

Laser-Enhanced Gas Phase Surface Modifications of Teflon AF1600 for Increased Copper Adhesion*

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Multilevel interconnect devices, made of alternating layers of a low permittivity polymer (e.g., Teflon AF1600TM) and a low resistivity metal (e.g., copper), are increasingly being used in microelectronics in order to decrease the RC signal transmission time delay. The mechanical stability of the multilevel interconnects is related to the adhesion developed at the metal-dielectric interface. Since Cu/Teflon AF1600 adhesion is moderate and may not satisfy the requirements of the microelectronics industry, new treatments of the fluoropolymer surface are needed to improve it. In this note, we present several surface modifications, such as the formation of reactive sites during intense X-ray exposure, and S- or N-grafting, activated by UV radiation in the presence of H₂S and NH₃; copper is well known to react with both thiols (R-SH) and amines (R-NH₂) to form strong bonds. Both X-ray exposure and N-grafting lead to enhanced adhesion.

Keywords: Adhesion; copper; fluoropolymer; excimer laser; X-ray damage

INTRODUCTION

The semiconductor industry requires higher speed III/V-based semiconductor structures for use in Ultra Large Scale Integration (ULSI).

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This requires that the signal transmission times through the multilayer devices which connect them must be reduced to values substantially below the inherent transistor signal transmission times. Because the signal transmission time through a multilayer device is simply $R \times C$, where R is the resistance along the metal line that the signal traverses and C is the capacitance of the surrounding insulator, R may conveniently be lowered by replacing the presently-used metal, Al, by one of lower resistivity, such as Cu; in a similar fashion, C may conveniently be lowered by replacing the presently-used insulator, SiO_2 or polyimide, by one of lower permittivity, such as a fluoropolymer.

A problem with the use of Cu and fluoropolymers is that they both react with difficulty, yet interfacial reaction is necessary to provide the adhesion necessary to overcome the effects of interfacial stresses. These stresses arise because each component, Cu and fluoropolymer, has hygroscopic and thermal expansion coefficients which differ substantially from one material to the other; the relief of these stresses through mechanical distortion can result in a loss of interfacial adhesion, capable of destroying the device.

In a recent paper [1], we showed that the interfacial adhesion developed on the evaporative deposition of Cu onto DuPont Teflon AF1600TM is substantially less than that of Cu deposited onto plasma-deposited fluoropolymers, and may not satisfy the needs of the semiconductor industry. On the other hand, Teflon AF1600 is an attractive candidate for a lower permittivity insulator and has the advantage that it is soluble in organic solvents and, thus, is capable of being deposited by spinning. Adhesion to Teflon AF1600 may be improved by the presence of chemical groups at the Teflon surface, such as thiols ($\text{R}-\text{SH}$) and amines ($\text{R}-\text{NH}_2$), which react with Cu. Here we explore several such possibilities: the production of surface reactive species on controlled X-ray damage, and the grafting of reactive groups to designated areas of the polymer surface through the UV laser exposure of the reactive gases H_2S (thiol) and NH_3 (amine).

Copper films, 1500 Å thick, were deposited by evaporation, and their adhesion to Teflon AF1600 was evaluated by microscratch testing. Initial results presented here are discussed in terms of chemical interfacial reactions analyzed by XPS and resulting changes in adhesion modification characterized by microscratch testing.

EXPERIMENTAL

Teflon AF1600 was purchased from DuPont as a clear solution containing 12% solids. After 75% dilution with Sigma Fluorinert FC-77TM, it was spun onto a freshly cleaned Si wafer at 4000 rpm. The samples were left to dry at room temperature before sequential annealing at 110, 165 and 330°C, as recommended by the manufacturer [2]. Teflon thicknesses of 1 to 2 μm were obtained.

Our VG ESCALAB 3 Mark II XPS instrument has a spectral resolution of 0.7 eV using Mg K_α radiation at 1253.6 eV, and a working pressure of 10⁻⁹ Torr. After background subtraction, peak separations were performed with a nonlinear least mean squares program developed in our laboratory, using individual peaks with FWHM and Gaussian/Lorentzian ratios similar to those determined by us for other fluoropolymers.

X-ray irradiation was performed in the analysis chamber of our VG ESCALAB. For surface modifications, an X-ray power of 240 W (12 kV and 20 mA) was intentionally used for 30 minutes. During exposure, surface degradation was monitored using XPS analysis of the C1s high resolution peak at a much lower power of 100 W, known not to degrade the substrate [3]. After irradiation, the samples were transferred to the preparation chamber for Cu deposition, without exposure to the atmosphere.

Excimer laser irradiation (1800 pulses at 190 mJ/cm²) in two different environments, H₂S and NH₃, took place in a specially-constructed stainless steel chamber using a LUMONIX TE861S KrF (248 nm) pulsed laser. The H₂S and NH₃ gas sources were directly connected to the reaction chamber at atmospheric pressure and a gas flow of about 500 sccm was used. Irradiated samples were transferred to the XPS preparation chamber for Cu deposition, using a nitrogen-filled transfer vessel.

Cu deposition was performed in the preparation chamber of our ESCALAB, using an electron beam evaporator of the Waldrop and Grant [4, 5] type at an initial pressure of 2 × 10⁻⁷ Torr. The thickness of the deposited copper was measured by a SYCON quartz crystal monitor placed near the sample and was found to be about 1500 Å.

The MST microscratch tester, made by CSEM (Switzerland), was used to evaluate the practical adhesion of Cu films. A hemispherical

indenter (0.8 mm in diameter) was linearly loaded at 10 N/min, at a fixed displacement speed of 5 mm/min across the sample. The critical load, at which a consistent delamination was observed by microscope, was used as a measure of adhesion strength.

RESULTS AND DISCUSSIONS

a) X-ray Irradiation

Figure 1 compares the C1s high-resolution spectra of original and intentionally X-irradiated Teflon AF1600. The degradation on irradiation was previously analyzed and discussed [3]. What was found was a loss of fluorine, graphitization, crosslinking and free radical formation at the interface. It is the reaction of Cu at this surface which is being studied here.

b) UV Irradiation

Initial testing of the effect of laser irradiation on the Teflon AF1600 substrate was carried out in the presence of both pure Ar and pure O₂;

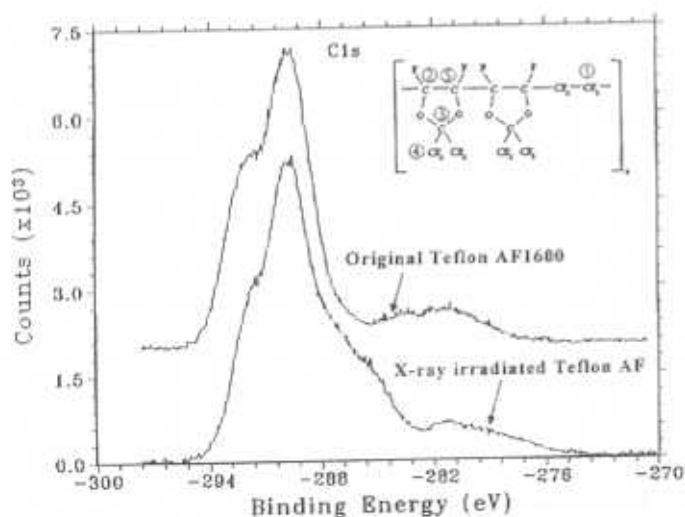


FIGURE 1 Typical C1s spectra of original and X-ray irradiated Teflon AF1600; the inset shows the Teflon AF1600 repeat unit.

XPS showed that the substrate was unaffected in either case, indicating no detectable chemical changes of the substrate at this laser energy. These gases were replaced by pure H_2S and pure NH_3 , and laser radiation was used to fragment these gas molecules into more chemically-reactive species, which might then graft onto the Teflon AF1600 surface to produce active thiol and amine sites for bonding with Cu.

H_2S

A typical XPS survey spectrum of Teflon AF1600, after exposure to excimer laser radiation in a H_2S atmosphere, is presented in Figure 2. It shows the presence of sulfur, which higher resolution showed to be uniquely elemental. That is, H_2S decomposed in the laser beam to give elemental S, which coated the entire inside of the reaction chamber, and H_2 ; XPS showed that the polymer surface was not attacked. The elemental sulfur, which did not chemically bond to the Teflon surface, sublimed from the XPS analysis chamber under the vacuum; as is seen

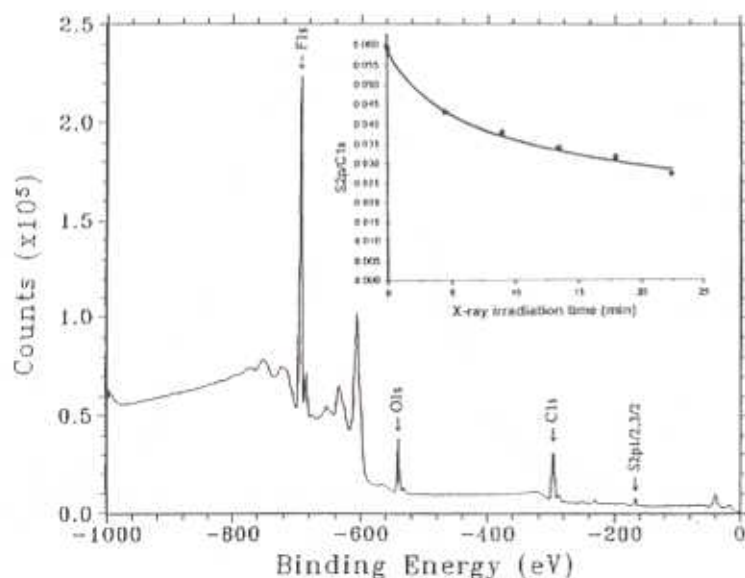


FIGURE 2. Typical XPS survey spectrum of Teflon AF1600 after excimer laser irradiation (248 nm, 150 mJ/cm^2 , 1800 pulses) treatment in a H_2S atmosphere; the inset shows the evolution of the S2p/C1s ratio.

in the inset to the Figure 2, the S2p/C1s ratio decreased continuously with exposure time.

NH₃

Figure 3 shows a high resolution N1s spectrum obtained on laser radiation in the presence of NH₃, and its separation into two peaks, one at 398.4 eV and the other at 397.1 eV. The original peak attributions, for untreated Teflon AF1600, were made in Ref. [6]. The C1s peak separation, after irradiation in the presence of NH₃ and subsequent to satellite subtraction, is presented in Figure 4; it indicates that two new peaks were formed, at 286.2 eV and 284.4 eV, at the expense of the original peaks 1 and 3 which have been attributed to sites 1 and 3, respectively, in the inset to Figure 1. Peak ratio intensities of the newly-formed C—N bonds were about 0.75 in both the N1s and C1s spectra (*i.e.*, $I[286.2 \text{ eV}] : I[284.4 \text{ eV}] \sim I[397.1 \text{ eV}] : I[398.4 \text{ eV}]$, where $I[B.E.]$ is the integrated intensity of the peak centered at

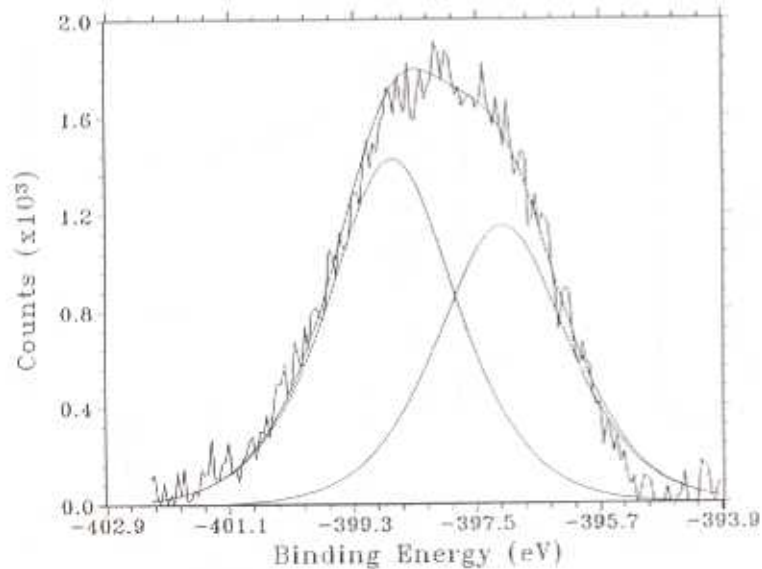


FIGURE 3. Peak deconvolution of the N1s spectrum after laser irradiation (conditions similar to those in Fig. 2) in an NH₃ atmosphere.

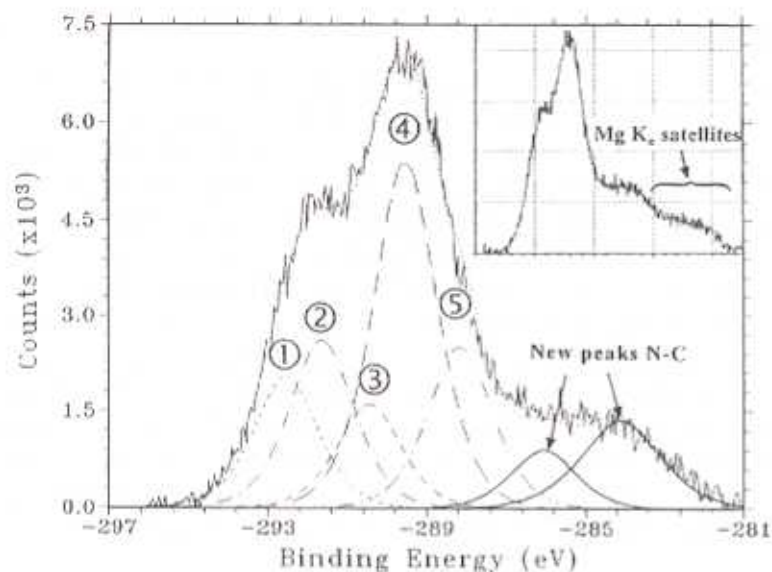


FIGURE 4 C1s spectrum and its deconvolution after NH_3 treatment. Two new peaks are formed at the expense of original peaks 1 and 3; the corresponding carbons are presented in the repeat unit (Fig. 1). Note that the peaks are numbered in order of decreasing binding energy, a more logical approach than the random numbering used in Ref. [6]. The inset shows the C1s spectrum before satellite subtraction.

B.E. eV). Their relative concentrations, when corrected by their sensitivity factors [7] and probe depths [8], as shown in Table I, were within 5%, well within experimental error. The purpose of the sensitivity factor correction is to convert intensity to relative concentration and the purpose of the probe depth (*i.e.*, $3\times$ electron mean free path) correction is to convert the relative concentrations to those at unit depth.

This analysis indicates that N is bonded only to C at positions 1 and 3.

TABLE I Sensitivity factors and mean free paths for N1s and C1s spectra

XPS peak	N1s	C1s
Sensitivity Factor	0.42	0.25
Mean Free Path (\AA)	13	15

c) Adhesion Measurements

The microscratch test results, presented in Figure 5, show a 25% improvement in adhesion in the case of X-ray treated surfaces, presumably due to Cu reaction with the free radicals and other reactive species formed. As expected, no detectable adhesion change was observed in the case of H₂S because the elemental sulfur does not chemically react with the Teflon surface. The microscratch test did not provide information regarding the NH₃-treated Teflon AF; however, visual analysis of the film scratch (Fig. 6) showed an abrupt fracture below the deposited copper layer. Thus, the failure mode analysis indicates that the delamination took place in the bulk Teflon, below the interface, demonstrating that the Cu adhesion to the Teflon AF1600 was stronger than the cohesion of the Teflon AF1600; the fact that it was a large flake which delaminated suggests that interfacial hardening may have occurred, although this is not evident by XPS.

d) Mechanism of N-grafting

In the absence of reactive gases, the 248 nm laser beam had no effect on the polymer substrate surface. This is due to the fact that its energy

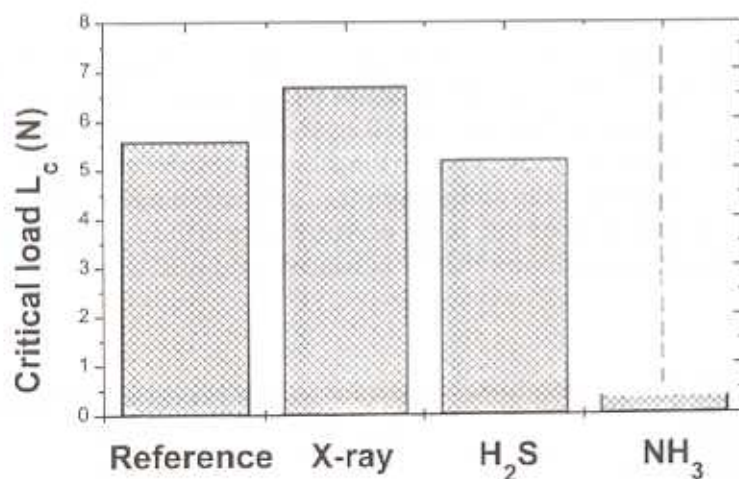


FIGURE 5. Microscratch test adhesion comparison for different treatments of the Teflon AF1600 surface.

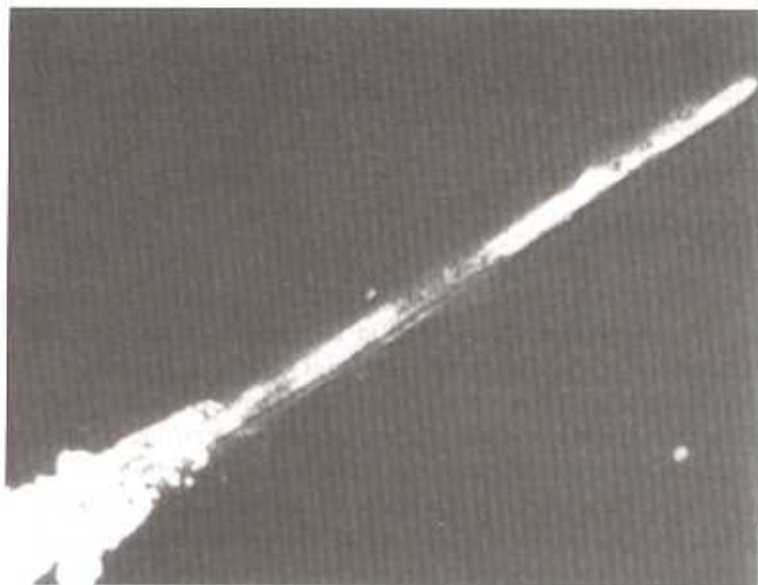


FIGURE 6 Failure mode of copper film fracture at the NH_3 -treated Teflon AF1600 surface, taken at 5x, indicating strong interfacial adhesion and interface hardening. Note the abrupt widening of the scratch and the exposure of the Teflon substrate. (See Color Plate 1).

is lower than that of the C—F bond, about 485 kJ/mole [9]. However, at energies higher than that of the C—F bond, fluoropolymers are readily attacked by O_2 [10–12], hydrazine [13, 14] and triethylamine [15], indicating that the attack is initiated by the generation of substrate free radicals through the breaking of the C—F bond.

Despite the fact that, in the present case, no C—F bonds were broken, reaction took place. Similar reactions have previously been observed for both NH_3 [16] and triethylamine [17], which clearly indicates that, in such cases, reaction is due to the laser-induced generation of highly reactive N-containing free radicals in the gas phase, which then attack the substrate. While it is conceivable that any free radical remaining on the substrate surface might react with nitrogen gas during transfer to the XPS apparatus in the nitrogen-filled transfer vessel, we have found [18] that even the intentional production of large amounts of free radicals, and their subsequent exposure to air, leads to both oxygen and nitrogen surface species detectable only by the

extreme sensitivity of static SIMS. In the case of the fragments produced from H₂S, reaction with the substrate was energetically far less favorable than reaction among the fragments, indicating why only elemental S was formed.

CONCLUSIONS

In situ X-ray irradiation, and excimer laser exposure, in both H₂S and NH₃ atmospheres, were used in an attempt to induce chemical modifications of the Teflon AF1600 prior to copper deposition. XPS analysis indicated surface degradation (free radical formation, graphitization) for the X-ray exposed samples, and the grafting of nitrogen-containing groups in the case of excimer laser radiation in a NH₃ atmosphere. The superficial deposition of elemental sulfur, in the case of excimer laser radiation in a H₂S atmosphere, did not lead to surface grafting. Adhesion testing demonstrated a 25% increase of interfacial adhesion following X-ray treatment and a significant, but unmeasurable, adhesion enhancement in the case of N-grafted surfaces.

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References

- [1] Alptekin, A., Sacher, E., Czeremuskin, G., Martinu, L. and DiRenzo, M., *Electrochem. Soc. Proc.* **47-8**, 58 (1997).
- [2] DuPont Specialty Polymers Technological Information Bulletins H-16577-1 and H-52454.
- [3] Popovici, D., Sacher, E., Martinu, L. and Meunier, M., *J. Appl. Polym. Sci.* **70**, 1201 (1998).
- [4] Waldrop, J. R. and Grant, R. W., *J. Vac. Sci. Technol.* **A1**, 1553 (1983).
- [5] Waldrop, J. R., Kowalczyk, P. and Grant, R. W., *J. Vac. Sci. Technol.* **21**, 607 (1982).
- [6] Sacher, E. and Klemberg-Sapieha, J. E., *J. Vac. Sci. Technol.* **A15**, 2143 (1997).
- [7] Wagner, C. D., Davis, L. E., Zeller, M. V., Taylor, J. A., Raymond, R. H. and Gale, L. H., *Surface Interface Anal.* **3**, 211 (1981).
- [8] Ke, R., Haasch, R. T., Finnegan, N., Dottle, L. E., Akire, R. C. and Farrell, H. H., *J. Vac. Sci. Technol.* **A14**, 80 (1996).

- [9] Okoshi, M., Toyoda, K. and Murahara, M., *Mat. Res. Soc. Symp. Proc.* **397**, 655 (1996).
- [10] ChtaiB, M., Roberfroid, E. M., Novis, Y., Pireaux, J. J., Caudano, R., Lutgen, P. and Feyder, G., *J. Vac. Sci. Technol.* **A7**, 3233 (1989).
- [11] Matienzo, L. J., Zimmerman, J. A. and Egitto, F. D., *J. Vac. Sci. Technol.* **A12**, 2662 (1994).
- [12] Girardeaux, C., Idrissi, Y., Pireaux, J. J. and Caudano, R., *Appl. Surf. Sci.* **96-98**, 586 (1996).
- [13] Niino, N. and Yabe, A., *Appl. Phys. Lett.* **63**, 3527 (1993).
- [14] Niino, N. and Yabe, A., *Appl. Surf. Sci.* **96-98**, 550 (1996).
- [15] Révész, K., Hopp, B. and Bor, Z., *Appl. Surf. Sci.* **109-110**, 222 (1997).
- [16] Bordeniuc, J., Chupka, W. and Crabtree, R. H., *J. Am. Chem. Soc.* **117**, 10, 119 (1995).
- [17] Ichinose, N., Maruo, M., Kawanishi, S., Izumi, Y. and Yamamoto, T., *Chem. Lett.* 943 (1995).
- [18] Léonard, D., Bertrand, P., Shi, M. K., Sacher, E. and Martinu, L., submitted to *Plasm. Polym.*