

THE SPONTANEOUS REACTION OF Cu (hfac) (TMVS) VAPOR WITH  
DUPONT TEFLON AF1600

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Preliminary X-ray photoelectron spectroscopic (XPS) and time-of-flight secondary ion mass spectroscopic (TOF-SIMS) measurements have confirmed the reaction of Teflon AF1600 with vapors of copper (hexafluoroacetylacetonate)(trimethyl vinyl silane) [C(hfac)(TMVS)], when exposed in the dark. XPS reveals the deposited copper to be in the  $\text{Cu}^{\text{II}}$  state, while TOF-SIMS has shown the organometallic to have lost its ligands in bonding to the surface.

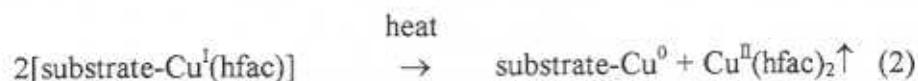
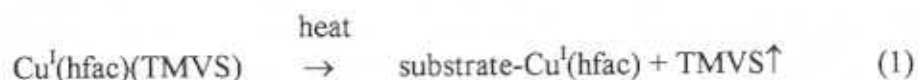
## INTRODUCTION

Future microelectronic multilayer devices will demand signal transmission times so short that the RC contribution must amount to no more than a small fraction of the overall delay time<sup>1</sup>. Here, R is the metal line resistance and C the capacitance of the interlayer insulator. There are three ways of accomplishing this: 1) reduce R with a more conductive metal; 2) reduce C with an insulator of lower permittivity; 3) reduce R by shortening the metal lines. R may be reduced by

replacing the presently used aluminum with copper, which has a resistivity ~50% lower. C may be reduced by replacing the presently used polyimide insulation with fluoropolymers, having dielectric constants ~40% lower. A recent addition to the Teflon<sup>®</sup> family of fluoropolymers, Teflon AF, is soluble in perfluorinated solvents, permitting its use in spin-on applications; it is available as AF1600 ( $T_g = 160^\circ\text{C}$ ) and AF2400 ( $T_g = 240^\circ\text{C}$ ).

The Teflon AF series differs from others Teflons in that the fluorocarbon chain,  $(\text{CF}_2)_n$ , is a minor component<sup>2</sup>. The major component is the 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole ring, containing two ether oxygens. The Teflon AF1600 repeat unit contains two dioxole rings to one  $\text{C}_2\text{F}_4$  moiety while the AF 2400 repeat unit contains seven dioxole rings to one  $\text{C}_2\text{F}_4$ .

Recent work in our group<sup>3</sup> has demonstrated the feasibility of the laser-induced deposition of Cu from the copper(I) precursor, copper (hexafluoroacetylacetonate) (trimethyl vinyl silane) [ $\text{Cu}(\text{hfac})(\text{TMVS})$ ]. Deposition was successful on both TiN and Teflon PFA substrates.  $\text{Cu}(\text{hfac})(\text{TMVS})$  is extremely stable and has a high vapor pressure at slightly elevated temperatures, making it suitable for chemical vapor deposition (CVD). A recent book<sup>4</sup> discusses the mechanism of copper deposition from  $\text{Cu}^{\text{I}}(\text{hfac})(\text{TMVS})$ . It begins with an activated reaction at the  $\text{SiO}_2$  substrate surface, leading to the loss of TMVS and the bonding of  $\text{Cu}^{\text{I}}(\text{hfac})$  to the surface. Subsequent reaction with  $\text{Cu}^{\text{I}}(\text{hfac})(\text{TMVS})$  leads to a disproportionation and the production of bonded  $\text{Cu}^0$  and  $\text{Cu}^{\text{II}}(\text{hfac})_2$ , which is subsequently lost as vapor. No explanation is offered as how elemental copper can bond and still retain its zero valency. Their overall mechanism is:



The present study was provoked by our finding that  $\text{Cu}(\text{hfac})(\text{TMVS})$  reacted with Teflon AF1600 (and Teflon PFA) surfaces at low temperatures, in the absence of laser light, giving a monolayer or less of Cu-containing product. Here, we report our initial findings on this unanticipated reaction between a non-reactive fluoropolymer and a stable organometallic. We use (1) X-ray photoelectron spectroscopy (XPS), comparing the spectra with those obtained on unreacted Teflon AF 1600<sup>5</sup>, and (2) time-of-flight secondary ion mass spectroscopy (TOF-SIMS), where the presence of fragments is used to indicate the state of the bonded copper.

## EXPERIMENTAL

As reported earlier<sup>5</sup>, Teflon AF1600, supplied by DuPont, was dissolved in Sigma Fluorinert FC-77 and spun onto a freshly cleaned Si wafer; it was then dried at 170°C for 3 hours and, finally, at 330°C for 10 minutes. Before exposure to Cu(hfac)(TMVS), purchased from the Schumacher Corporation as CupraSelect, the Teflon AF1600 was heated to 110°C for 10 minutes.

Exposure was carried out in the following manner: a 100 sccm flow of H<sub>2</sub> carrier gas was passed through a bubbler of CupraSelect, held at 45°C. This vapor, containing CupraSelect at a partial pressure of 0.5 Torr, was passed into a chamber containing the Teflon AF1600 sample at 55°C; the exposure lasted 10 minutes. Samples were then submitted for XPS and TOF-SIMS analyses, with an unavoidable exposure to air: several minutes in the case of XPS and several days in the case of TOF-SIMS.

Both XPS and TOF-SIMS techniques are well adapted for this type of study. Similar applications have recently been reviewed<sup>2</sup>. XPS is based on the photoelectric effect: irradiation by high energy monoenergetic X-rays causes the emission of electrons, whose binding energies indicate the orbitals from which they were emitted and whose chemical shifts, caused by the electron density at the emitting atom as influenced by its neighbors, indicates the chemical environment at the atom. TOF-SIMS is a form of SIMS carried out under "static" conditions, in which less than a monolayer of surface is removed during the course of the experiment; the use of a TOF spectrometer assures a high mass resolution ( $M/\Delta M \approx 10^4$  at lower masses), a high sensitivity due to its high transmission, and a high detection efficiency.

XPS analysis was carried out on a VG ESCALAB Mark II apparatus, using Mg K<sub>α</sub> radiation at 1253.6 eV. Survey scans were obtained at an analyzer pass energy of 100 eV and at a grazing angle of incidence. TOF-SIMS analysis was carried out on a Charles Evans & Associates TRIFT mass spectrometer, using a pulsed Ga ion beam, as recently described<sup>6</sup>. Secondary ions were extracted at an acceleration voltage of 3 kV, electrostatically deflected 270° and mass analyzed by measuring their time-of-flight distributions from the sample surface to the position-sensitive detector.

## RESULTS AND DISCUSSION

Cu(hfac)(TMVS) was found to react with Teflon AF1600 after a short exposure, in the absence of laser light, and at a temperature of 55°C, substantially below the conventional CVD temperature range of 120-130°C. This unexpected reaction is shown by the XPS survey scan in Figure 1 and the TOF-SIMS spectra in Figure 2.

The XPS scan in Figure 1 indicates the presence of C, O, F and Cu. Satellites in the Cu2p region (930-970 eV) indicates the presence of divalent Cu, although Cu(hfac)(TMVS) contains monovalent Cu. A high resolution scan of the

Cu2p region, not shown, indicates the presence of only one divalent species, although zerovalent Cu is expected<sup>4</sup>; while air oxidation is a possible reason for the presence of divalent Cu, it is our experience that such oxidation is slow and, were it to have taken place, both monovalent and divalent Cu would have been in evidence. High resolution scans of the C1s, O1s and F1s regions showed no obvious changes when compared to untreated spectra<sup>5</sup>; they are not shown. A blank was also run: Teflon AF1600 was exposed under the same conditions but in the absence of Cu(hfac)(TMVS).

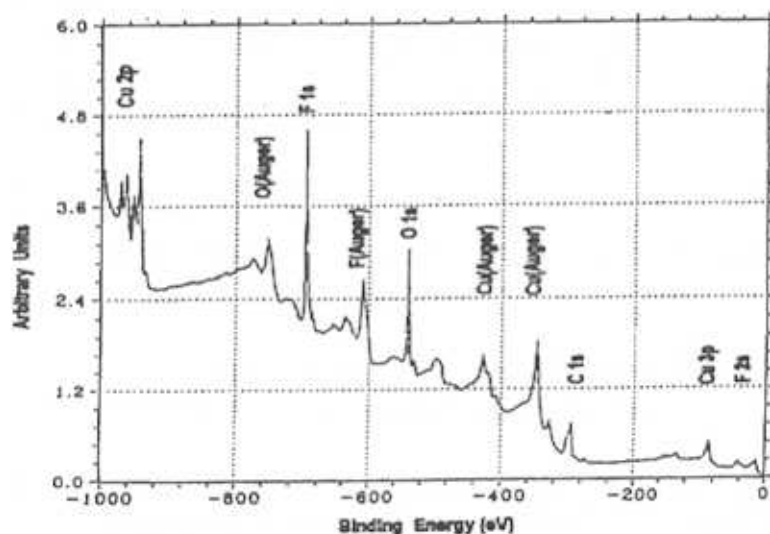


Figure 1. An XPS survey scan of the Teflon AF1600 surface after reaction with Cu(hfac)(TMVS).

Its spectrum was identical to that in Figure 1, except for the absence of all Cu peaks. It, too, is not shown.

The TOF-SIMS scans are found in Figure 2, where treated (a) and untreated (b) Teflon AF1600 spectra are shown; both general (0-200 amu) and Cu-specific (62.05-65.65 amu positive scans are shown for each. Both treated and untreated Teflon AF samples are characterized by the same high intensity peaks, relating to the AF structure: C<sup>-</sup> (12 amu), CF<sup>+</sup> (31 amu), CF<sub>2</sub><sup>+</sup> (50 amu), CF<sub>3</sub><sup>+</sup> (69 amu), C<sub>2</sub>F<sub>3</sub><sup>+</sup> (81 amu), C<sub>2</sub>OF<sub>3</sub><sup>+</sup> (97 amu), C<sub>3</sub>OF<sub>3</sub><sup>+</sup> (109 amu), C<sub>3</sub>F<sub>5</sub><sup>+</sup> (131 amu) and C<sub>3</sub>F<sub>7</sub><sup>+</sup> (169 amu). In the Cu specific spectra, <sup>63</sup>Cu and <sup>65</sup>Cu, in the natural isotopic ratio of 70:30, are observable only on the treated Teflon AF; peaks at 63 and 65 amu, observable on both treated and untreated Teflon AF, are due to C<sub>2</sub>HF<sub>2</sub><sup>+</sup> and C<sub>5</sub>F<sub>5</sub><sup>+</sup>, respectively. No other copper-containing fragments were found.

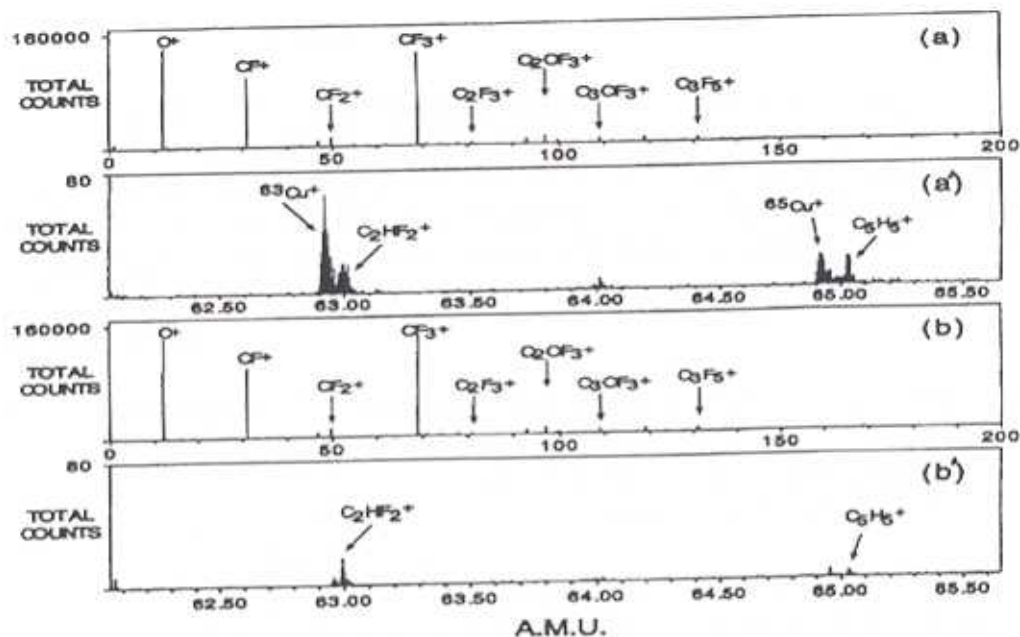


Figure 2. General and Cu-specific, respectively, TOF-SIMS scans of (a,a') treated and (b,b') untreated Teflon AF1600.

It is important to note that only  $^{63}\text{Cu}^+$  and  $^{65}\text{Cu}^+$  are found in the TOF-SIMS spectra, despite the XPS identification of  $\text{Cu}^{\text{II}}$ . This suggests, first, a bond between  $\text{Cu}^{\text{II}}$  and the Teflon AF surface which, when broken, causes an increased electron density at the Cu. Second, it is clear that the  $\text{Cu}^{\text{II}}$ , on bonding to the substrate, has also lost its hfac ligand; the observation of such intact fragments is expected<sup>7</sup> if the ligand were still bonded to the Cu.

The fact that the spectra remain unchanged for long periods of time under UHV condition in the spectrometers, and that  $\text{Cu}^{\text{I}}$  has been oxidized to  $\text{Cu}^{\text{II}}$  on reaction with Teflon AF1600, clearly shows the *chemical* nature of this reaction.

The mechanism for this chemical reaction is unclear. While the  $\text{Cu}^{\text{I}}$  has clearly undergone an oxidation to  $\text{Cu}^{\text{II}}$ , the reduction portion of the couple is not yet identified. It may involve the lost hexafluoroacetylacetonate fragment.

## CONCLUSIONS

The present results indicate that  $\text{Cu}(\text{hfac})(\text{TMVS})$  reacts spontaneously with Teflon AF1600. Although the site of the reaction is unidentified, it is most probably the oxygen of the dioxole rings. In reacting, the copper loses both ligands and is oxidized to  $\text{Cu}^{\text{II}}$ . This is in contradistinction to the mechanism proposed in the literature<sup>4</sup>, based on transmission FTIR studies carried out on high surface area  $\text{SiO}_2$  substrates<sup>5</sup>. It may well be that both mechanisms are substrate-dependent.

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