seen as the most promising alternative metal, while fluoropolymers such as the Teflons, which have dielectric constants near 2, are considered as potential replacements for polyimides and SiO_2. The well-known chemical inertness of the fluoropolymers has created a strong interest in the metal-fluoropolymer interface and any specific reactions between them, in situations in which strong interfacial adhesion is required. This is the case for multilevel interconnect devices, which are made of alternating layers of polymer and metal. Thermal and hygroscopic expansion coefficient mismatches introduce interfacial stresses during the fabrication process. Any tendency to breakdown of the device due to these stresses must be prevented by strong interfacial adhesion[2].

Diffusion barriers, such as TiN or Ta were not considered at this stage because the extensive diffusion of copper into Teflon AF1600 has not yet been demonstrated. In the present work, we focused on the copper/Teflon AF1600 interface. Copper provides benefits from a reduced resistivity and a relatively good electromigration resistance. In addition, it can be deposited with excellent step coverage and is capable of filling narrow, high aspect ratio contacts and vias. It can also be deposited at relatively low temperature, which is a technological advantage[3]. Teflon AF1600, the Teflon we have chosen to consider, is a copolymer of 35% tetrafluoroethylene (TFE) and 65% 2.2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole (TDD) and is manufactured by DuPont; it has the repeat unit structure $-(TFE)-(TDD)_2-$. Teflon AF1600 also has the distinct advantage of being soluble in perfluorinated solvents, permitting its deposition by spin-on techniques[4].

The copper metallization of different types of Teflon, such as Teflon PFA and FEP, has been studied in our laboratory in an attempt to elucidate chemical interactions at the interface[5,6]. We showed that these surfaces are not easily attacked by copper. In our previous study of copper deposition onto Teflon AF1600[7], we provisionally related adhesion to the presumed formation of Cu-O bonds at the interface. Here, we consider specific reactions, based on the separated peaks of XPS spectra.

EXPERIMENTAL

The copper/Teflon AF1600 interface was studied using X-ray photoelectron spectroscopy (XPS), which is a convenient method because of its high surface

sensitivity. The base pressure in the analysis chamber of our VG ESCALAB 3 Mark II spectrometer was 10^{-9} Torr. No electron flood gun was used to reduce sample charging during the data accumulation. The spectral resolution for our Mg K_{α} source was measured to be 0.8 eV. The XPS spectra were accumulated under conditions of minimal exposure to the X-ray source (10 mA and 6 kV), in order to avoid degradation of the Teflon surface during analysis[8].

Teflon AF1600 was purchased from DuPont as a clear solution containing 12% solids and was further diluted 50% in Sigma Fluorinert FC-77 before application. For both vapor deposition and sputtering, the Teflon AF1600 was spun onto a freshly cleaned Si wafer at a spin speed of 3000 rpm. After air drying at room temperature, the samples were baked at 115°C for 15 minutes and then annealed at 165°C for 3 hours. To obtain maximum uniformity of coating thickness and enhanced adhesion, a supplementary heating was performed at 300°C for 15 minutes, as recommended by the manufacturer[4]. A final Teflon thickness of 1-2 μm was obtained.

The spectrometer possesses a preparation chamber where vapor deposition and sputtering were carried out without exposing the samples to air. Our evaporation unit is an electron beam evaporator similar to the one developed by Waldrop and Grant[9,10]. A thin wire of pure copper was positioned 9 cm from the sample and biased at +6 kV. A nearby wire filament acted as an electron source. Evaporation of the target took place at electron bombardment currents of 15 mA, at a pressure of 2×10^{-8} Torr. An evaporation rate of 0.2 nm/sec. and vapor deposition times of 2, 4, 6 and 12 seconds gave nominal copper layer thicknesses of about 0.4, 0.8, 1.2 and 2.4 nm, respectively, as measured by our quartz crystal monitor.

Our sputtering unit was also mounted in the preparation chamber of the spectrometer. The target was a 99.9% pure copper plate and was sputtered by Ar^{+} ions at an energy of 6 kV. The intensity of the Ar beam was controlled by a focusing electrostatic lens, using an excitation potential of 4 kV. The Teflon samples were positioned at a distance of 5 cm from the sputter source at an angle of 65°. A sputtering rate of 0.4 nm/min and sputtering times of 1, 2, 4 and 10 minutes gave nominal copper layer thicknesses of 0.4, 0.8, 1.6 and 4 nm, respectively (in the case of sputtering, our angle-resolved studies showed that was no metallic copper layer on the Teflon AF1600 surface but, rather, the reacted copper was uniformly distributed throughout the observable depth).

For evaporated copper, two sorts of samples were used for the measurement of practical adhesion: after the evaporation of 0.15 μm of high purity copper onto 0.7 μm Teflon substrates on glass, one sample was post-annealed in vacuum at 200°C for 30 minutes. Practical adhesion was determined by a microscratch tester (MST) developed at CSEM, Switzerland[11], using a Rockwell C hemispherical diamond stylus of 0.8 mm radius. At a table speed of 5 mm/min, a progressively increasing load ranging from 0.01 to 3 N was applied at a rate of 1 N/min. The critical load failure criterium was arbitrarily considered to be the

moment when the copper layer began to be completely and consistently removed from the Teflon surface. It was determined by optical examination, using an optical microscope and a scanning electron microscope (SEM). For both non-annealed and annealed samples, five scratch tests were carried out and the results were averaged.

Spectral peaks were separated using an in-house nonlinear least-mean-squares program. The Gaussian / Lorentzian ratios and the Full Width at Half Maximum (FWHM) values used were those determined by us for other fluoropolymers[12], as it is seen in Table 1.

Table 1. Gaussian/Lorentzian ratios and FWHM for C, O and F XPS spectra.

	C1s	O1s	F1s
G/L	40/60	60/40	30/70
FWHM (eV)	1.8	2.0	2.0

A Shirley background subtraction was made prior to peak separation, and charge compensation was carried out by peak alignment: the $Cu2p_{3/2}$ peak for the thickest vapor-deposited copper layer was arbitrarily placed at a binding energy of 931 eV, which is a value attributed to bulk copper[13]. This places the major F1s peak, to be discussed below, at 687.3 eV. This shift, subsequently carried out for all the samples, gave C1s, O1s and F1s peak alignments for all the spectra to within ±0.1 eV.

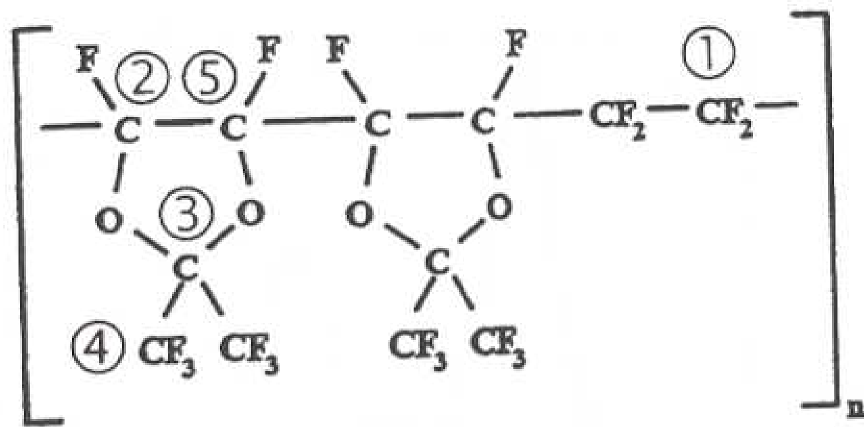
The relative concentration of each element of interest was determined from the peak area divided by the atomic sensitivity factor, also determined in our laboratory. To compare elements having different electronic mean free paths, the concentrations were corrected using the ratios of the mean free paths of the element being compared[14].

RESULTS

The repeat unit of the pure Teflon AF1600 and its XPS spectrum was discussed in a previous paper[12]; it is seen in Fig.1. As it can be noticed in this figure, the five peaks under the envelope are attributed to the five carbon environments shown.

Vapor Deposition

1) C1s spectra. A typical C1s spectrum is presented in Fig. 2a. The spectrum of the pure Teflon AF1600 is easily recognizable in the spectrum of the



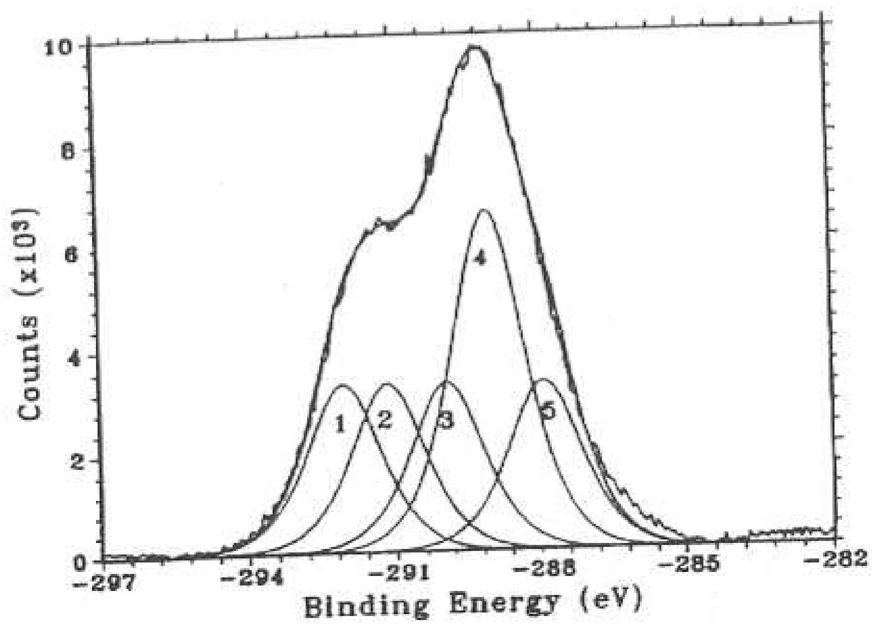
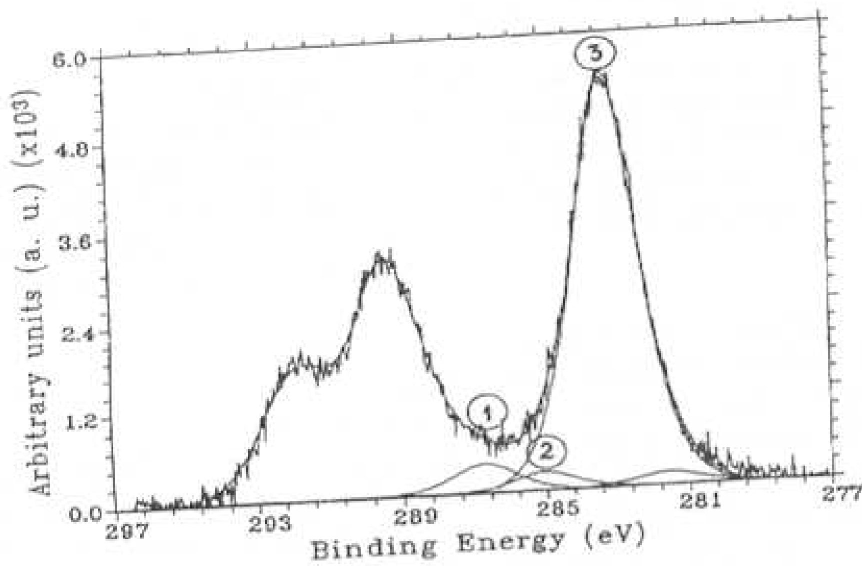


Figure 1. The structure of the Teflon AF1600 repeat unit and its XPS spectrum.

metallized sample above a binding energy of 287 eV. The new contribution arising at lower binding energy was too wide to accommodate one peak. Three supplementary peaks, placed at 283.7, 285.4 and 287.3 eV were necessary to fit the envelope. A fourth peak was infrequently required at 282.0 eV but there are



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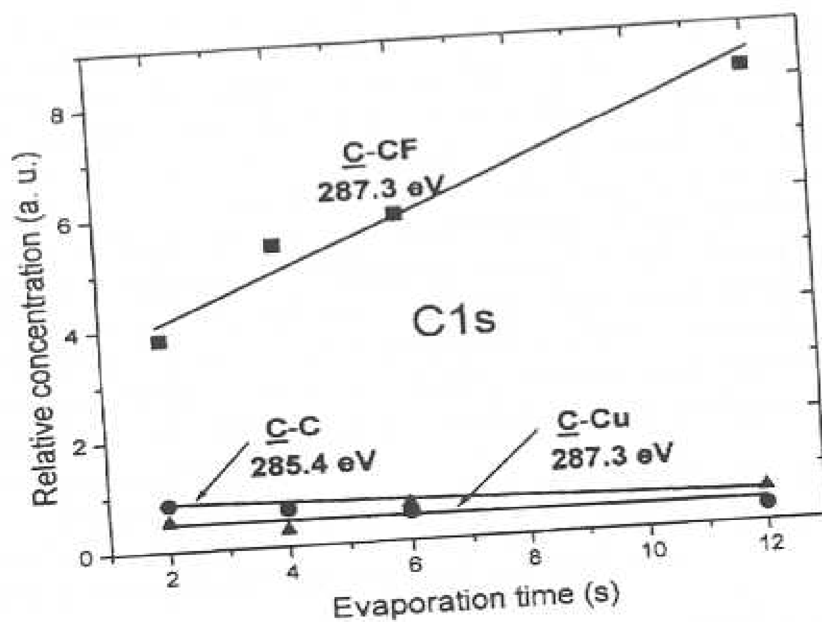


(b)

Figure 2. a) C1s spectrum for 12 seconds of vapor deposition. Peaks 1, 2 and 3 are attributed to the formation of C-CF, C-C and Cu-C, respectively; b) Evolution of the newly formed C1s peaks on vapor deposition.

serious doubts about its existence; its relative area represents 4.6% or less of the total area. Peak 1, 2 and 3 are attributed to C-CF, C-C and C- Cu, respectively[15].

The evolution of these three supplementary peaks is shown in Fig. 2b. Peak 3, which is associated with carbide formation, increases linearly. Because it does not extrapolate to zero, there is evidently a high initial rate of carbide formation. Peaks 1 and 2 are due to the partial and total loss of fluorine, respectively. These processes occur at the onset of deposition and remain constant thereafter. Their similar evolution suggests that both processes are triggered by the initial deposition of copper.

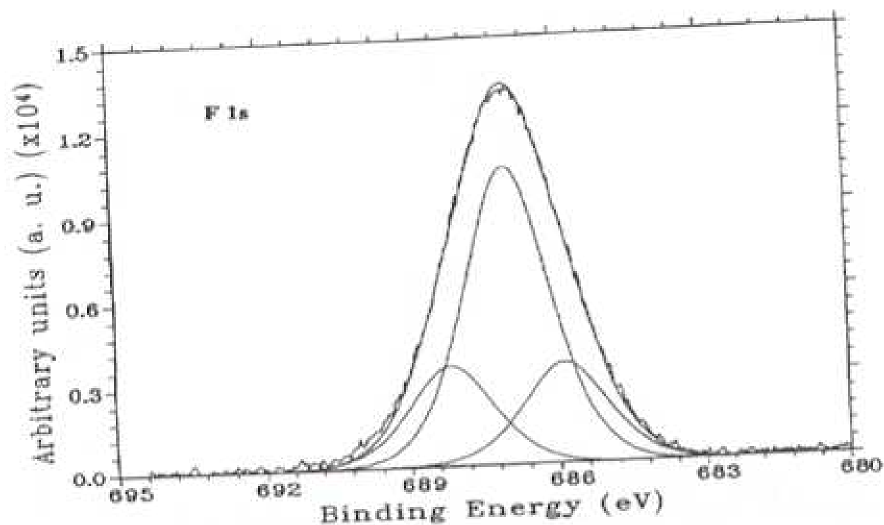
2) F1s spectra. A typical F1s spectrum is presented in Fig. 3a. The area under the envelope decreases slowly, showing a total loss of about 10% fluorine, which is in good agreement with the degradation of C1s spectra. As reported in an earlier paper[14], the fluorine spectrum in pure Teflon AF1600 could be separated into three peaks assigned to CF, CF_2 and CF_3 in the ratio 1:1:3. The evolution of F1s peaks is shown in Fig 3b. The original three peaks decrease essentially in the same ratio of 1:1:3, suggesting that the fluorine is lost uniformly.

3) O1s spectra. Fig. 4a shows a typical O1s spectrum. It was separated into four peaks, the two original peaks of Teflon AF1600 at 532.6 and 533.4 eV, and two newer ones at 529.6 and 530.4 eV appearing on copper deposition. Pairs of peaks at identical chemical shifts indicate that the two slightly different oxygen environments of Teflon AF1600 have equal probabilities of attack by copper.

The chemical shift of the newer peaks toward lower binding energies indicates a more electronegative environment, suggesting the possible generation of oxygen free radicals via O-C bond breaking. Thus, the formation of $-O^{\bullet}$ is expected to produce a shift to lower binding energies; the $-C^{\bullet}$ simultaneously produced may react with another similar free radical to form C-C bonds, contributing to peak 2 in the previously discussed C1s spectrum (Fig. 2a), or it may be obscured by other peaks. Another possible attribution of the new peaks, the formation of C-O-Cu, is discounted because associated peaks in the C1s and $Cu2p_{3/2}$ spectra do not exist.

The evolution of the O1s peaks is shown in Fig. 4b. Vapor deposition occurs with little loss of oxygen. The rate of formation of oxygen free radicals is higher at the beginning before falling to a constant value.

4) $Cu2p_{3/2}$ spectra. A typical $Cu2p_{3/2}$ spectrum is presented in Fig. 5a. As the amount deposited increases, the envelope becomes narrower, with FWHM values decreasing from 2.48 to 1.81 eV, indicating the noticeable presence of Cu^0. As already mentioned, this latter peak was arbitrarily placed at 931 eV.
The relative concentration of carbide present at the interface was determined from the ratio between the total amount of copper and the concentration of C-Cu measured from the C1s spectra. This ratio remained essentially unchanged,



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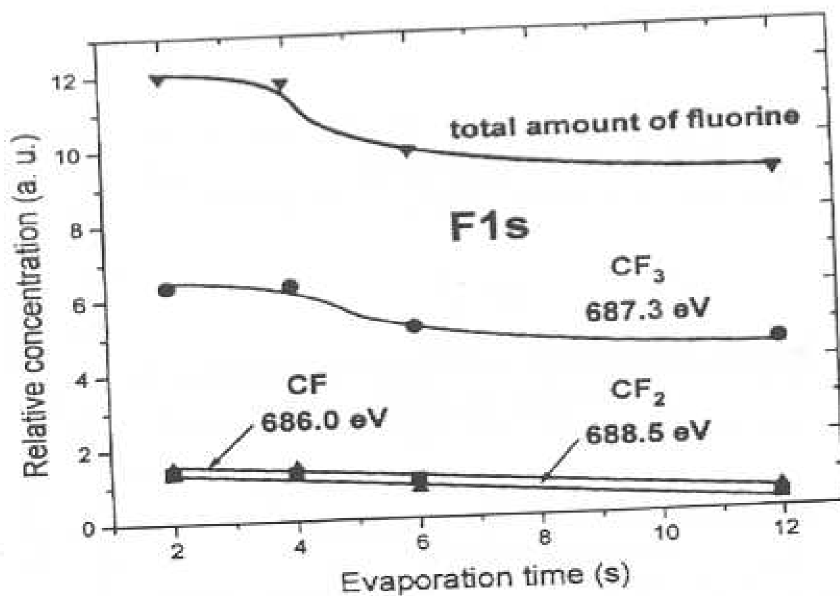

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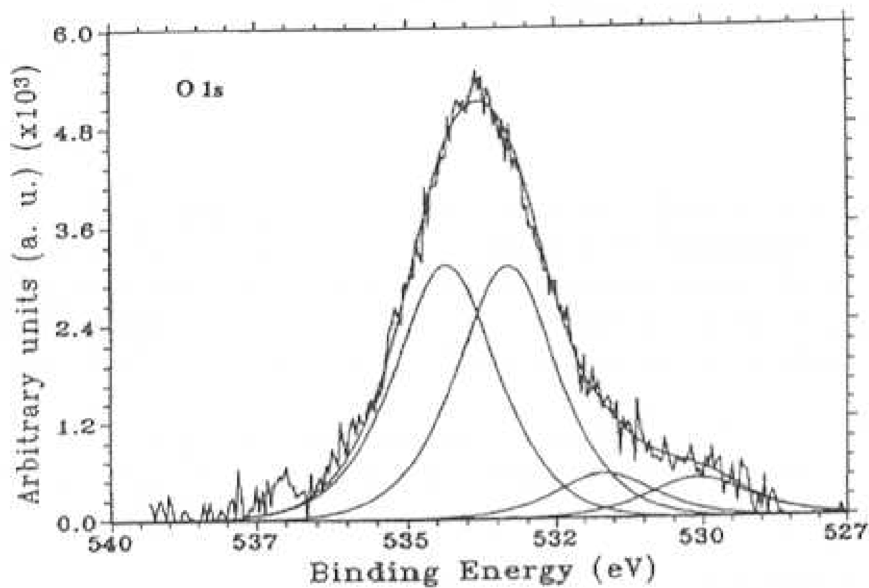
Figure 3. a) F1s spectrum for 2 seconds of vapor deposition; b) Evolution of the F1s peaks, as well as the total change of fluorine on vapor deposition.



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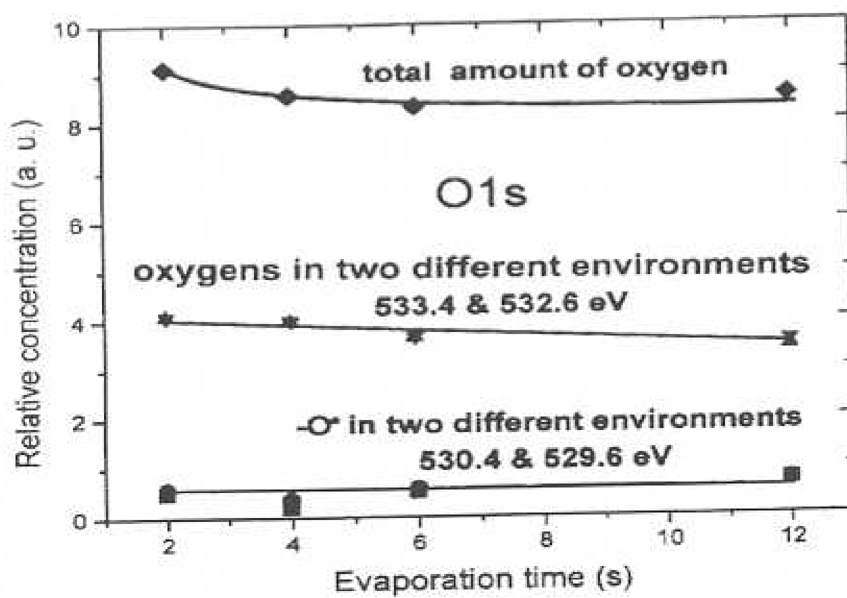


(b)

Figure 4. a) O1s spectrum for 6 seconds of vapor deposition; b) Evolution of the O1s peaks, as well as the total change of oxygen on vapor deposition.

showing that about 50% of the deposited copper remained in the metallic state. The evolution of the Cu^{I} peak and the carbide peak from the C1s spectra are shown in Fig. 5b.

Sputtering

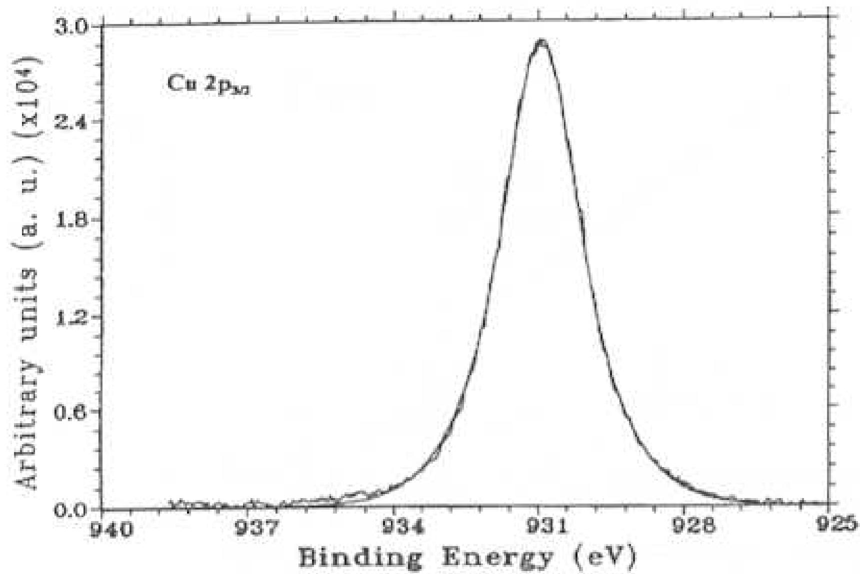
In general, the spectra of sputtered samples show characteristics qualitatively similar to those found for vapor deposited samples. The positions of the separated peaks remained identical to those in the case of vapor deposition to within ±0.1 eV. Nevertheless, there are several differences in the evolution of the peaks. Further, some new peaks indicate the formation of additional species.

1) C1s spectra There are no important differences compared to the spectra of vapor deposited samples. Similar evolutions are found for the C-CF, C-C and C-Cu, as seen in Fig.6.

2) F1s spectra As shown in Fig. 7a, the spectrum indicates a new peak at a binding energy of 682.5 eV. Its evolution, presented in Fig. 7b, indicates it increases with the amount of coverage. It is attributed to F^{-} ion[15]. The other peaks are the ones normally found in pure Teflon AF1600 in a constant 1:1:3 ratio.

3) O1s spectra Unlike the case of evaporation, where the loss of oxygen was negligible, the amount of oxygen lost on sputtering was about 30%. The total amount of oxygen declined at the onset of the deposition before stabilizing after 4 minutes. The loss of bonded oxygen from the continually forming $C\text{-}O^{\bullet}$ free radicals accounts for this behavior. An equilibrium between these two oxygen species is established after several minutes, as seen in Fig. 8.

4) $Cu2p_{3/2}$ spectra The $Cu2p_{3/2}$ spectrum, which is presented in Fig. 9a, differs qualitatively from the spectrum of vapor deposited copper sample in Fig. 5a. The position of the major peak during sputtering was established, relative to the fluorine peak at 687.3 eV, to be at 932.0 eV; this indicates that there is no Cu^{0} left unreacted, nor is any found visually. A new structure develops at the higher binding energy side of the $Cu2p_{3/2}$ spectrum. Two additional peaks, at 943.3 and 936.0 eV, are necessary to fit the envelope. These positions suggest a second, more electropositive, Cu^{I} environment and the presence of Cu^{II}, respectively. In addition, the presence of a shake-up (not shown) is clear proof for the existence of the Cu^{II} state. Figure 9b shows the correlation between the concentration of elements for different species after the sensitivity and probe depth corrections. Thus, the continuous lines represents the evolution of the three copper peaks shown in Fig. 9a. The continuous thicker line represents the sum of fluoride peaks ($\underline{Cu}^{I}F^{-}$ (934.3) eV and $\underline{Cu}^{II}F_2$ (936.0 eV) and it is easily seen to correlate very well with the evolution of the fluoride peak F^{-} (682.5 eV), represented as a dashed line.



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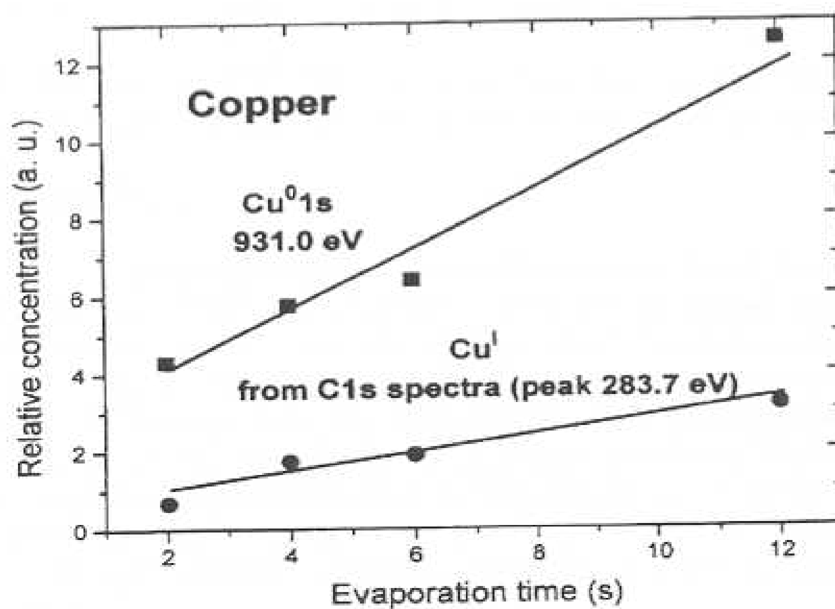


(b)

Figure 5 a) $Cu2p_{3/2}$ spectrum for 6 seconds of vapor deposition; b) Evolution of Cu^0 and Cu^I (estimated from peak 3 of the C1s spectrum, assuming CuC formation).

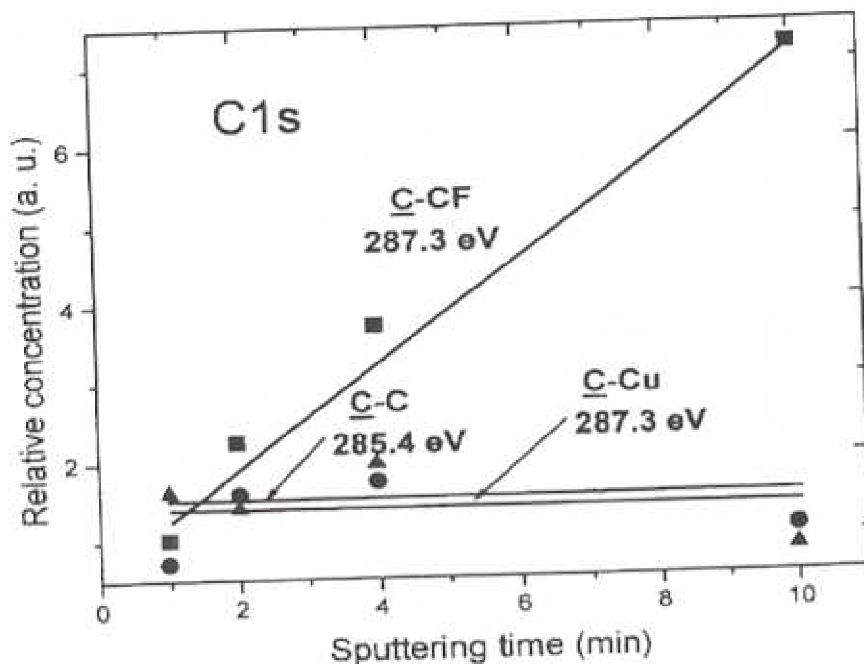


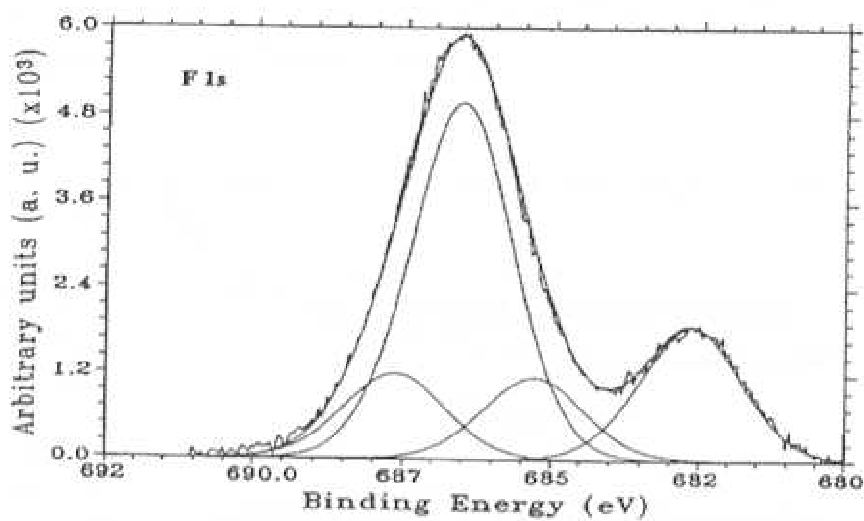
Figure 6. Evolution of the newly formed C1s peaks on sputtering.

The carbide correlation dashed between the continuous line, CuC (932.0 eV) and line, CuC (287.3 eV), supports the assumption that Cu_nC species are formed.

Adhesion Results

a) Vapor deposition For unannealed samples, failure during scratch testing began at an average load of 0.12 N. With increasing load, small delaminations were evident at 1.65 N and, at an average of 2.2 N, larger Cu delamination were seen. In the post-annealed case, tiny cracks appeared at an average 0.28 N. As the force increased, these tiny cracks became small delaminations along the path. It appears that failure under tension, occurring at an early stage for nonannealed samples, delays the delaminations to higher force values. Nevertheless, failure in unannealed samples began earlier than in annealed ones. While both samples showed weak adhesion properties, annealing to 200^{0}C caused an increase in adhesion.

b) Sputtering For unannealed samples, failure manifested itself as the sudden onset of delaminations at a load of 0.56 N. Annealing at 200^{0}C caused some cracking of the copper coating without delamination, suggesting a marked



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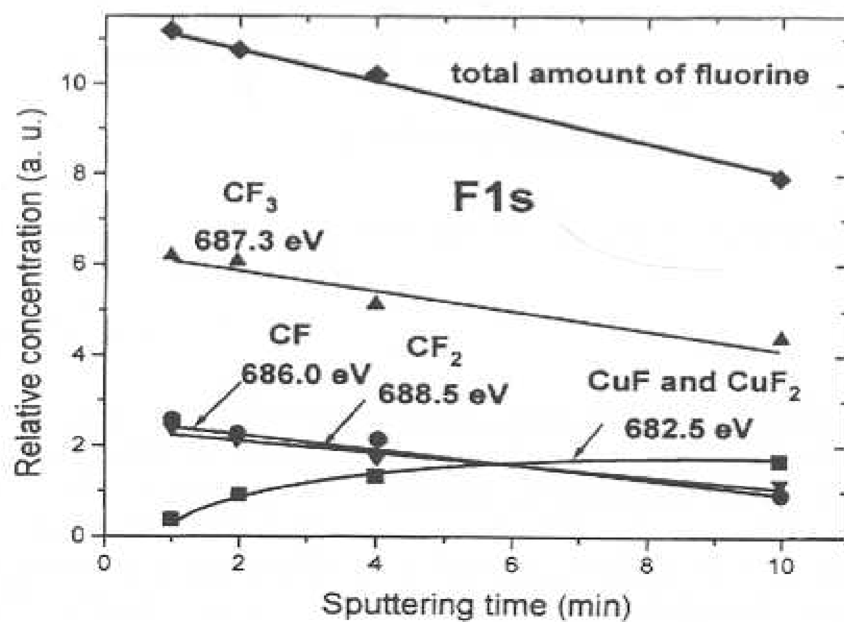


(b)

Figure 7 a) F1s spectrum for 10 minutes of sputtering; b) Evolution of the F1s peaks, as well as the total change of fluorine on sputtering.

increase in adhesion. Evaluation of the adhesion in areas between the cracks showed substantially improved adhesion values: failure occurred as plastic deformation, with delamination at 2.04 N.

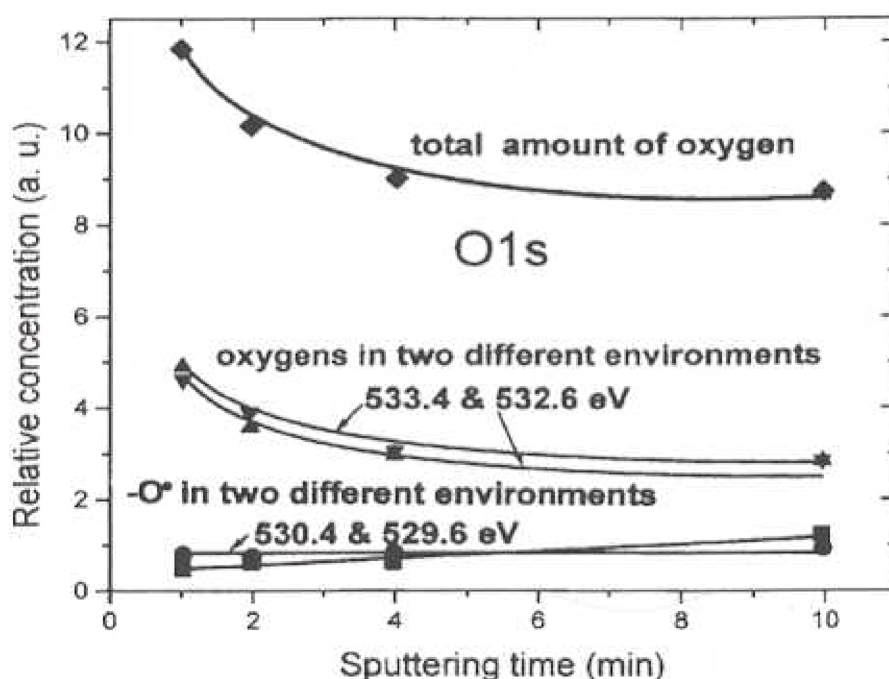
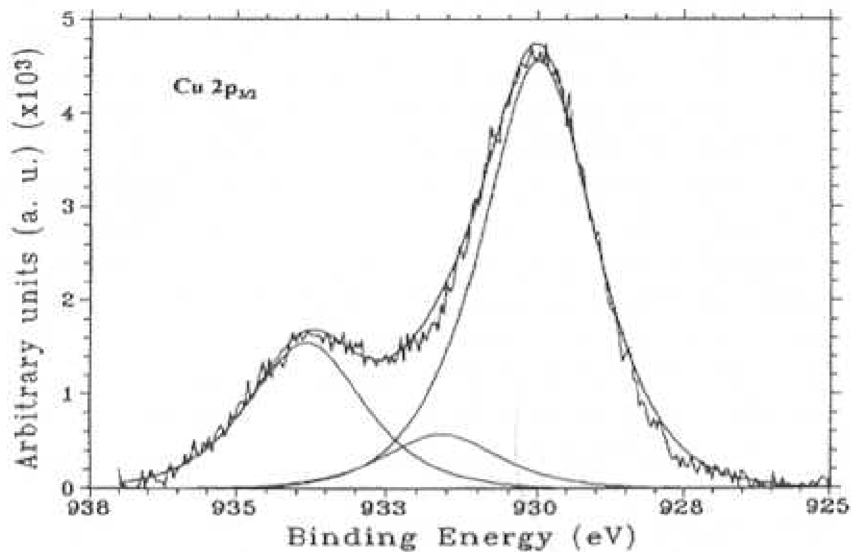


Figure 8. Evolution of the O1s peaks, as well as the total change of oxygen on sputtering.

DISCUSSION

An overall picture of the chemical reactions provoked by evaporation and sputtering may by gained from an analysis of the XPS spectra. The driving force for such reactions on the deposition of evaporated copper is the energy of condensation of the metal[16]. The increased temperature at the interface induces degradation reactions in the initial structure of Teflon AF1600, as revealed by the XPS spectra; These processes occur only on initial deposition. Degradation is due to the uniform loss of fluorine, as revealed in Fig. 3b. The copper bonds uniquely to carbon, forming carbide throughout the deposition, although approximately half of the depositing copper atoms remain in the metallic state in the thickness range used. There is no important oxygen loss, although modifications of the pure Teflon AF1600 O1s spectrum indicate single bond breaking of the oxygen of the dioxole rings, to produce free radicals. No evidence of C-O-Cu bond formation was found in this analysis.



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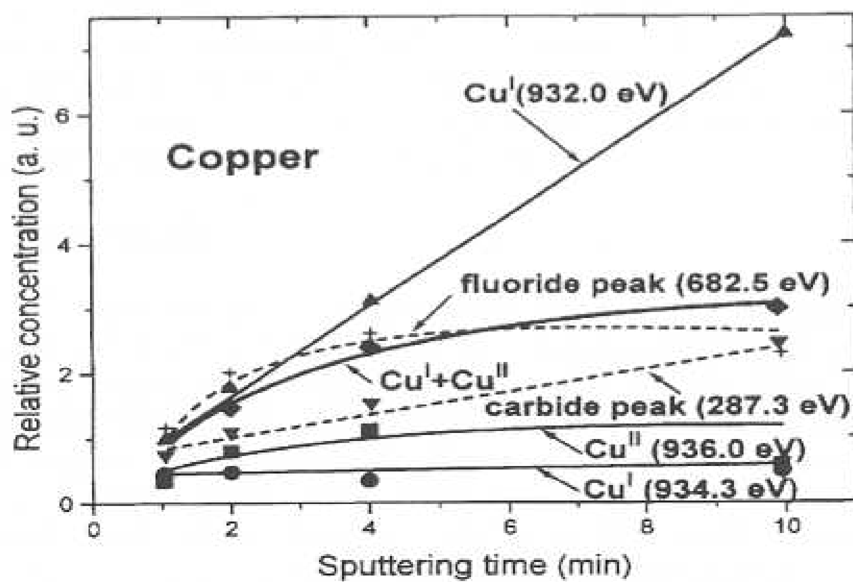

(b)

Figure 9. a) $Cu2p_{3/2}$ spectrum for 1 minute of sputtering; b) Correlation between concentration of elements for different species. Carbide (Cu-C) and fluoride ($Cu^{2+}F^{-}_2$ and $Cu^{+}F^{-}$) formation correlations support the assumption of Cu_nC formation.

In the case of sputtering, the kinetic energy of the copper atoms, which is at least an order of magnitude greater than the condensation energy released by the condensation of evaporated copper[17], leads to new reactions. The depositing copper reacts entirely, with the formation of carbide and fluoride species, while the carbon spectrum indicates degradation processes similar to those found in the case of evaporation. Oxygen is lost during sputtering: the intense energy causes not only single bond breaking to produce -C-O$^{\bullet}$, but the breaking of the second C-O bond, as well, resulting in the loss of oxygen atoms. The loss of fluorine and oxygen atoms do not radically change the C1s spectra because both species are lost uniformly: the five carbon peaks decrease uniformly with the same ratio. While C-F bonds are broken, not all the F is lost: some is retained as copper fluorides. As shown in Fig. 9b, correlations between Cu and F concentrations reveal a consistent overall picture of chemical reactions at the interface. No such attempt at analysis was made in our previous study[7], where the new feature in C1s spectrum was provisionally attributed to the formation of both C-C and Cu-O-C bonds when a very small amount of Cu was deposited. The present, more complete and accurate study, using a range of Cu thicknesses, gives no indication of Cu-O-C formation. Rather, as we show for the first time, copper reacts exclusively with carbon during both evaporation and sputtering.

For both vapor deposition and sputter deposition, adhesion is less than desired. For unannealed samples, the critical load for copper delamination appears to correlate qualitatively with the extent of Cu-C bonding at the copper/fluoropolymer interface. Annealing shows substantial improvement, with adhesion values increasing in both cases. The reason for these marked improvement is presently being investigated.

CONCLUSIONS

XPS analysis was used to assess the interaction of vapor deposited and sputtered copper with Teflon AF1600. For evaporation, half of the depositing copper reacted at the interface, forming carbide. The higher energies of the sputtered incident atoms led to the complete reaction of copper for the sputter deposition. Carbide and fluoride formation were the principal reaction products. Reacted copper did not remain accumulated at the Teflon surface but, rather, was uniformly distributed throughout the observation depth. Metal adhesion was stronger in the case of sputtering, increasing on annealing at 200^{0}C.

ACKNOWLEDGMENTS

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