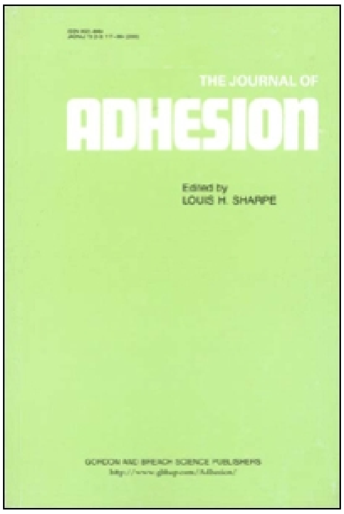

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The Adhesion of Evaporated Copper to Dow Cyclotene 3022®, Determined by Microscratch Testing

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THE ADHESION OF EVAPORATED COPPER TO DOW CYCLOTENE 3022®, DETERMINED BY MICROSCRATCH TESTING

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The mechanical integrity, stability, and strong interfacial adhesion between Cu, a high conductivity metal, and Dow Cyclotene 3022®, a low permittivity polymer, are important for their application in future high-speed microelectronic devices. In the present study, Cu was deposited by both evaporation and sputtering, and various Cyclotene surface modifications were carried out. These modifications included low pressure N_2 *plasma and* Ar^+ *treatments and the use of a Ti interlayer. The adhesion was evaluated by use of the microscratch test, and complemented by an adhesive tape peel test and XPS. The* N_2 *plasma treatment was found to lead to a dramatic increase in adhesion, which was influenced to a minor extent by the adhesion promoter that was used at the Cyclotene/Si substrate interface. This significant Cu/Cyclotene adhesion enhancement is interpreted in terms of the chemical groups present at the Cyclotene surface and the bonds formed on Cu deposition.*

Keywords: Adhesion; Evaporated Cu; Cyclotene; Interfacial reactions; Microscratch testing; Surface modifications

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1. INTRODUCTION

The digital signal delay time in microelectronic devices, τ, is a function of the resistivity of the metal carrying the signal and the permittivity of the surrounding dielectric. In order for a device to be used, the value of τ must be reduced to an insignificant fraction of the inherent delay time. In terms of the newer, high speed III/V semiconductors, this requires the use of higher-conductivity metals and lower-permittivity dielectrics [1].

While copper is certainly the high conductivity metal of choice for these newer devices, several candidate low permittivity dielectrics are presently being considered; these include fluorinated SiO_2 [2], fluorinated polyimides [3], foams [4], and plasma-polymerized fluorocarbons [5, 6]. Dow Cyclotene 3022, the Diels-Alder addition product of 1,3-bis(2-bicyclo[4.2.0]octa-1,3,5-trien-3-ynetheny)-1,1,3,3-tetramethyldisiloxane, a bis-benzocyclobutene-terminated divinyl siloxane [7], is another attractive material. As with all new metal/dielectric combinations, integration issues must be overcome; among these, interfacial adhesion is particularly important. Its understanding and improvement require the development of new techniques to enhance and control it, as well as the development of sensitive techniques to evaluate it.

The integrity of the metal/dielectric interface must be maintained not only during the hostile chemical and thermal excursions seen throughout the manufacturing process but during the prolonged, less hostile exposures seen during the device lifetime as well. Previous studies were carried out on the adhesion of copper evaporated [8, 9] and sputtered [10] onto Cyclotene. While one group used adhesive tape peel measurements [8] to establish adhesion and another group used stud-pull measurements [9], the values these groups obtained are inconsistent and are in qualitative disagreement with our own, which were obtained on treated and untreated Cyclotene [11] using microscratch testing. For this reason, we detail here our far more systematic study, leading to consistent microscratch results.

Adhesion is a film characteristic of great concern, and numerous testing methods have been proposed and reviewed [12–14]. Basically, three types of tests may be distinguished: (1) tensile-type tests, such as the direct-pull (or toggle) test; (2) shear-type tests, the simplest being the adhesive tape peel test; and (3) scratch tests.

Scratch testing is increasingly being used for the evaluation of adhesion because it can provide rapid qualitative, semiquantitative, or quantitative information. It consists of drawing a stylus (or indenter) of known radius over a film or coating, under a linearly increasing load. During the scratching procedure, the stresses induced by indentation and friction combine to contribute to the total compressive and tensile stresses at the leading and trailing edges of the stylus [15]. As a result, the film begins to delaminate. Various delamination patterns may be distinguished, thus providing qualitative information on adhesion [16].

A critical load, Lc, indicates the start of delamination. Such values may be determined from abrupt changes in the acoustical signal or frictional force during scratching, or from microscopic observation [14]. Lc values may be viewed as semiquantitative measures of adhesion.

Theoretical analyses and models have been used to derive the adhesion force and the reversible work of adhesion (W_a) from the Lc values. Laugier [17] used a Griffith energy balance approach to obtain W_a by considering the compressive stress ahead of the indenter and the thickness and elastic modulus of the film. The model assumes fully elastic behavior, which is often not the case in real situations. Burnett and Rickerby [18] identified three contributions to the stress responsible for delamination: an elasto-plastic indentation stress, an internal film stress, and a tangential friction stress. The model of Bull and Rickerby [19] relates these stress components to W_a; it has been successfully applied to various film-substrate combinations [20].

2. EXPERIMENTAL

Samples were prepared by depositing the commercially available 46% (w/w), B-staged Cyclotene 3022 in mesitylene solution onto cleaned Si wafers which might be treated with adhesion promoter, as described in our previous studies on Cyclotene [7]. After spinning, the wafers were cured by being linearly raised to 250°C and permitted to cool, the process occurring under N_2. The conditions used gave a Cyclotene layer about 1.3 μm thick.

In the present case, two adhesion promoters were used: Dow AP3000, triacetoxy vinyl silane, and Dow AP8000, triethoxy γ-aminopropyl silane. Each was applied as a 2% (w/w) solution in water. After spinning, the wafers were dried at 110°C for five minutes.

Two types of Cyclotene surface treatment were used prior to metallization: (1) argon ion bombardment took place at a pressure of $< 5 \times 10^{-6}$ torr, using a Vacuum Generators AG21 ion source whose source voltage was 2 kV; (2) low pressure N_2 plasma treatments were carried out in a microwave plasma (2.45 GHz). The N_2 plasma conditions used were previously found [21–23] to yield the best adhesion enhancement for various combinations of materials; the discharge was excited in N_2 at a pressure of 200 mtorr, a power of 250 W and a N_2 flow rate of 95 sccm. Copper was deposited, at a rate of ~3 nm/min, to a thickness of 200 nm.

Film adhesion was evaluated using the MST microscratch tester manufactured by CSEM (Neuchatel, Switzerland). A 0.4 mm radius hemispherical Rockwell C diamond stylus was drawn across the sample while the applied load was linearly increased from 0 to 30 N over a distance of 1 cm, at a speed of 1 cm/min. The scratching process was evaluated by simultaneously observing the emitted acoustical signal and the frictional force. The scratch track was inspected by optical microscope, using a calibrated x-t stage. Of these, optical observations were found to be the most reliable for adhesion determinations of the present system.

During scratching, several critical loads associated with the delamination process were distinguished, corresponding to the onset of failure at different interfaces (see Figure 1). They are (1) Lc1, the critical load at which defects are initially observed in the film surface, (2) Lc2, the critical load at which the complete loss of copper adhesion permits the copper to tear, and (3) Lc3, the critical load at which adhesion is lost between the Cyclotene and the Si substrate. At least two samples were used for each condition; for each sample, the Lc values reported represent the average of at least 5 scratches.

For comparison, Cu adhesion was also evaluated using the traditional adhesive tape peel test, which was performed in the following manner: a strip of 3M type 853 Scotch® tape was gently placed across the sample and a 2 kg roller was rolled twice over it. Immediately thereafter, the tape was peeled by pulling perpendicular to the surface. The percentage of the area of Cu remaining on the sample was then estimated by optical microscopic observation.

Surface composition before and after Cyclotene treatment was evaluated by XPS. We used a VG ESCALAB 3 Mark II equipped with a nonmonochromated Mg K_α source.

3. RESULTS AND DISCUSSION

Before we can analyze the adhesion measurements between the Cu and the underlying Cyclotene, we must first discuss the methodology and reliability of the scratch test measurements used to assess the adhesion. The MST and adhesive tape peel test results are found in Tables 1 and 2. Table 1 contains values for unmetallized (samples 1–3) and untreated surfaces (samples 4–6), while Table 2 contains the values for N_2 treatments under various exposure conditions. As seen in Figure 2, these values indicate relationships between the area of Cu remaining

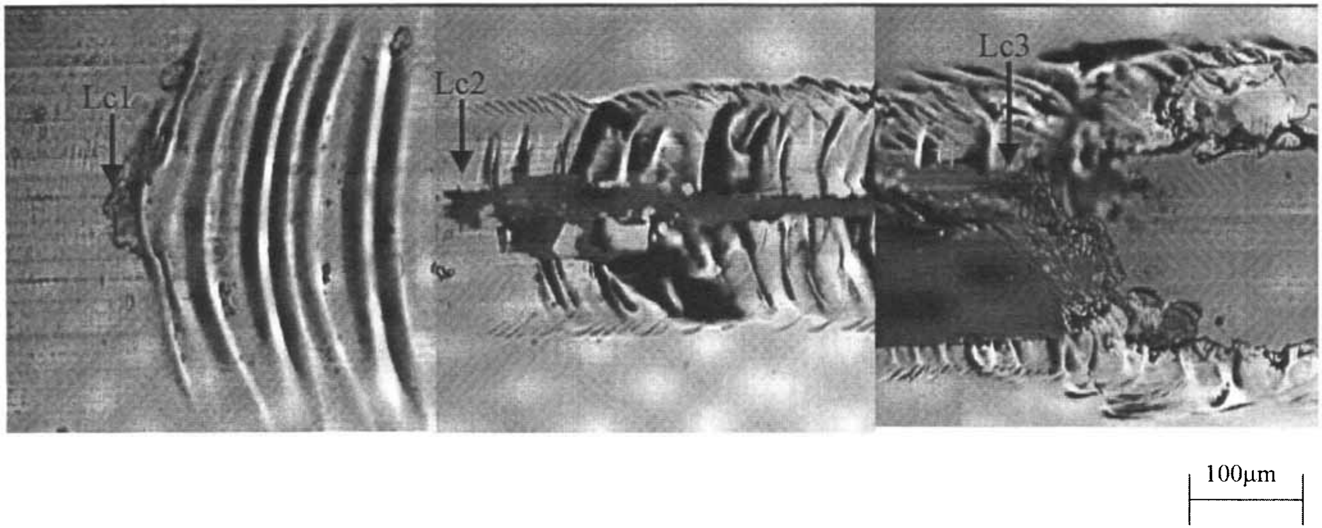

FIGURE 1 Photomicrographs of scratch tracks showing Lc1 (at which defects are observed in the Cu), Lc2 (at which the Cu begins to tear), and Lc3 (at which adhesion is lost between the Cyclotene and the Si substrate).

TABLE 1 Reference Microscratch Adhesion Data

Group	Adhesion promoter[a]	Lc1 (N)	Lc2 (N)	Lc3 (N)	Peel test (%Cu)
Reference 1	—	17.2[b]	—	17.6	—
Reference 2	A	19.2[b]	—	20.9	—
Reference 3	B	22.7[b]	—	26.0	—
Reference 4	—	2.9	10.2	15.2	0
Reference 5	A	1.9	9.8	15.3	0
Reference 6	B	1.8	14.5	24.2	0

[a] A is AP3000 and B is AP8000.

[b] These values, for samples without deposited copper, indicate the loads for initial deformation of the Cyclotene®, normally hidden by the copper deposit.

TABLE 2 Microscratch Adhesion Data for N_2-plasma Treated Cyclotene®

Group	N_2 plasma (s)	Adhesion promoter	Copper	350°C annealing (min)	Lc1 (N)	Lc2 (N)	Lc3 (N)	Peel test (%Cu)	Coefficient of friction ±0.02
Plasma 1	60	—	—	—	18.2[b]	—	18.7	—	—
Plasma 2	60	A	—	—	22.6[b]	—	22.8	—	—
Plasma 3	60	B	—	—	25.5[b]	—	26.9	—	—
Plasma 4	30	A	+	—	6.4	11.0	15.4	30	0.09
Plasma 5	30	B	+	—	6.7	15.6	24.1	40	—
Plasma 6	60	—	+	—	16.4	17.1	17.5	90	—
Plasma 7	60	A	+	—	15.7	16.8	17.4	85	0.08
Plasma 8	60	B	+	—	18.1	19.0	24.4	100	—
Plasma 9	60	A	+	60	17.0	17.3	18.1	80	—
Plasma 10	60	B	+	60	18.5	18.5	24.8	100	—
Plasma 11	180	A	+	—	15.8	16.2	16.4	100	0.07
Plasma 12	180	B	+	—	17.4	17.6	17.9	100	—
Plasma 13	360	A	+	—	15.2	15.5	15.7	70	0.08
Plasma 14	360	B	+	—	14.3	15.9	16.2	60	
Plasma 15	600	A	+	—	14.4	14.7	14.9	0	0.10
Plasma 16	600	B	+	—	13.7	15.8	16.0	0	

[a] A is AP3000 and B is AP8000.

[b] These values, for samples without deposited copper, indicate the loads for initial deformation of the Cyclotene®, normally hidden by the copper deposit.

after peeling and both Lc1 and Lc2 values. We may thus conclude that these Lc values are directly related to the area of residual Cu, both scratch test and peel test values increasing systematically, indicating that both types of Lc failure are related to Cu adhesion. Of these, Lc1 is the value at which the Cu delaminates from the Cyclotene, permitting

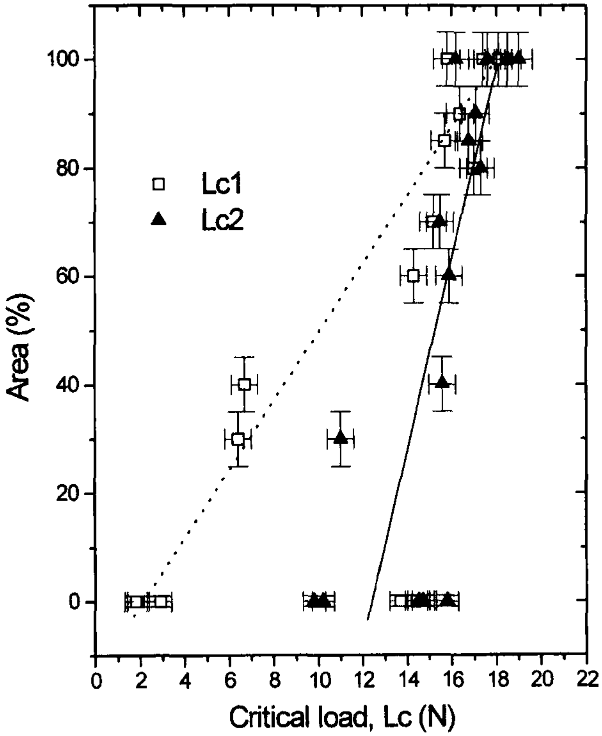

FIGURE 2 A plot of the correlations between the critical loads Lc1 and Lc2 and the % area of retained Cu.

contaminant atmospheric gases to access the Cu/Cyclotene interface, and we apply it to the remainder of our study, as our assessment of adhesion. It should be noted that this correlation of Lc and peel test values has been found for other systems as well, such as Cu on plasma-treated Teflon PFA [22]. In fact, scratch test measurements are very convenient, the associated statistics are very good because many scratches can be performed in a small area, and Lc values may be obtained even where peel tests show no sign of metal loss.

Complementary measurements were performed on the bare Cyclotene (Table 1, samples 1–3). Here, Lc1 indicates the load at which defects first form on the bare Cyclotene, while Lc3 indicates the load at which the Cyclotene delaminates from the Si wafer. These results indicate that the AP8000 adhesion promoter is marginally better than the AP3000 adhesion promoter, which is marginally better than no adhesion promoter.

The effect of N_2 plasma treatment time on the Lc values is seen in Figure 3. The most pronounced change is found for Lc1, which rises rapidly to a maximum near $t = 60$ s, beyond which it decreases; both Lc2 and Lc3 behave similarly. None of these values demonstrates a systematic correlation with the coefficient of friction values also found in Table 2, in contradistinction to the correlations found for hard coatings on plastic lenses [20]. In our case, the coefficient of friction remains very low ($\sim$0.07–0.10; see Table 2), with all values falling within experimental error.

The decay of the Lc values with prolonged N_2 plasma treatment time ($t > 60$ s) is related to the change in Cyclotene surface structure and the resultant formation of a weak boundary layer [22]. The change of interfacial adhesion with treatment time is related to the change in chemical composition of the treated surface. In Figure 4, we show that

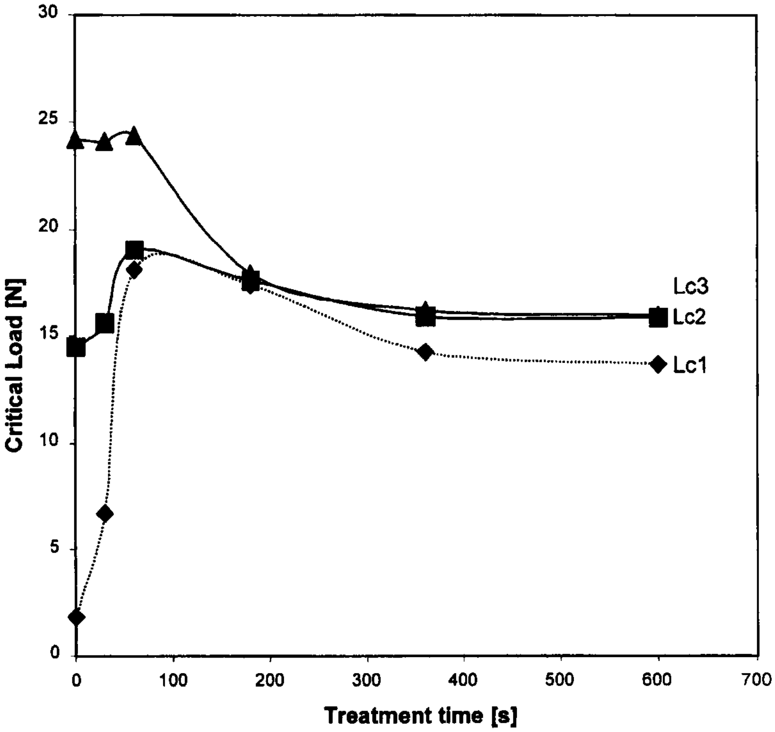

FIGURE 3 A plot of Lc1, Lc2, and Lc3 values as an function of N_2 plasma treatment for samples using AP8000.

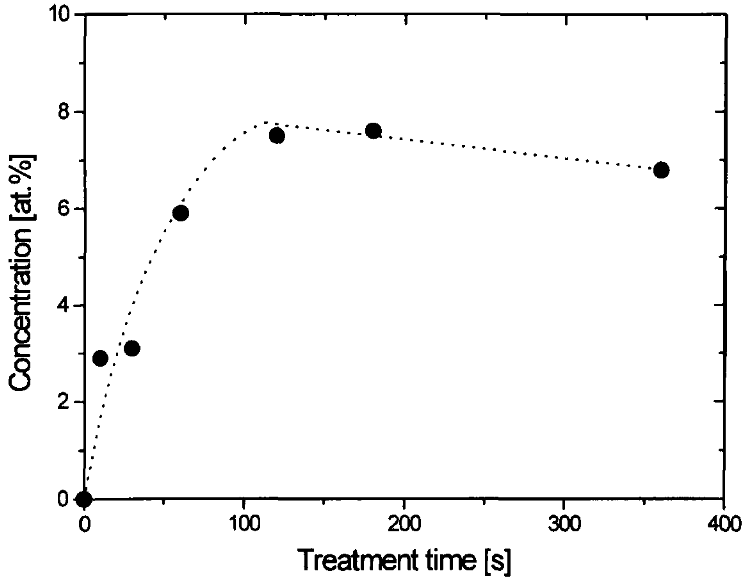

FIGURE 4 A plot of the introduction of N-containing groups to the Cyclotene surface as a function of N_2 plasma treatment time.

the total concentration of N (at. %) with treatment time under our experimental conditions reaches a maximum above 100 s of treatment time, following the same trend seen in Figure 3.

The correlation between Lcl and nitrogen concentration is seen in Figure 5, which confirms that the increase in adhesion is directly related to the presence of N-containing groups on the Cyclotene surface. In fact, the formation of strong Metal-N bonds and their beneficial effects on adhesion have been observed for different materials combinations, such as Ag on polyethylene [24] and Cu on Teflon PFA [22]. In fact, this enhancement of adhesion by plasma treatment seems to be related to several adhesion mechanisms [25, 26]: (1) it cleans the surface and removes possible weak boundary layers; (2) it may increase the substrate microroughness; (3) it may increase the surface energy, leading to an increased interaction with surface metal atoms which then form smaller clusters; and (4) in the case of a N_2 plasma, it grafts N-containing groups that form strong Metal-N bonds. It should be noted that such surfaces remain active for long periods of time, extending from hours to days [27].

At this point, convinced that the use of AP8000 gave better adhesion of the Cyclotene to the Si substrate, we used only that adhesion

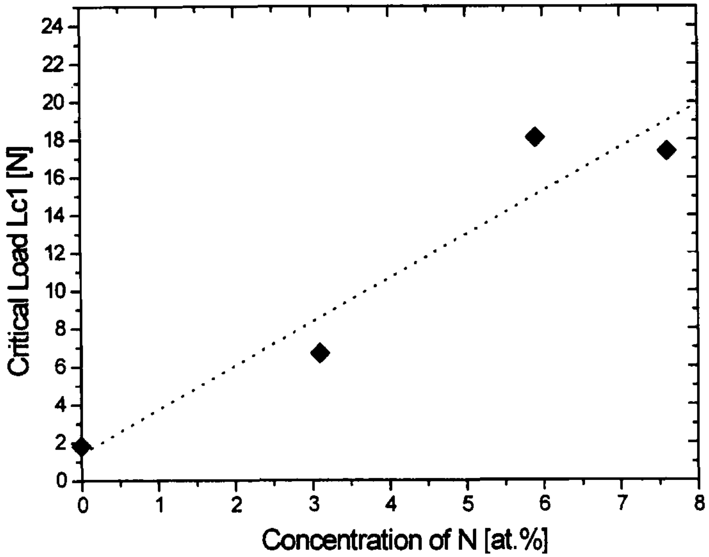

FIGURE 5 A plot of Lc1 values as a function of N-containing groups subsequent to N_2 plasma treatment.

promoter in our evaluation of the results obtained on sputtering the Cyclotene surface with an Ar^+ beam. The sputtering results are seen in Table 3. Quite clearly, no adhesion enhancement was obtained, even after sputtering for 600 s. The reason is found in a recent paper from our group [11] that shows the following: sputtering causes surface degradation and the formation of -Si-O· and -Si·, as well as -C· fragments. Both -Si-O· and -C· react with evaporated Cu^0 to form -Si-O-Cu and -C-Cu; these bonds to Cu are too weak to prevent lateral surface diffusion of the Cu, a key criterion in the evaluation of the Cu/Cyclotene adhesion [28, 29].

We have recently analyzed, in considerable detail, the Cyclotene surface and the effect of chemical modification on the strength of the Cyclotene-Cu bond. The Cu does not diffuse into the Cyclotene [28] but, instead, diffuses across its surface to form clusters. The ease of cluster growth (*i.e.*, the ability of the clusters to enlarge) is directly related to the bond formed between the deposited cluster and the Cyclotene. In the present study, both Ar^+ sputtering (sputtering 1–6, Table 3) and, subsequent to air exposure, N_2 plasma treatment (Plasma 4–16, Table 2) introduce groups capable of giving -O-Cu bonds, but only plasma treatment introduces groups capable of giving

TABLE 3 Microscratch Adhesion Data for Ar$^+$-treated Cyclotene®

Group	Ar$^+$ sputtering (s)	Lc1 (N)	Lc2 (N)	Lc3 (N)	Peel test (%Cu)	Coefficient of friction ±0.02
Sputtering 1	0	1.8	14.6	24.0	0	0.08
Sputtering 2	60	2.2	14.6	23.9	0	0.09
Sputtering 3	120	2.2	14.8	23.8	0	0.10
Sputtering 4	180	2.4	15.0	21.5	0	0.11
Sputtering 5	360	2.5	12.6	19.2	0	0.09
Sputtering 6	600	1.2	12.8	19.8	0	0.10

-N-Cu bonds [28]. The results in Table 4 strongly suggest that the increased adhesion seen there is due to the formation of -N-Cu bonds. The metal clusters that form on the Cyclotene surface on Cu deposition are most stable in the case of N_2 plasma treatment, with little evidence of coalescence, even at a temperature of 350°C [30].

Discussions with industrial workers have led us to conclude that Lc1 is the most important critical load value for comparison purposes because it is the load at which contaminant ingress to the Cu/Cyclotene interface can begin. Using the Lc1 criterion, not only is the N_2 plasma treatment better at providing increased copper adhesion, it

TABLE 4 The Effects of Various Surface Treatments on Cu Adhesion, and the Interfacial Interactions Responsible

Deposition methods	Surface treatment	Adhesion[a]	Structure giving adhesion
Evaporation	None	0.7 (poor)	Cu-aromatic ring orbital overlap [16]
Evaporation	Ar$^+$ cleaning	1.3 (poor)	Cu-O bonding with surface free radicals formed on sputtering [6]
Sputtering[b]	None	7.4 (moderate)	Cu-O bonding with surface free radicals formed on sputtering; Cu clusters implanted below surface [17]
Sputtering[b]	Ar$^+$ cleaning	6.7 (moderate)	Cu-O bonding with surface free radicals formed on sputtering; Cu clusters implanted below surface [17]
Evaporation	N_2 plasma treatment	10 (good)	Cu-N bonding with grafted NH_2 [11]

[a] On a scale of 0–10, where 0 is no adhesion and 10 is our best adhesion, obtained on N_2 plasma treatment.

[b] Deposition rate: 0.67 Å/min.

is also seen that such adhesion is optimized after the relatively short exposure time of 60 s. This is because the grafting of reactive N-containing groups reaches a steady state after 60 s of plasma treatment [28] (see Tables 2 and 4, and Figure 3). In addition, small but consistent differences are seen between samples using AP3000 and AP8000, despite the fact that the interface being tested is not that to which the adhesion promoter was applied.

4. CONCLUSIONS

A summary of Cu adhesion as a function of Cyclotene surface treatment is found in Table 4. Of the several Cyclotene surface treatments evaluated, N_2 plasma treatment produces by far the highest Cu adhesion. This is shown to be due to the presence of N-containing groups, introduced by the plasma treatment. The microscratch technique is shown to be very suitable for the assessment of adhesion at the Cu/Cyclotene interface and permits us to optimize the surface treatment conditions.

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