## Refersnces


[1] S.P. Murarka, R.J. Gutmann, A.E. Kaloyeros, W.A. Lanford, Thin Solid Films, 236(1993) 257.

[2] S.P. Murarka and M. C. Pecker, Electronic Materials, Science and Technology, Edited by H.B. lovanovich, Academic Press, London, (1989) 269.

[3] S.Poulin, D.-Q. Yang, E. Sacher, C.Hyett, T.H. Ellis, Appl. Surf. Sci., 165(2000)15.

[4] N. Schuhler, P.Oelhafen, J. Vac. Sci. Technol., A15 (1997) 2529.

[5] F.S. Shieu, M.H. Shiao, J.Adh. Sci. Technol., 12 (1998) 19.

[6] K.W.Paik, A.S. Cole, R.J. Saia, J-J. Chera, J. Adh. Sci. Technol., 7(1993) 403.

[7] D.-Q. Yang, E. Sacher, Appl. Surf. Sci. submitted.

[8] D.Q., Yang, L. Martinu, E. Sacher A. Sadouhg. Vanini, Appl. Surf. Sci. Submitted.

[9] A.Sadough-Vanini, D.Q., Yang, L. Martinu, E. Sacher, J.Adhesion, Accepted for publication.

[10] L.Martinu, in Plasma Processing of Polymers, R.d'Agostino, P.Favia and F.Fracassi, Eds. Kluwer, Boston, 1997, p. 247.

[11] A.Alptekin, E. Sacher, G.Czeremuzkin, L. Martinu, M. DiRenzo, in Low and High Dielectric Constant Materials: Materials Science, Processing and Reliability Issues, H.S. Rathore, R. Singh, R.P.S. Thakur and S.C. Sun, eds. Electrochemical Society Penington, NJ, 1997, P. 58.

[12] E. Griswold, L. Martinu, m. Meunier, V. Pigaks, S. Poulin, S. Rodrigues, E. Sacher, A. Sadough-Vanini, G. M. Smith and D. Q. Yang, in preparation.

[13] D.Q. Yang, E. Sacher and A. Sadough. Vanini, in preparation.

[14] J.E.E.Baglin, in Fundamentals of Adhesion, L.-H. Lee, ed. Plenum, New York, 1991, p. 363.

## Table (1) Cu adhesion results

| Group | $N_2$ Plasma Sec | Adhesion Promoter | Copper | 350 °C Annealing min | $Ar^+$ Sputtering sec | Lc1 N | Lc2 N | Lc3 N | Peel Test % Cu |
|---|---|---|---|---|---|---|---|---|---|
| Reference 1 | - | - | - | - | - | 17.25[a] | - | 17.61 | - |
| 2 | - | AP3000 | - | - | - | 19.23[a] | - | 20.9 | - |
| 3 | - | AP8000 | - | - | - | 22.75[a] | - | 25.97 | - |
| 4 | - | - | + | - | - | 2.89 | 10.2 | 15.2 | 0 |
| 5 | - | AP3000 | + | - | - | 1.88 | 9.78 | 15.33 | 0 |
| 6 | - | AP8000 | + | - | - | 1.83 | 14.48 | 24.2 | 0 |
| Plasma 1 | 60 | - | - | - | - | 18.18[a] | - | 18.74 | - |
| 2 | 60 | AP3000 | - | - | - | 22.57[a] | - | 22.78 | - |
| 3 | 60 | AP8000 | - | - | - | 25.55[a] | - | 26.92 | - |
| 4 | 30 | AP3000 | + | - | - | 6.45 | 10.98 | 15.45 | 30 |
| 5 | 30 | AP8000 | + | - | - | 6.7 | 15.6 | 24.1 | 40 |
| 6 | 60 | - | + | - | - | 16.42 | 17.15 | 17.48 | 90 |
| 7 | 60 | AP3000 | + | - | - | 15.66 | 16.85 | 17.42 | 85 |
| 8 | 60 | AP8000 | + | - | - | 18.11 | 19.01 | 24.39 | 100 |
| 9 | 60 | AP3000 | + | 60 | - | 16.98 | 17.27 | 18.14 | 80 |
| 10 | 60 | AP8000 | + | 60 | - | 18.54 | 18.55 | 24.8 | 100 |
| 11 | 180 | AP3000 | + | - | - | 15.76 | 16.16 | 16.4 | 100 |
| 12 | 180 | AP8000 | + | - | - | 17.4 | 17.6 | 17.9 | 100 |
| 13 | 360 | AP3000 | + | - | - | 15.18 | 15.5 | 15.7 | 70 |
| 14 | 360 | AP8000 | + | - | - | 14.27 | 15.93 | 16.2 | 60 |
| 15 | 600 | AP3000 | + | - | - | 14.4 | 14.7 | 14.9 | 0 |
| 16 | 600 | AP8000 | + | - | - | 13.7 | 15.8 | 15.96 | 0 |
| Thermal 1 | - | AP8000 | + | 20 | - | 1.99 | 14.8 | 23.5 | 0 |
| 2 | - | AP8000 | + | 40 | - | 2.54 | 14.2 | 15.7 | 0 |
| 3 | - | AP8000 | + | 60 | - | 2.72 | 12.87 | 15.56 | 0 |
| Sputtering 1 | - | AP8000 | + | - | 20 | 1.85 | 14.56 | 24 | 0 |
| 2 | - | AP8000 | + | - | 60 | 2.18 | 14.61 | 23.9 | 0 |
| 3 | - | AP8000 | + | - | 120 | 2.20 | 14.8 | 23.8 | 0 |
| 4 | - | AP8000 | + | - | 180 | 2.41 | 15.01 | 21.5 | 0 |
| 5 | - | AP8000 | + | - | 360 | 2.54 | 12.59 | 19.18 | 0 |
| 6 | - | AP8000 | + | - | 600 | 1.16 | 12.8 | 19.8 | 0 |
| Silicon | - | - | + | - | - | 7.23 | 11.31 | - | 0 |
| Glass Slide | - | - | + | - | - | 8.52 | 12.5 | - | 0 |

**a. These values, for samples without deposited copper, indicate the loads for initial deformation of the Cyclotene, normally hidden by the copper deposit.**

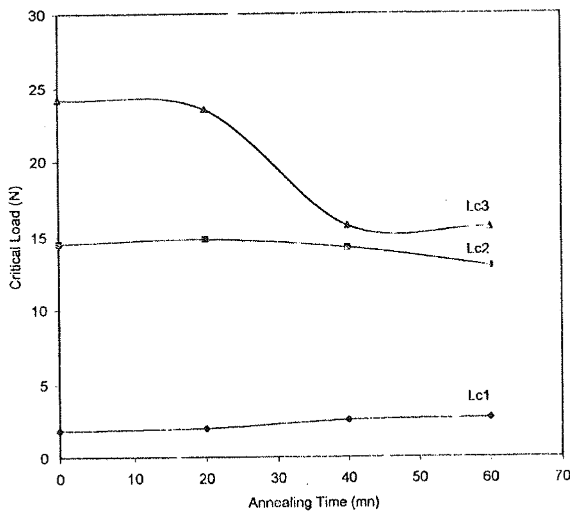


**Figure (3) Critical loads as a function of annealing time at 350°C for AP 8000 adhesion promoter.**

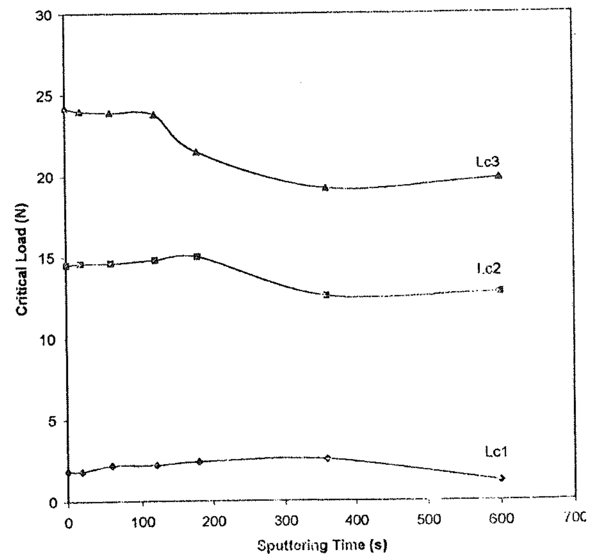


**Figure (4) Critical loads as a function of sputtering time prior to copper deposition for AP 8000 adhesion promoter.**

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.

In previous work (see,e.g., references 10 and 11), a qualitative correlation was found to exist between Lcl and peel test data. This is generally true here, as well (see Table 1), although there are exceptions. These exceptions are due to the fundamentally different ways in which these two tests measure adhesion, one in compression/ tension [11] and the other, in tension [14]. That there is any correlation at all is gratifying.

## Conclusions

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 - $NH_2$ groups introduced by the plasma treatment, and their capacity to form Cu-N bonds.

## Acknowledgements

The author wishes to thank the Natural Sciences and Engineering Research Council of Canada for support, and H. Nentwich, Nortel, for furnishing samples

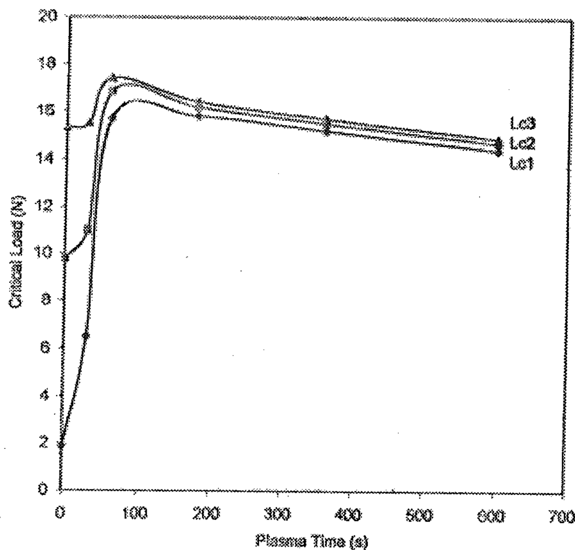


**Figure (1) Critical loads as a function of $N_2$ plasma treatment time for AP 3000 adhesion promoter.**

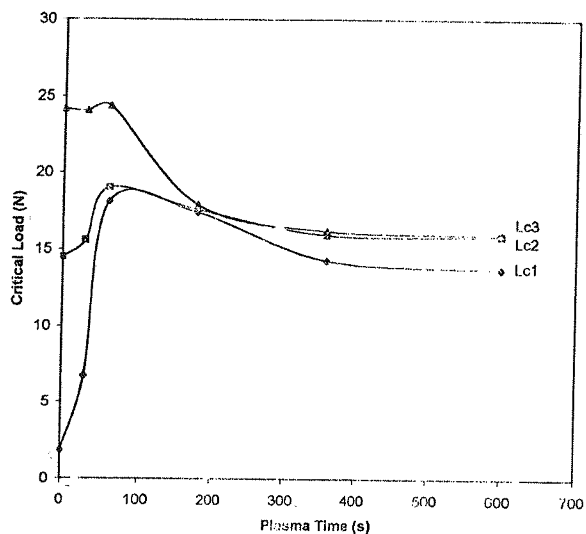


**Figure (2) Critical loads as a function of $N_2$ plasma treatment time for AP 8000 adhesion promoter.**

deposited (Reference 1-3 and Plasma 1-3), the Lcl values indicate the loads for the onset of initial deformations in the Cyclotene layers. In all six cases, they are found to be extremely close to the respective Lc3 values, for Cyclotene separation from the Si substrate. $Ar^+$ sputtering prior to Cu deposition (Sputtering 1-6) seems to do little good. The reason is found in a recent paper [7] that shows the following: sputttering 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° to form Si-O-Cu and -C-CU; these bonds to Cu are too weak to prevent lateral surface diffusion of the Cu to form clusters, a key criterion in the evaluation of Cu/Cyclotene adhesion [12].

Reference 3-6 show little difference in Lcl as a function of adhesion promoters but a clear preference for AP8000, the amine-terminated adhesion promoter in the cases of Lc2 and, especially, Lc3. This is explained in our recent XPS study of the effect of a $N_2$ plasma on Cyclotene [13]: the plasma process introduces both $-NH_2$ and -OH groups, which result in strong reaction with evaporated $Cu^0$ [12].

This was borne out in our $N_2$ plasma treatment experiments, designed to increase Lcl through the introduction of $-NH_2$ groups. These valuse are plotted in Figure 1 (AP3000) and 2 (AP8000). The data clearly demonstrate not only an optimum treatment time but also the fact that mechanical properties at each interface (i.e., Cu/Cyclotene and Cyclotene/Si) are interdependent.

The noticeably better performance of the AP8000 prompted us to limit the rest of the study to the use of that adhesion promoter. Short time thermal treatment did not appear to affect critical loads in the case of $N_2$ plasma treatment (Plasma 9, 10) but caused some degradation of Lc3, without affecting Lcl and Lc2, in its absence (Thermal 1-3); this is seen in Figure 3. Simmilar results were found for $Ar^+$ sputtering times prior to copper deposition, as seen in Figure 4, despite the fact that only the outer surface was affected by the sputtering treatment.

## Discussion

As will be detailed in the paper presently in preparation [12], the Cu does not diffuse into the Cyclotene 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 fromed between the deposited cluster and the Cyclotene. In the present study, both $Ar^+$ sputtering (Sputtering 1-6) and $N_2$ plasma treatment (Plasma 4-16) introduce groups capable of giving -O-Cu bonds but only plasma treatment introduce groups capable of giving-N-Cu bonds. The results in Table I clearly show that the capacity to form-N-Cu bonds provides the increased adhesion found.

One may ask, as we did, which critical load value is more industrially important in the case of metal adhesion. Is it Lcl, at the onset of metal adhesion, or Lc2, where a sufficient area of the metal interface has lost adhesion to produce a scratch in the metal film? Discussions with industrial workers have led us to conclude that Lcl is more important because it is the load at which contaminant ingress can begin.

Using this criterion, not only is $N_2$ plasma treatment better at providing increased copper adhesion, it is also seen that such adhesion is optimized after a relatively short exposure time. This is because the grafting of reactive groups is in competition with material loss due to sputtering, the latter beginning to predominate after 60 seconds of plasma treatment [13] (see Table I), In addition, small

Previous studies were carried out on the adhesion of copper evaporated [4,5] and sputtered [6] onto Cyclotene. While one group used peel measurements [4] to establish adhesion and another group, stud pull measurements [5], the values obtained are inconsistent and disagree with our own on treated and untreated Cyclotene [7,8]. For this reason, we detail here our far more consistent and understandable results, obtained by microscratch measurements.

Microscratch measurements use an indenter of fixed radius, which is linearly loaded as it is drawn across a sample. Such samples may consist of one or more layers deposited onto a substrate.Each layer ultimately undergoes delamination due to the combination of compressive and tensile stresses exerted by the indenter [9]. The type of delamination determined optically, and its precise critical load, determined optically, acoustically or by a change in the friction force, help to determine the type of failure and, at least semiquatitatively, its value. The technique has recently been reviewed [10] and has recently used it to study the adhesion of copper films on fluoropolymers [11].

## Experimental

Cyclotene, samples were prepared by depositing the commercially available 46% (w/w) B-staged Cyclotene 3022 in mesitylene solution onto cleaned Si wafers treated with adhesion promoter. After spinning, the wafers were cured by being linearly raised to 250°C and permitted to cool, the process occurring under $N_2$ [3]. The conditions used gave a Cyclotene layer 1.3 μm thick.

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

Metal was deposited, at a rate of ~0.5 Å/sec, to a thickness of 2000 Å. Samples were evaluated in a microscratch tester manufactured by CSEM, Neuchatel, Switzerland. A 0.4 mm Rockwell C diamond stylus was drawn across the sample and linearly loaded to 25 N over a distance of 1 cm. The progress of the scratch test was followed by microscope, and by measuring the emitted acoustical signal and the frictional force. Of these, optical observations are by far the most reliable because the otheres are often too insensitive to give precise values.

As previously described (9), there are several critical loads which were evaluated: Lcl, the critical load at which adhesion is initially lost between the copper and the Cyclotene surface; Lc2, the critical load where a sufficient loss of copper adhesion permits the copper to tear; Lc3, the critical load at which adhesion is lost between the Cyclotene and the Si substrate. The average values recorded are for at least five scratches and are to within ± 1.5 N or better.

## Results

Adhesion measurements were performed under several conditions, including no surface treatments (referred to as Reference), exposure to $N_2$ plasma for various lengths of time, with and without 350°C annealing (Plasma), 350°C annealing (Thermal) and $Ar^+$ sputtering prior to copper deposition (Sputtering). In addition, copper deposition was carried out directly onto Si wafers containing native surface oxide and glass microscope slides; these are presented for comparison purposes.

The results are shown in Table 1. In the six casses where copper layers were not

# *Surface Modification of a Polymer to Enhance Metal/Polymer Interface Toughness*

A.Sadough-Vanini
Associate Professor
Mech.Engineering Department,
Amirkabir University of Technology

## Abstract

*The mechanical stability of the multilevel interconnects used in microelectronics is related to the adhesion developed at the metal-dielectric interface. Microscratch measurements have been carried out on the system: evaporated Cu/Dow Cyclotene 3022/Si substrate, using various Cyclotene surface treatments meant to enhance Cu adhesion. $N_2$ plasma treatment of the Cyclotene surface leads to a dramatic increase on adhesion, influenced to a minor extent by the adhesion promoter used at the Cyclotene/silicon substrate interface.*

## Keywords

*Adhesion, Microscratch, Surface treatments, interface, sputtering.*

## Introduction

The drive for higher circuit speeds has led to the examination of new materials for the replacement of the presently used Al-polyimide technology, which provides signal delay times too long to be used in ULSI and GSI applications [1]. New materials, having lower resistivities and permitivities, are required for decreased digital signal delay time in microelectronic devices, $\tau = RxC$ [1], where R is the resistance along the line the signals travels and C is the capacitance of the surrounding dielectric. Additionally, these new materials and their associated metallization techniques must meet several conditions for long-term stability and reliability [2]: interfacial adhesion, diffusion and electromigration are among the more important physical characteristics, which can seriously affect the choice of a particular material or technological process.

Metal diffusion into an insulator during manufacture or use-life strongly affects the stability of electronic circuits. When the deposited metal diffuses into the insulator, 1) the metallic layer thickness decreases, which leads to an increased resistivity, 2) the effective insulator thickness and permittivity are modified, changing the circuit impedance and 3) the probability of a fatal short-circuit increases, affecting the overall reliability of the device.

While copper is certainly the high conductivity metals of choice, several candidate dielectrics are presently being considered. Among them is Dow Cyclotene 3022, a bis-benzocyclobutene-terminated tertramethyl divinyl siloxane prepolymer, which cures through a Diels-Alder addition [3]. As with all new metal/dielectric combinations, integration issues must be overcome; among these is interfacial adhesion.

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, as well, during the prolonged, less hostile exposures seen during the device liftime.