# REACTIVE ION ETCHING OF POLY(TETRAFLUOROETHYLENE) IN $CF_4/O_2$ PLASMAS FOR IMPROVEMENT OF COPPER ADHESION

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## ABSTRACT

The improved adhesion of Cu to PTFE, treated in $CF_4/O_2/Ar$ plasmas, was found to be associated with: (1) increasing atomic oxygen concentration at the modified surface at the expense of fluorine atom concentration, (2) decreasing advancing contact angle of distilled water droplets at a given exposure time, and (3) increasing surface roughness for treatments performed in the oxygen-rich regime.

## INTRODUCTION

To achieve high density electronic packaging products that perform at greatly enhanced signal processing speeds, low dielectric constant polymers, such as poly(tetrafluoroethylene) (PTFE), are being considered as substrates onto which copper circuit lines are placed. Excellent adhesion between the Cu and PTFE surface is essential for the production of these devices [1].

Without surface modification, the Cu-PTFE adhesion is weak and the film is easily removed by a peel test using Scotch tape. Bombarding PTFE with 500eV $Ar^+$ ions, increases the adhesion up to 50 times due to changes in surface morphology and chemical bonding between Cu and the modified PTFE. Exposure of the treated PTFE to air prior to sputter deposition of Cu showed no effect on the strong adhesion [2,3].

Plasma treatment using Ar, $Ar/O_2$ (50/50%), and $CF_4/O_2$ (22/78%) containing radio-frequency (RF) discharges have also been reported to cause changes in the surface topography of PTFE which enhance adhesion of electrolytically plated Cu to the modified fluoropolymer substrate [4].

$CF_4/O_2$ mixtures are frequently used to etch/modify organic polymer surfaces in RF plasmas [5]. At a given RF power, etch rates of PTFE are greatest with pure $O_2$ and decrease upon addition of $CF_4$. At constant peak-to-peak voltages, compositions from 0-80% $CF_4$ in $O_2$ are found to reactive ion etch PTFE equally well. Etching of PTFE was, therefore, proposed to be initiated by ion indiscriminate bombardment-induced radical generation [5].

In the present work [6], a systematic study is undertaken of the adhesion of magnetron-sputtered Cu to RF plasma-treated PTFE as a function of the relative concentrations of $O_2$ and $CF_4$ with 5% Ar in the plasma gas mixture. Peel test measurements of the degree of adhesion of the sputtered Cu films to PTFE exposed to the plasma for various times up to 60 minutes are correlated with plasma gas composition, film surface chemical composition (XPS), surface energy (as reflected by contact angle measurements), and polymer film surface morphology (SEM).

## EXPERIMENTAL

Films of Dupont PTFE were first washed with hot water and detergent, rinsed with distilled water, air dried, cleaned in acetone vapor and again air dried.

The circular (2.5 in. diameter) film samples were mounted directly on the water-cooled cathode of the aluminum-walled RF plasma reactor. The ratio of the areas of the powered electrode to the grounded chamber wall is 1:210, ensuring that the voltage drop across the dark space is essentially the total applied RF voltage, resulting in energetic ion bombardment of the substrate. The plasma gases, $CF_4$, $O_2$, Ar mixtures, were admitted to the chamber through variable leak mass flow controllers; for all experiments the total flow rate was 50 SCCM and the total pressure was 0.3 Torr. The relative concentrations of the constituent gases and the total treatment time were varied. RF power at 13.56 MHz was applied to the system through an impedance matching network with a blocking capacitor and maintained at 50 W. After exposure to the plasma, the sample was exposed to air and cut in halves, one half for contact angle determinations or SEM/XPS analysis and the other for adhesion (copper deposition/peel test) measurements. Measurements of the distilled water contact angle were made within five minutes of removal from the reactor. Cu was sputtered onto the other treated film sample in a separate chamber, using a 2" diameter planar magnetron with a Cu target mounted 7.5 in. from the sample [7]. Argon was admitted to the chamber at a flow of 7.5 SCCM and a total pressure of $2 \times 10^{-3}$ Torr. An Inficon quartz crystal monitor (Model No. XTM) was used to define the deposition rate (0.2nm/s); the thickness of the deposited Cu films was approximately 200 nm. Adhesion was determined by a 90° peel test using Scotch tape. The amount of Cu remaining on the surface after the peel was taken as a measure of the quality of adhesion.

XPS analyses were carried out in a PHI 5500 multiprobe spectrometer using Al K$\alpha$ radiation. Survey and high resolution spectra for the regions of interest were obtained for each sample described in the present study.

## RESULTS AND DISCUSSION

The peel test measurements showed that the percentage of sputtered Cu remaining on the treated PTFE surface increased from about 60 to 95% as the percentage of $O_2$ in $CF_4$ (with 5% Ar) increased from 0% to 95%, respectively. The best adhesion was achieved with pure $O_2$ or Ar gas feed resulting in 90-100% and 80-

90%, respectively, of the Cu remaining on the modified PTFE surface following the peel test.

Results from the surface morphological studies were consistent with the adhesion measurements. Untreated PTFE had a very smooth surface and remained relatively smooth upon plasma treatment with 85% $CF_4$, 10% $O_2$, 5% Ar for up to 45 min. exposure. When the $O_2$ content in the plasma gas was increased, etch pits on the film surface appeared, increased in size and density as the $O_2$ concentration was further increased, and were larger for 100% $O_2$ than those observed for 100% Ar treatment. Increasing the exposure time expanded these individual pits into an interconnected surface structure. The roughest surfaces were observed with oxygen-rich plasma treatment at longer exposure times, in agreement with results reported for the plasma etching of PTFE using $O_2$-$CF_4$ mixtures [5]. Previous investigations have also reported enhanced adhesion of Cu onto PTFE surfaces topographically modified by plasmas containing Ar [3,4], a 50/50% Ar/$O_2$ mixture [4] and a 22/78% $CF_4/O_2$ mixture [4].

Table 1 shows the surface composition of the treated and untreated PTFE films as determined by XPS analysis. Except for the pure Ar treated samples which will be discussed separately below, the C-atom percentage and the C/F ratio remain roughly constant at about 33% and 0.5, respectively. The O atom percentage varies considerably from 0.37% to 5.54% depending on the gas feed composition and time of exposure. For samples treated predominently with $O_2$ in the plasma mixture, the O/F ratio increases with exposure time.

In general, improved adhesion of Cu correlates well with increasing O atom percent, decreasing F atom percent and increasing O/F ratio on the treated surface.

Oxygen found on the surface of the Ar-treated PTFE was probably incorporated during the transport of the samples from the plasma reactor to the XPS spectrometer. Similar effects have been observed following $He^{2+}$ ion [8], UV(193nm) photon [9] and vacuum UV photon bombardment [10] of PTFE, which caused defluorination, formation of C=CF bonds and enrichment in C-O bonding.

Consistent with the results of this study, Burkstrand [11] has shown that the formation of metal-oxygen-polymer complexes on oxygen-plasma-treated polymer surfaces correlates with adhesion of the metal film. Improvement in the adhesion of Ag to polymer surfaces also occurs upon plasma treatment with oxygen [12]. Oxygen-containing polymers normally show good adhesion since they form a chemical bond between the metal and a functional group [4]. The adhesion of electrolytically plated Cu on PTFE is also improved by the deposition of a thin metallic interlayer (Pd, Pt, Au, Cu) on a pre-etched PTFE surface with $CF_4/O_2$ by PECVD processes [4].

Schonborn and Hansen [13] have suggested that cross linking by activated species of inert gases (CASING) such as He ions in an RF plasma resulted in increased bondability to PTFE. Treatment of PTFE with X-rays and 2 keV electrons resulted in a modified layer of cross linked or branched PTFE that accounted for improved wetting and adhesion of Ni and Au films [14].

**Table 1.** X-Ray Photoelectron Spectroscopic Analysis of PTFE Films Exposed to $O_2/CF_4/Ar$ RF Plasma as a Function of Plasma Gas Feed Composition and Time of Exposure

| Gas feed composition,% | | | Exposure time, | Element$^a$ | | | Atom Ratio | |
|---|---|---|---|---|---|---|---|---|
| Ar | $O_2$ | $CF_4$ | min. | C | O | F | C/F | O/F |
| - | - | - | 0 | 33.93 | 0.22 | 65.85 | 0.515 | 0.003 |
| 5 | 95 | 0 | 5 | 33.93 | 2.66 | 63.40 | 0.535 | 0.042 |
| 5 | 50 | 45 | 5 | 33.42 | 0.96 | 66.62 | 0.502 | 0.014 |
| 5 | 10 | 85 | 5 | 32.70 | 1.14 | 66.16 | 0.494 | 0.017 |
| 5 | 0 | 95 | 5 | 33.41 | 2.04 | 64.55 | 0.518 | 0.032 |
| 0 | 100 | 0 | 5 | 33.37 | 2.66 | 63.96 | 0.522 | 0.042 |
| 100 | 0 | 0 | 5 | 37.00 | 5.58 | 57.42 | 0.644 | 0.097 |
| 5 | 95 | 0 | 45 | 32.72 | 5.54 | 61.74 | 0.530 | 0.090 |
| 5 | 90 | 5 | 45 | 32.37 | 2.72 | 64.91 | 0.499 | 0.042 |
| 5 | 50 | 45 | 45 | 31.76 | 2.73 | 65.50 | 0.485 | 0.042 |
| 5 | 10 | 85 | 45 | 32.93 | 0.37 | 66.70 | 0.494 | 0.006 |
| 5 | 0 | 95 | 45 | 33.31 | 0.72 | 65.97 | 0.505 | 0.011 |
| 0 | 100 | 0 | 45 | 33.81 | 4.68 | 61.51 | 0.550 | 0.076 |
| 100 | 0 | 0 | 45 | 37.68 | 9.44 | 52.88 | 0.713 | 0.179 |

a Calculated atom percent values for PTFE ($-[CF_2-CF_2]_n-$) are C, 33.33; O, 0.00; F, 66.67.

Fig. 1 shows the advancing contact angle of water on treated PTFE as a function of the plasma treatment time for a variety of plasma gas compositions. The equilibrium contact angle of water on PTFE, a highly non-wettable surface, decreases from 108° to 86° in the first 15 minutes of exposure to an Ar plasma and then remains constant at longer exposure times. Similar behavior was previously observed when PTFE was exposed to vacuum UV radiation from He and Ar plasmas where the value of the contact angle at the plateau decreased as the wavelength of exposure decreased [10]. For pure $O_2$ and the $CF_4/O_2/Ar$ mixtures, the contact angle increases from 108° as a function of increasing exposure time according to Wenzel's Law [15] which predicts that for non-wettable surfaces ($\theta > 90^o$) the effect of roughening the surface makes the surface more non-wettable. The SEM results reported earlier showed enhanced roughening of PTFE as the $\%O_2$ increased in the plasma. For the $CF_4/O_2/Ar$ mixtures, the rate of increase of contact angle with exposure time decreases as the $\%O_2$ increases (Fig. 1).

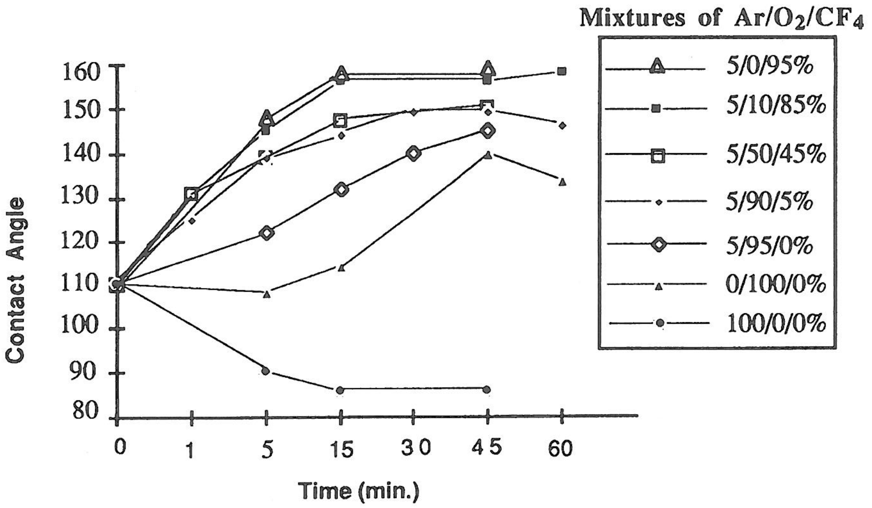

FIGURE 1 Advancing contact angle on plasma treated PTFE films

## CONCLUSION

Improved Cu adhesion to modified PTFE was correlated with increasing atomic oxygen and decreasing atomic fluorine on the surface, increasing surface roughness and decreasing advancing contact angle of distilled water at a given exposure time.

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