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SHEAR STRENGTH OF METAL - SiO$_2$ CONTACTS

by Stephen V. Pepper
Lewis Research Center
Cleveland, Ohio 44135

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Stephen V. Pepper, NASA - Lewis Research Center
21000 Brookpark Rd., Cleveland, Ohio 44135

ABSTRACT

The strength of the bond between metals and SiO_2 is studied by measuring the static coefficient of friction of metals contacting α-quartz in ultrahigh vacuum. It was found that copper with either chemisorbed oxygen, nitrogen or sulphur exhibited higher contact strength on stoichiometric SiO_2 than did clean copper. Since the surface density of states induced by these species on copper is similar, it appears that the strength of the interfacial bond can be related to the density of states on the metal surface.

INTRODUCTION

The useful electrical properties of the interface between different solids has led to the fabrication of solid state electronic devices and a parallel investigation of the physical basis of these properties. The investigation into the physical nature of the adhesive forces between solids required in fabrication of electronic devices has not progressed as rapidly. This lack of progress is partly due to the experimental difficulty of obtaining a measure of interfacial strength (1, 2) that can be interpreted as due to only one of the many different forces that can act between solids (3). Adhesion problems that have arisen in device fabrication have been dealt with rather empirically, without fundamental understanding in which to act.

A system that should benefit from a fundamental investigation of interfacial strength is the metal-SiO_2 system. This system is considered to be a "problem" in that noble metals do not adhere well and must be joined to SiO_2 with intermediate layers of Ti or Cr.

In this paper changes in the shear strength of Cu-SiO_2 contacts induced by chemisorbed O, S and N on Cu are studied. The shear strength has been shown to be correlated to thin film adhesion via the popular scratch test (2, 4). This correlation is the principle justification for associating the results obtained here with what is generally considered to be adhesion. The use of O, S and N is motivated by recent work (5) indicating that they induce similar changes in the Cu surface valence electron density of states. Since it is the valence electrons of a solid which determine the chemical interaction of the solid with other species, the contact strength should change in similar ways due to the presence of those elements on the Cu of in fact the adhesive bonding between Cu and SiO_2 is due to a chemical interaction.

APPARATUS

Contact shear strength is measured in ultrahigh vacuum by pressing a copper sphere onto an SiO_2 flat and then subjecting the contact to a tangential force. The maximum tangential force that the contact can support divided by the normal force yields a static coefficient of friction, μ_S. Changes in μ_S due to chemisorbed O, S and N on Cu, from the value obtained for the clean surfaces, are the principle experimental results. This method has been used to study metal - Al_2O_3 contact strength (6). Fig. 1 depicts the shear apparatus.
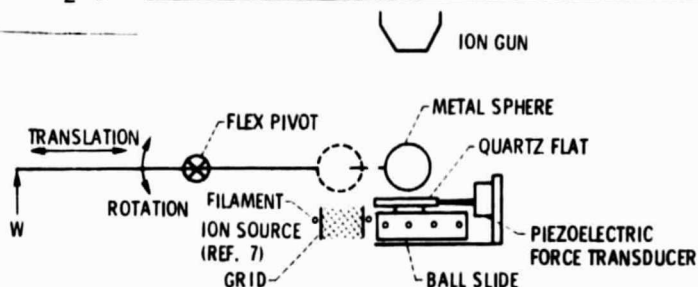

Figure 1. Shear apparatus in ultrahigh vacuum.

The load of the metal on the SiO_2 flat is provided by vertical force W. A differential screw provides tangential motion and tangential force is measured by the piezoelectric force transducer in vacuum. The sphere is retracted (dotted line) to allow specimen cleaning by Ar^+ bombardment of the SiO_2 (ion gun) or of the sphere by the electron bombardment ion source (7). This source also "activates" N_2 which does not chemisorb on Cu in molecular form (5). For "activated" chemisorption the metal sphere is grounded and the source operated at 5×10^{-5} torr N_2 with the ion pump on.

Surface analysis with a single pass cylindrical mirror analyzer with coaxial electron gun was performed in another part of the vacuum chamber, but with the specimens and ion sources removed from the shear apparatus. Auger electron spectroscopy (AES) and energy loss spectroscopy (ELS) for SiO_2 were used to characterize the surfaces after ion bombardment and after exposure to gases. Since the same surface preparation procedures were used both prior to contact and prior to surface analysis, it is assumed that the analysis is valid for the contacting surfaces. Polycrystalline metal and single crystal α-quartz were used.

SURFACE CHARACTERIZATION

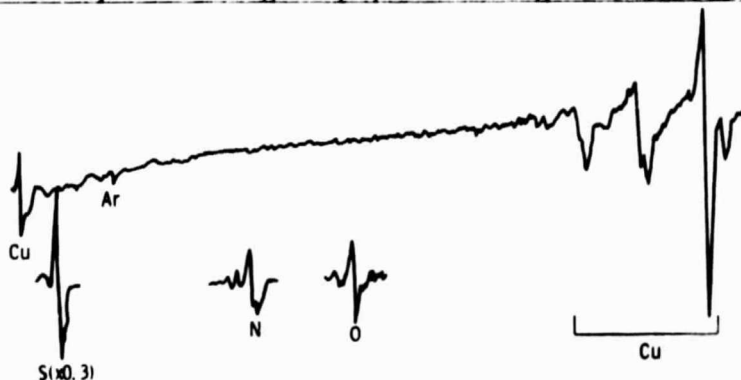After Ar^+ bombardment, the Cu Auger spectrum in Fig. 2 resulted.

Figure 2. Auger spectrum of clean Cu and adsorbate Auger peaks.

The usual contaminants are absent and there is some Ar. Subjecting this clean Cu surface to exposure of either 10^3 L O_2 or 10^2 L H_2S yields either the 0 or S Auger peaks indicated. Subjecting the clean Cu surface to activated N_2 for 3 min. yields the N Auger peak indicated. Analysis of the fine structure of the adsorbate peaks showed good agreement with those obtained by Tibbetts et al (5). Assuming the peak-peak heights are proportional to elemental concentration, taking into account the linear energy dependence of the sensitivity of the CMA and the Auger yields of the elements (8), it is found that the elemental concentrations for 0, N and S are in the ratio 1:.73:.77. Thus the relative concentrations are quite similar. The absolute concentrations are probably on the order of ½ monolayer (5).

The Auger spectrum of Ar^+ bombarded SiO_2 indicated that the surface was free of impurities and the Si LVV structure is shown in Fig. 3a.

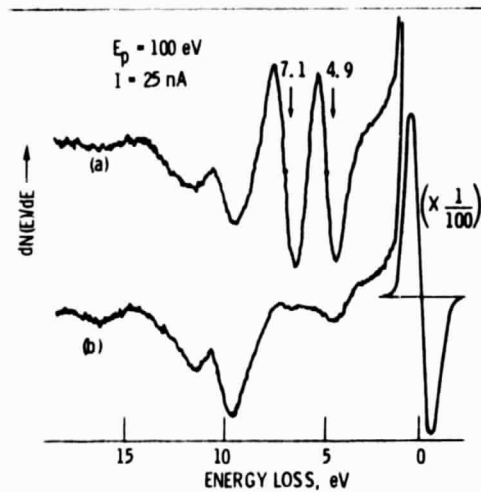Figure 3. Si LVV Auger peak (a) after Ar^+ bombardment and (b) after O_2^+ bombardment.

Figure 4. Energy loss spectrum of SiO_2 (a) after Ar^+ bombardment and (b) after O_2^+ bombardment.

The virtual absence of the 92eV transition indicates that the surface was not reduced to elemental Si by the Ar^+. However, the structure at 78eV is absent after 1 keV O_2^+ bombardment, Fig. 3b. Since the latter surface is probably stoichiometric SiO_2 (9, Fig. 3), it appears that Ar^+ reduces the surface, but not all the way to elemental Si. This is corroborated by ELS, Fig. 4. A comparison with the second derivative ELS of SiO_2 (9, Fig. 5) indicates that the spectrum of Fig. 4b is close to that of stoichiometric SiO_2, but that Fig. 4a contains large peaks at 4.9eV and 7.1eV that have been attributed to the presence of a "surface phase of approximately monoxide composition" (10). The stoichiometric surface is the better defined of the two and may be easier to handle analytically in a future theory of the SiO_2 - metal interface. Both surfaces were investigated because the reduced surface is generated by the sputter-etch step in thin film deposition and thus the results may be applicable to thin film adhesion.

RESULTS AND DISCUSSION

The results for stoichiometric SiO_2 are presented first. Both surfaces were cleaned by Ar^+ bombardment, the SiO_2 was oxidized by O_2^+ bombardment and finally the Cu was recleaned to prepare a clean Cu – SiO_2 system. Although the static friction coefficient varied from one experimental run to another (due perhaps to differing contact geometrics on the metal sphere), the changes in static friction following the exposures were quite reproducible. In Fig. 5 are depicted force-displacement curves for the clean contact and
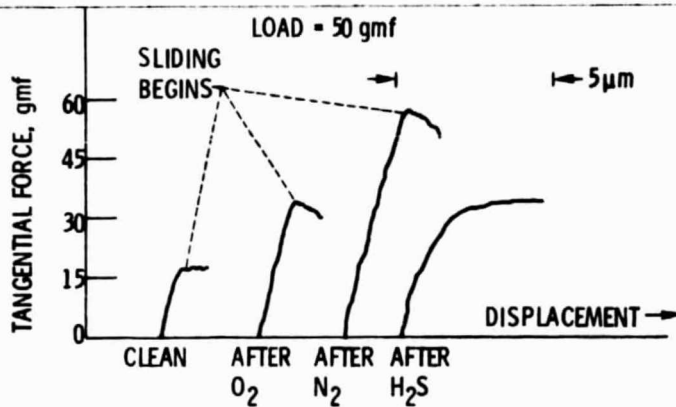

Figure 5. Force-displacement curves for contact on stoichiometric SiO_2.

for contact after exposure to O_2, N_2 and H_2S. The clean contact has $\mu_s \sim .3$ and significant increases over this value are exhibited after all the exposures. The largest increase was due to N_2. Smaller increases were found after O_2 and H_2S, even though the force-displacement curves that illustrate the approach to sliding are (reproducibly) different. The contact strength on the reduced SiO_2 was somewhat different: the clean contact strength and the effect of N_2 was the same as for the stoichiometric SiO_2, but little, if any, increase was observed after the O_2 or H_2S exposures. Motivated by recent work which showed that the density of states induced by O, N and S on Ag were also quite similar to those observed on Cu (11), experiments were performed with a Ag sphere. For this relatively inert metal, all adsorption on the clean surface was by electron beam activation. The results were similar to Cu, although here increased contact strength was observed only on the stoichiometric SiO_2 and not on the reduced surface, even for N_2 exposures.

In considering these results, first note that the increased strength due to the presence of these adsorbates is contrary to the view that maximum interfacial strength is obtained by removing all foreign species from both surfaces prior to joining. Although this may be the case in joining similar materials as in metal-metal contacts, it is certainly not the case in the situation considered here. Secondly, a previous study of metal – Al_2O_3 contact strength (6) has assumed the need for two separate theories of interfacial strength to understand the effect of adsorbed oxygen on the metal – one for clean metal – Al_2O_3 and one for metal oxide – Al_2O_3. Here, however, we deal not with the copper oxide but with a partial monolayer chemisorbed surface species. Thus one theory of contact strength should be sufficient – for copper and its surface modifications – rather than for the very different entities Cu and Cu_2O in contact with SiO_2.

The adsorbates that change the valence electron density of states in similar ways have led to similar changes in contact strength only on stoichiometric SiO_2. A different situation prevailed on reduced SiO_2, where only N_2 increased the contact strength. The contact strength cannot be understood solely in terms of the surface properties of one of the partners and requires a more complicated, as yet undeveloped, understanding of the interaction. An important finding, however, is the effect of adsorbed N. This large effect was not anticipated on grounds other than the induced valence electron density of states and thus lends some confidence to this approach to understanding contact strength.

Finally, the enhanced bonding observed here can have the practical effect of improving thin film adhesion. This has been noted for some time for rather thick intermediate oxide films (2) but results here show that the enhancement may also be possible by monolayer concentrations. This has in fact been observed by the author in preliminary experiments with the $Cu-N-SiO_2$ system by R. F. sputter deposition in a partial pressure of N_2.

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