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Thin gold films placed in contact on compliant elastomeric poly(dimethylsiloxane) supports weld together. This "cold welding" is remarkable both for the low loads required and for the fact that it occurs under ambient laboratory conditions, conditions in which the gold surfaces are covered with films of weakly adsorbed organic impurities. These impurities are probably displaced laterally during the welding. Welding can be prevented by the presence of a self-assembled gold(I) alkylthiolate monolayer on the gold surfaces. The welded contacts have low electrical resistivity and can be made thin enough to transmit light. This system is a promising one with which to study interaction between interfaces.

WELDING OF METALS UNDER AMBIENT conditions ("cold welding") has been practiced for more than 700 years, but only with high applied pressures (such as under the impact of a smith's hammer) or with frictional work (*1–3*). The adhesion of metals in ultrahigh vacuum (UHV) under light loads is also known (*4*) but requires flat, ductile, and atomically clean surfaces. In this report we describe the self-adhesion of thin gold films on elastomeric supports, under ambient laboratory conditions, with very small applied loads (Fig. 1). Adhesive bonding of metal surfaces under ambient laboratory conditions—that is, in the presence of air, humidity, and volatile organic contaminants—and with very small applied loads (<0.1 to 0.2 g/cm^2) (*5*) is therefore remarkable. For self-adhesion of these "dirty," supported films of gold, an underlying elastomeric support is required. The self-adhesion is inhibited or prevented by monolayer films [self-assembled monolayers (SAMs)] less than 1 nm thick on the gold.

We prepared the systems by the procedure summarized in Fig. 1. Treatment of a film of poly(dimethylsiloxane) (PDMS) (*6*) with a radio frequency, oxygen plasma formed a thin [<50 Å by x-ray photoelectron spectroscopy (XPS)] silica-like layer on its surface. We denote this oxidized surface as PDMS/SiO_2: its surface chemistry is similar to that of SiO_2 (*7*). Chemisorption of 11-trichlorosilylundecyl thioacetate [$Cl_3Si(CH_2)_{11}SCOCH_3$] from the vapor phase onto PDMS/SiO_2 produced a monolayer of the corresponding alkylsiloxane (*8, 9*). Thin films of gold (~20 nm), thermally evaporated onto the surface of the PDMS-bound SAM (*9–11*), adhered well to it (*9, 12, 13*).

When placed in contact, two gold films supported on 1 cm by 1 cm squares of PDMS adhered strongly across the gold-gold interface. Failure occurred by decohesion within the polymer (the tear strength of the PDMS used here is 2.7×10^3 g/cm) (*14*). We hypothesize that the elasticity and compliance of PDMS allow the gold surfaces to conform to one another, increasing the area of gold-gold contact and tangentially displacing loosely adsorbed contaminants (*15*). This hypothesis implies the possible formation of "islands" of the contaminants at the gold-gold interface.

We measured the strength of adhesion by using an apparatus reported separately (*8*). A small (radius of curvature = 1.31 to 1.34 mm) hemispherical lens of PDMS and a flat sheet of PDMS were allowed to come into contact in the absence of an applied load. For two surfaces of unmodified PDMS, the pull-off force was 0.034 dyne for an initial area of contact at zero load of 4.45×10^{-4} cm^2. We characterize this adhesion as "tacky," because the area of contact decreased with increasing negative load. The pull-off force for the two gold films supported on PDMS was 3.33 dyne for an initial area of contact of 3.53×10^{-4} cm^2. In this case, the area of contact did not decrease with increasing negative load; rather, cohesive failure occurred within the flat sheet of PDMS. We conclude that this pull-off force is a lower limit of the strength of adhesion across the gold-gold interface and that these results rule out the possibility that the welding is actually tacky adhesion arising from organic contaminants at the interface.

Chemisorbed monolayers of alkyl thiolates at the surfaces of these gold films prevented welding. Treatment of one of the films with ethanoethiol vapor for 5 to 10 s greatly reduced the strength of adhesion; that is, the films were easily separated and adhesive failure occurred at the "gold-gold" interface. This "weak" adhesion was similar in strength and character to the tackiness between sheets of unmodified PDMS (*16*). As expected, gold films bearing ordered SAMs of longer chain alkyl thiolates (*17*)

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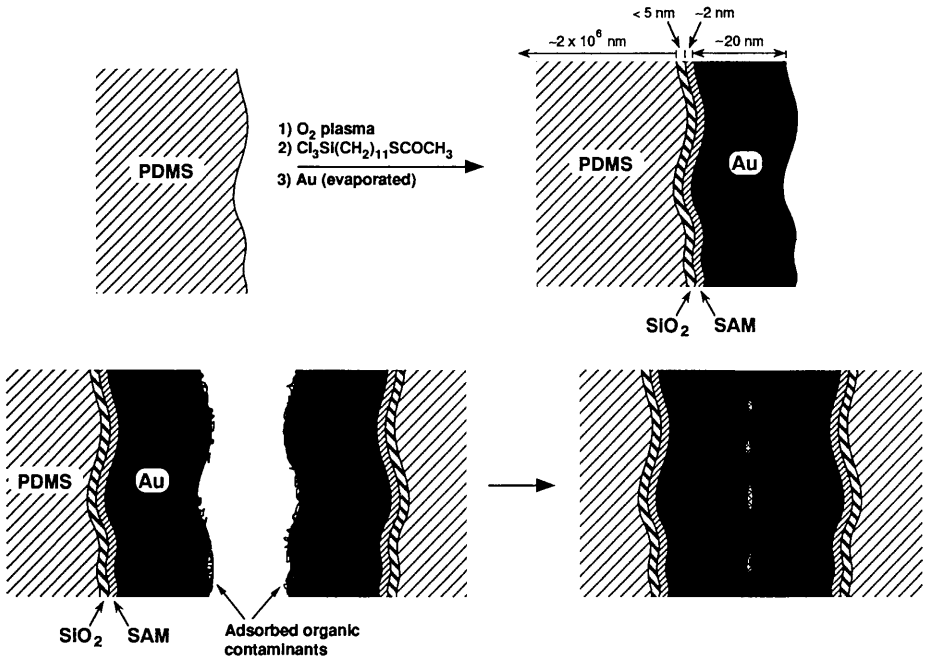

Fig. 1. Schematic illustration of the structure of the supported films of gold and gold-gold welding. PDMS = poly(dimethylsiloxane); SiO_2 = silicon dioxide overlayer; SAM = self-assembled monolayer prepared by adsorption of 11-trichlorosilylundecyl thioacetate; Au = evaporated film of gold.

$[HS(CH_2)_{10}CH_3$, $HS(CH_2)_{11}CH_3$, and $HS(CH_2)_{15}CH_3]$ also showed only weak adhesion. The pull-off force for two of these surfaces [bearing SAMs of $HS(CH_2)_{11}CH_3$] was 0.037 dyne for an initial area of contact of 3.50×10^{-4} cm^2. We presume that these thin (5 to 25 Å) films exert their influence by preventing atomic contact of the gold surfaces.

It seems to be necessary to have at least one gold film supported on a compliant elastomer in order for cold welding to occur under these conditions. We observed welding between a sample of the gold on a PDMS square 1 cm by 1 cm and gold condensed very slowly (0.3 to 0.4 Å/s) onto a glass, microscope cover slip (*18*). We observed only weak (tacky) adhesion, however, between samples of gold on PDMS and gold condensed at or above 1 to 3 Å/s onto a glass microscope slide (*19*).

The composite films ($PDMS/SiO_2$/monolayer/Au/Au/monolayer/SiO_2/PDMS) described in this report were optically transparent and provide an opportunity for optical microscopic and spectroscopic (ultraviolet-visible) analysis of the gold-gold interface. Preliminary experiments, in which we used simple patterned surfaces formed by shadowing portions of the polymer film during evaporation of the gold, have established that the gold-gold contacts show little electrical resistance (<0.4 ohm/cm^2) (*20*).

Cold welding requires atomic contact between the surfaces that are joining. These clean surfaces are probably generated in the system described here by lateral displacement of contaminants on the gold surface. This displacement is facilitated by the elastomeric and compliant support. Although cold welding is a well-known phenomenon in other circumstances, its occurrence between "dirty" metal surfaces, under ambient atmospheres, at very small applied pressure is unexpected. A number of characteristics of this system make it a particularly attractive one with which to study cold welding. The mechanical properties of the PDMS elastomer are easily varied. The thicknesses of the SiO_2 layer, the gold film, and the SAM coupling layer can be controlled. The system is very sensitive to alkane thiolates adsorbed on the gold, and the techniques developed in studying these SAMs (*17*) are applicable to understanding this sensitivity. The entire system is optically transparent and can be examined by absorption spectroscopy. The welds are electrically conducting: this conductivity may be useful in characterizing them and may also provide the basis for methods of fabricating novel types of electrical circuits.

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5. In some cases, external loads were not deliberately applied; the values given reflect the approximate mass of a sheet of PDMS.
6. The PDMS was synthesized with a commercially available kit (Dow Corning Sylgard-184, Midland, MI). The reaction mixture contained a vinyl end-capped oligomeric dimethylsiloxane, a methylhydrogensiloxane as a cross-linking agent, and a platinum complex as a catalyst for the hydrosilation reaction.
7. The exact structure of this layer is unclear. Most reports, however, agree that it contains silanol groups. For instance, see D. W. Fakes, M. C. Davies, A. Brown, J. M. Newton, *Surf. Interface Anal.* **13**, 233 (1988); D. W. Fakes, J. M. Newton, J. M. Watts, M. J. Edgell, *Surf. Interface Sci.* **10**, 416 (1987); M. Morra *et al.*, *J. Colloid Interface Sci.* **137**, 11 (1990).
8. For a description of the procedure used for formation of monolayers on $PDMS/SiO_2$, see M. K. Chaudhury and G. M. Whitesides, *Langmuir* **7**, 1013 (1991).
9. S. R. Wasserman, H. A. Biebuyck, G. M. Whitesides, *J. Mater. Res.* **4**, 886 (1989). Contact angles (a, advancing; r, receding) of water: $PDMS/SiO_2$/monolayer: $\theta_a = 78°$ to 83°; $\theta_r = 72°$ to 78°. Si/SiO_2/monolayer: $\theta_a = 78°$ to 80°. Both SAMs were wet by hexadecane (θ_a <15°). XPS confirmed that the interface contained sulfur.
10. Gold was condensed onto the substrates at rates of 0.3 to 3 Å/s at 20° ± 2°C.
11. Scanning electron micrographs of $PDMS/SiO_2$ bearing monolayers and 200 Å of thermally evaporated gold were featureless on a length scale greater than 1 μm. A gridlike distribution of fine cracks (<0.1 μm wide) separated by 20 to 40 μm was observed in the gold film. XPS analysis indicated the presence of silicone contaminants on the gold surface.
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13. The yield strength for the adhesion between gold and a SAM prepared by adsorption of 11-trichlorosilylundecyl thioacetate onto a silicon wafer is >84 g/cm (*9*).
14. *Dow Corning Materials for High Technology Applications*, Form No. 10-008C-86 (1986). This technical brochure is available from Dow Corning Corporation, Midland, MI.
15. An alternative explanation is that sufficient stress may accrue at the surface of the films supported on PDMS to cause the formation of small cracks that expose fresh, uncontaminated surfaces of gold. On bending of the films, tiny cracks in the gold were visible to the naked eye and appeared as a hazy finish on the reflective surface. This haziness disappeared when the films were released. Direct observation of the area of contact between two of these films by optical microscopy, however, revealed no evidence of cracking. In addition, the inhibition of adhesion by adsorbed SAMs argues against this hypothesis.
16. The strength of adhesion between two sheets of unmodified PDMS is less than 1% of that between two of the gold surfaces (without monolayers). Pull-off forces were measured by the procedure described in (*8*).
17. For a review, see G. M. Whitesides and P. E. Laibinis, *Langmuir* **6**, 87 (1990).
18. We treated the glass cover slip with 11-trichlorosilylundecyl thioacetate in the vapor phase before evaporation of the gold film, following a procedure analogous to that used with the $PDMS/SiO_2$ surfaces.
19. Although we have not examined this difference in detail, the results may reflect differences in the surface morphology or topology of the gold films. For recent studies, see A. Putnam, B. L. Blackford,

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20. We made these measurements with thick gold films (~80 nm) using a four-probe method to avoid errors due to the resistance of the electrical contacts (silver epoxy) to the gold films. In addition to the possibility of practical applications of these experiments, careful measurement of resistivity may allow an estimation of the degree of atomic (gold-gold) contact between the two surfaces.

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