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Abstract
We show that there is a predictable correlation between the macroscopic critical load for the loss of adhesion of a thick copper film to the low-permittivity polymer, Dow Cyclotene, as determined from microscratch testing, and the kinetic coalescence coefficient of the initially formed copper nanoclusters on the same surface.

The purpose of this article is to show the existence of a correlation between nanoscopic and macroscopic measures of adhesion, in the case of Cu evaporated onto Dow Cyclotene. This demonstrates the importance of nanoscale interactions in the control of macroscopic behaviour. We are interested in the interaction of Cu clusters and Dow Cyclotene, a low-permittivity polymer that is a candidate for use in the new, high-speed VLSI and GSI technologies [1–3]. The condensation energy of Cu, 335 kJ mol^{-1} [4], is lower than the energies of any of the bonds in Cyclotene [5], which means that no chemical reactions, leading to interfacial adhesion, are expected to be provoked on Cu deposition. In fact, only a minor extent of orbital overlap exists, between one side of the A_{2u} orbitals of the Cyclotene aromatic rings and the A_{1g} orbitals of the Cu atoms [1].

As a result, the atoms are free to diffuse across the surface, to form spherical clusters. We have studied this cluster growth and diffusion process [6–9], and an important conclusion of these studies is that the ability for clusters to diffuse depends strongly on the extent of cluster–substrate interaction. That is, the cluster coalescence (diffusion) coefficient (see [7, 8] and references therein) can vary over several orders of magnitude, depending on the extent of surface interaction, to the point where the clusters become essentially immobile in the case of strong interaction.

In a recent study [10], samples of Cyclotene on silica wafers were subjected to variable-angle spectroscopic ellipsometry in the 260–1700 nm region, using a J A Woollam Company VASE ellipsometer. This permitted spectra to be taken from the sample underside, through the transparent silica and Cyclotene, as various thicknesses of Cu were deposited. The spectra,

evaluated by effective medium theory, using the instrument software, indicated the following: as more and more Cu is deposited, the spaces between the clusters are not filled in. Rather, a uniform Cu film deposits *onto* the clusters. Thus, the original clusters remain, forming the interphase between substrate and Cu film. It is, then, the interaction between cluster and substrate that determines the adhesion of the Cu film.

Macroscopic adhesion measurements take many forms [11–15]. Our preferred technique [15] is scratch testing, in which an indenter of known radius is drawn over the coating at a constant rate, under a linearly increasing load. Stresses induced by pressure and friction contribute to the total compressive and tensile stresses at the leading and trailing edges of the indenter [16]. The critical load, L_c, at which delamination initiates, is detected optically.

Several theoretical analyses have been proposed for the scratch process [17–21]. The one which best lends itself to this discussion is that of Benjamin and Weaver [17]. They showed that, for an indenter of radius, r, the shear force per unit area of surface, F, caused by the deformation, is related to the critical load, L_c, by

$$F = \frac{aP}{(r^2 - a^2)^{1/2}}, \tag{1}$$

where the radius of the circle of contact, a, is

$$a = \left(\frac{L_c}{\pi P}\right)^{1/2}. \tag{2}$$

Here, P is the indentation hardness of the substrate.

Cluster coalescence on surface diffusion is described by the coalescence coefficient, D_s, given by (see [7] and references therein)

$$D_s = \frac{\langle l^2 \rangle}{4t}, \tag{3}$$

where $\langle l \rangle$ is the mean cluster displacement over time, t. A coalescence coefficient, D_s, may be evaluated [8] from either of the following processes: the thickness-dependent cluster size change, measured *in situ* during the initial stages of deposition (a process that we call dynamic coalescence) or the time-dependent coalescence measured subsequent to deposition (static coalescence). Various mechanisms have been proposed to be responsible for cluster coalescence: these include two-dimensional evaporation and/or condensation, in which atoms leave, and subsequently reattach to, the cluster surface [22–26], used for metal clusters on metal substrates. Movement may also occur through a gliding-like motion of the whole cluster [27–30], a mechanism widely used to describe the motion of large two- and three-dimensional clusters on non-metallic solid surfaces, such as HOPG and metal oxides. Our clusters are only weakly held to the surface [1–3], making gliding the more likely process. Thus, we propose that the whole cluster diffuses on the surface, using a portion of the energy from the thermal background, kT. That is, the frictional work, W, overcome on cluster displacement, is

$$W = F_c \langle l \rangle = nkT, \tag{4}$$

where F_c is the frictional force between cluster and substrate, and $n < 1$; whether or not this form, nkT, is correct does not affect our final conclusions. From this point of view [29], the friction is essentially the shear strength and the adhesion, the tensile strength, of the junction formed at the point of real contact [31]. Converting F_c to the force, F, per unit area of contact, Ω, we write

$$F_c = F\Omega. \tag{5}$$
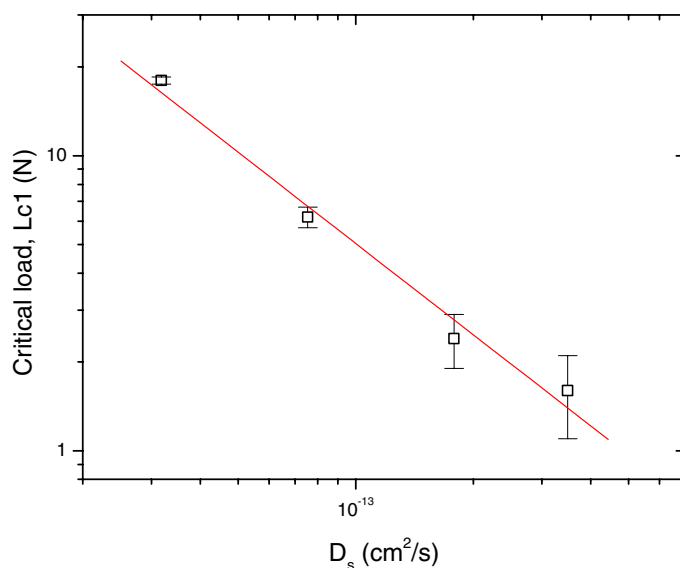
Figure 1. A plot of critical loads, L_c, from scratch tests on 200 nm Cu, versus dynamic nanocluster coalescence coefficients, D_s, for a nominal 1 Å of Cu, evaporated onto variously treated Cyclotene surfaces; each treatment provides a different level of adhesion [15].

(This figure is in colour only in the electronic version)

Substituting these equations into (1), we obtain, by assuming that, to a good approximation, $r^2 - a^2$ is a constant (since $r \gg a$),

$$L_c = \frac{r^2 - a^2}{\Omega^2} \frac{\pi}{P} \frac{(nkT)^2}{4D_s t},$$ (6)

which may be written logarithmically as

$$\log L_c = A - \log D_s.$$ (7)

Using our previously published dynamic D_s-data for Cu evaporated at a deposition rate of 0.3 Å s^{-1} to a nominal thickness of 1 Å [8], and our L_c-data obtained on these samples after the additional deposition of 200 nm Cu [15], a plot of equation (7) was made. This is seen in figure 1, where the data points represent various Cyclotene surface treatments, from none (upper left: weak Cu bonding) to N$_2$ plasma (lower right: strongest Cu bonding attained). As seen in the figure, the prediction of a linear plot with a negative slope is fulfilled. Each point represents the average of three measurements. Despite the limited range of values, they extend from the weakest to the strongest bonding, and clearly fit a straight line, as predicted by equation (7). The equation of the line is

$$\log L_c = -(12.66 \pm 1.20) - (1.03 \pm 0.09) \log D_s,$$ (8)

with a correlation coefficient of $-0.991\,94$ indicating a statistical significance of >0.9995. In summary, on the basis of our finding that Cu clusters initially formed persist at the interface between Cyclotene substrates and thick Cu films, we have predicted, and found, a quantitative correlation between nanoscopic and macroscopic measurements of interfacial adhesion.

Acknowledgment

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