

# MECHANICAL AND DIELECTRIC PROPERTIES OF LOW PERMITTIVITY DIELECTRIC MATERIALS

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## ABSTRACT

The dielectric and mechanical properties of low permittivity dielectric/metal system consisting of fluoropolymers and copper were studied. The types of polymers in this study include sputtered Teflon, plasma-deposited fluoropolymers and the soluble Teflon AF1600. All these fluoropolymers have dielectric constants below 2.0 and dissipation factors below 0.001. Copper was either evaporated or sputtered. Adhesion of copper to fluoropolymers was studied using scratch and peel tests. Different thermal treatment techniques were applied to enhance adhesion, including preannealing in vacuum or in atmosphere, as well as postannealing in vacuum. The results show generally poor adhesion for evaporated copper, with substantial improvement for sputtered copper; however thermal treatments enhance adhesion in some cases. FTIR, surface tension and XPS experiments were carried out in an effort to understand these effects. Our findings will be discussed in terms of the various effects contributing to copper/fluoropolymer adhesion.

## INTRODUCTION

Advances in the fields of very-large-scale integration (VLSI), ultra-large-scale integration (ULSI) and giga-scale integration (GSI) require new metal-insulator combinations compatible with the high speed requirements. With increasing miniaturization and integration levels, the transmission delay time also increases, due to the increase in capacitance between interconnection metal lines. This transmission delay time,  $\tau$ , is the product of the resistance of the line carrying the signal and the capacitance of the surrounding insulator. To reduce  $\tau$ , the line resistance may be lowered by using a more conductive metal and/or the capacitance may be lowered by using an insulator with a lower permittivity [1].

In the present study we propose to replace the commonly used Al-polyimide metal-insulator combination with a Cu-fluoropolymer system. Cu has the second lowest resistivity after Ag, and fluoropolymers have the lowest permittivities among the organic materials. Copper has a resistivity of  $1.67 \mu\Omega\text{-cm}$ , only 5% higher than Ag, but it has better adhesion to dielectrics and it is expected to diffuse at a much lower rate. Fluoropolymers have other beneficial properties than their low permittivities and

dissipation factors: this includes low water absorptivity, good heat and chemical stability, and surface inertness [2]. Unfortunately, this surface inertness leads to low adhesion at the Cu-fluoropolymer interface [3-5].

The major part of this work was concerned with increasing the adhesion of Cu deposited onto the fluoropolymers. Using the microscratch tester to evaluate this adhesion, we measured the critical load at which metal delamination started for samples treated under various thermal conditions. We evaluated the dielectric properties of various fluoropolymer structures sandwiched between evaporated copper electrodes. Thermal stability was also evaluated by thermally cycling the samples.

## EXPERIMENTAL

Fluoropolymer samples evaluated include plasma-polymerized (PP)  $C_2F_4$  and  $C_2F_3H$ , sputtered (SP) Teflon PTFE, and spin-deposited (SD) Teflon AF1600. Both sputtering and plasma polymerization of fluoropolymers were performed in an RF plasma system operating at 13.56 MHz and at a pressure of 20-40 mTorr. In the case of SP films, a disc of conventional PTFE was placed on the RF electrode and glass or silicon substrates were placed on the grounded electrode; Ar and  $CF_4$  gases were used at a flow rate of 10 sccm, and the RF power was about 250 W. For PP films,  $C_2F_3H$  or  $C_2F_4$  monomers were used at the same flow as for sputtering but with an RF power of about 20 W. The AF1600 solution was diluted in Fluorinert Sigma FC-77, and spin-deposited. The fluoropolymer films were about 1  $\mu m$  thick.

High purity copper (99.999 %) was either thermally evaporated from a filament at a pressure of around  $10^{-5}$  Torr, or it was sputtered, using a DC planar magnetron at a pressure of 10 mTorr of Ar, using a flow rate of 6 sccm, a current of 0.5 A and a negative target bias of 355 V. Copper thickness was about 200 nm.

The CSEM microscratch tester (MST) was used to measure adhesion. A linearly increasing force, over the range of 0-3 N, was applied to a 0.8 mm hemispherical diamond tip moving across the surface at a speed of 5 mm/min using a loading rate of 1 N/min. The scratches were analyzed, using both optical microscopy and SEM, to determine the critical load necessary to delaminate copper from the polymer substrate. Type 600 3M Scotch tape peel test was used to provide additional information about adhesion. The tape was placed gently over the sample and a roller of mass 2 kg was rolled twice over it. Immediately thereafter, the tape was peeled from the surface perpendicularly and the percentage of remaining copper was estimated.

Dielectric measurements were performed, using a HP 4274A multi-frequency LCR meter, at frequencies ranging from 100 Hz to 10 MHz. The samples were stabilized by annealing at 200°C for 30 minutes in a vacuum chamber kept at  $10^{-2}$  Torr. The permittivity at high frequency in the visible range ( $\sim 10^{15}$  Hz) was evaluated from the refractive index.

Chemical structure of the films and interfaces was also evaluated: FTIR spectra were obtained in transmission (volume) and photoacoustically (surface) on a MATTSON RS-1 FTIR spectrometer using an MTEC model 300 photoacoustic sample attachment. XPS spectra were obtained using a VG ESCALAB MKII instrument with  $MgK_{\alpha}$  radiation (1253.6 eV) operated at 12 kV and 20 mA. Angle-resolved XPS of metallized fluoropolymers, as a function of heat treatment, gave details on Cu diffusion. Film stress was measured as a function of temperature for both bare and metallized fluoropolymers,

using the Tencor FLX-2900 system under  $N_2$ .

## RESULTS AND DISCUSSION

Microscratch and peel test results are shown in Fig.1 for samples exposed to various heat treatments. The abbreviation "pre" indicates annealing prior to copper deposition, and "post" indicates annealing after the copper deposition. The abbreviations "atm" and "vac" indicate, respectively, annealing under the atmosphere or in vacuum. All these treatments were performed at 200 °C for 30 min. The results show that preannealing in atmosphere significantly increases adhesion for the PP and SP fluoropolymer samples. We believe that the free radicals produced during the plasma deposition are thermally activated to react with air to produce chemical groups capable of reaction with copper. In fact, formation of C-O-Cu and C-N-Cu chemical linkages at the Cu/fluoropolymer interface were detected earlier using XPS [6]. For AF1600, however, since no such free radicals exist, lower adhesion is observed, and preannealing in atmosphere does not improve the adhesion. One can see in Fig.1 that sputtered copper adheres better than evaporated copper. This is most probably due to higher energies associated with sputtering, possibly leading to more extensive surface reactions. Postannealing also improves the adhesion. This appears to be due to enhanced diffusion of copper into the polymers as confirmed by XPS analysis.

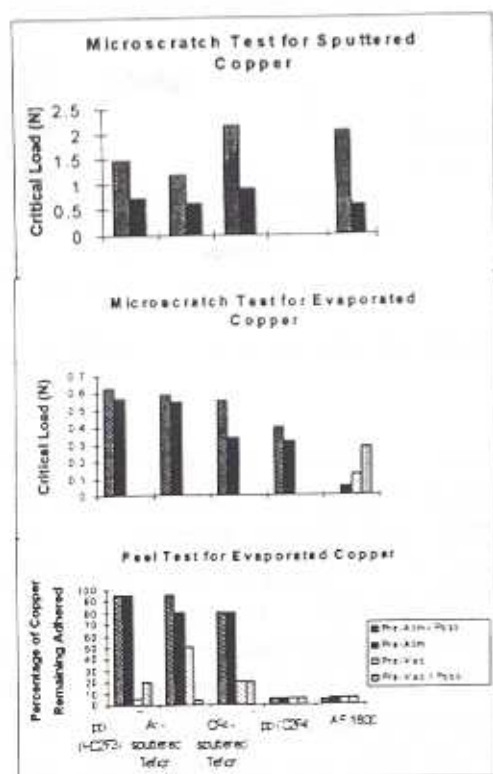


Fig.1: Adhesion of Cu on different fluoropolymers measured by MST and peel test.

As-deposited fluorocarbon films exhibited unstable dielectric properties. Stability was obtained after annealing at 200 °C for 30 minutes in vacuum which generally leads to desorption of water vapor [7], low molecular weight species and reduction of free radicals. Mass spectroscopy analyses performed in the present work further indicated that the annealing process is accompanied by the loss of low molecular weight species in the case of the SP and PP fluoropolymers, and by the loss of retained solvent in the case of Teflon AF1600. Subsequent exposure to air caused slight increases in the dielectric constant values, which returned to their former values on evacuation. With the exception of PP( $C_2F_3H$ ), which frequently short circuited above room temperature, all other fluoropolymers showed permittivity values below 1.9 after vacuum annealing. Dielectric behaviour of the fluoropolymer films is illustrated in Figs.2 and 3 by the effect of temperature and frequency on the dielectric constant  $K$  and the dissipation factor  $\tan\delta$ .

The  $K$  and  $\tan\delta$  values agree quite well with the data published earlier for the PP and SP fluoropolymers [7-9] and for the Teflon AF1600 [10]. In the present case the increase of  $\tan\delta$  with temperature for the SP films (Fig.2b) can be associated with the increased chain mobility [7]. On the other hand,  $K$  decreases very slightly with the frequency over a very

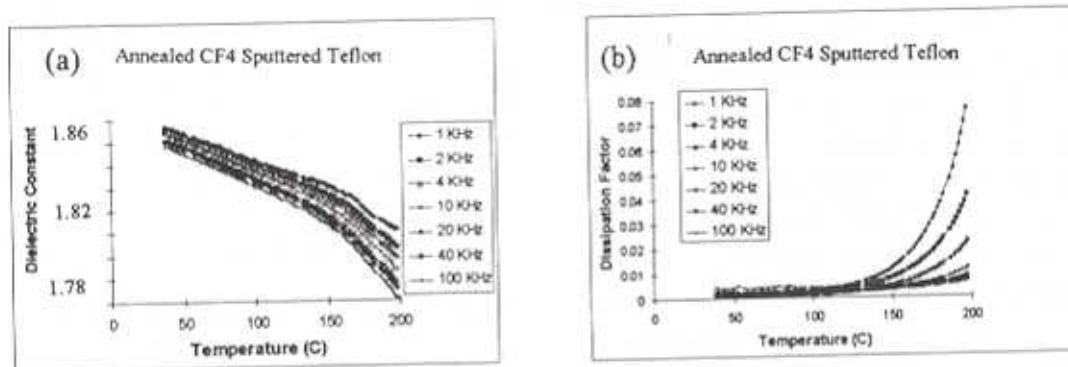


Fig 2: Dielectric constant (a), and dissipation factor (b) as a function of temperature.

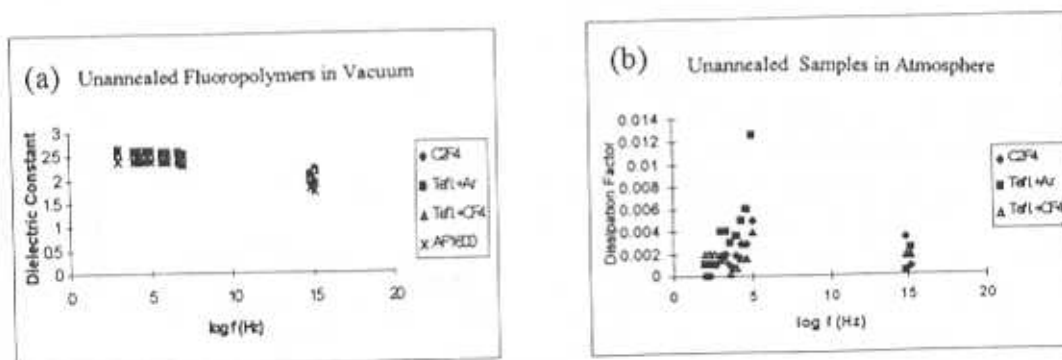


Fig. 3: Dielectric constant (a) and dissipation factor (b) as a function of frequency.

large frequency range, while  $\tan\delta$  increases with frequency on the lower frequency side (see Fig.3): the latter effect may suggest that a loss peak may exist between  $10^5$  and  $10^{10}$  Hz, but its presence has not been confirmed yet. Such a peak may be related to the presence of  $C=O$  polar groups in the films, also detected by FTIR measurements [8].

Infrared spectra originated from the near-surface region were measured by PA-FTIR, and they are illustrated in Fig.4 for PP(C2F4) and SD Teflon AF1600. The PP film shows a typical broad peak around  $1200\text{ cm}^{-1}$ , mostly due to stretching of  $CF_2$  groups [7,11,12]. In addition, a broad peak around  $1700\text{ cm}^{-1}$  confirms the presence of carbonyl ( $C=O$ ) groups, mostly due to the reaction of the films free radicals with the atmospheric oxygen upon the sample exposure to air [7,8,12]. Weak absorption around  $3400\text{ cm}^{-1}$  suggests the presence of  $-OH$  groups due to sorption of water vapor. For the SD Teflon AF1600, the characteristic peaks are due to  $CF_2$  stretching and due to the fluorinated dioxole component ( $1250\text{ cm}^{-1}$  and  $1150\text{ cm}^{-1}$ ), and due to  $CF_3$  vibrations ( $980\text{ cm}^{-1}$ )[10].

In both cases, residual atmosphere in the measuring compartment contained some CO<sub>2</sub> molecules contributing a symptomatic peak around 2400 cm<sup>-1</sup>.

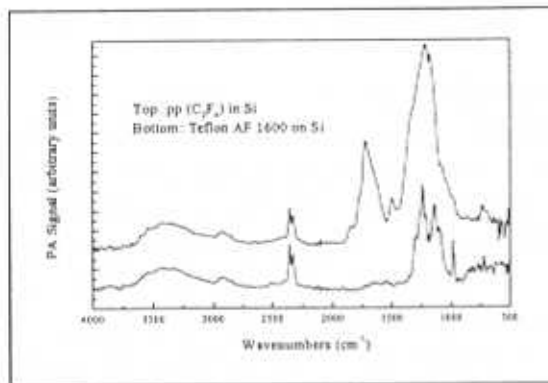


Fig.4: PA-FTIR signal for Teflon AF1600 and PP(C<sub>2</sub>F<sub>4</sub>)

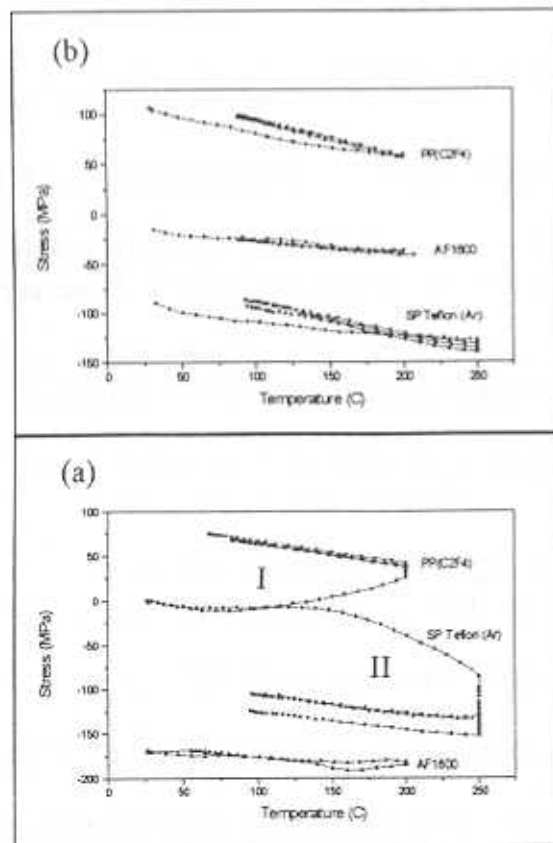


Fig.5: Stress as a function of temperature for fluoropolymers without (a) and with (b) an evaporated Cu layer.

evaporated Cu layer: the latter one contributed by its tensile stress to the overall stress values for all the evaluated films (Fig.5b). The stress did not appreciably change upon

XPS survey scans at 0° (perpendicular), 35° and 70° take-off angles were made for both unannealed and samples annealed at 100, 150, 200, and 250 °C. The annealing and XPS analyses were performed in-situ. Because the depth probed varies with the cosine of the angle of incidence, this depth could be varied by a factor of 4 between take-off angles of 0° and 70°. Atomic profiles so obtained indicate increased Cu diffusion toward the film bulk at elevated temperatures.

The effect of temperature on the evolution of film stress is shown in Fig.5. Stress measurements of unmetallized and metallized samples behaved differently from each other, showing the effect of metallization on stress. Irreversible changes in the stress of bare PP and SP fluoropolymer films can be seen during the first heating cycle (see curves I and II in Fig.5a). For both types of the plasma-deposited fluoropolymers the stress is initially very low (~0 MPa). With increasing the temperature, the stress values increase above 100 °C for the PP(C<sub>2</sub>F<sub>4</sub>), and this material adopts a tensile stress which is then reproducibly stable in the subsequent thermal cycles. This effect may suggest a loss (desorption) of low molecular weight species. On the other hand, the SP-Teflon film develops a compressive stress upon annealing, suggesting a film densification upon annealing to 250 °C. Trapped gases (such as Ar) may also contribute to the higher compressive stress. The stress values for Teflon AF1600 are negative and stable with varying annealing temperatures. After the initial stress measurements the fluoropolymers were coated with an

further thermal cycling, and the slight changes can be tentatively related to the stress relaxation at the Cu/fluoropolymer interface and to partial Cu diffusion.

## CONCLUSION

In the present work, we studied low permittivity dielectric/metal system consisting of fluoropolymers and copper. The plasma polymerized  $C_2F_4$ , sputtered Teflon and the spin-deposited Teflon AF1600 provided, after annealing to 200 °C for 30 min in vacuum, permittivity values below 1.9 and dissipation factors below 0.001. We found that for evaporated copper, adhesion to PP and SP fluoropolymers improves with preannealing in atmosphere, as well as postannealing in vacuum. For AF1600, adhesion is improved by postannealing alone. Adhesion is greater for sputtered copper, compared to evaporated copper, because of more extensive surface reaction during the more energetic sputter deposition. Suitable film stability was achieved upon postannealing in vacuum at 200 °C for 30 minutes. Following this treatment fluoropolymers do not exhibit thermal stability problems at temperatures below 200 °C.

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