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The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

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Online publication date: 08 September 2010

To cite this Article Schneider, Marc , Möhwald, Helmuth and Akari, Sabri(2003) 'Quantitative measurement of chromium's ability to promote adhesion', *The Journal of Adhesion*, 79: 6, 597 – 607

To link to this Article: DOI: 10.1080/00218460309539

URL: <http://dx.doi.org/10.1080/00218460309539>

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QUANTITATIVE MEASUREMENT OF CHROMIUM'S ABILITY TO PROMOTE ADHESION

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Using atomic force spectroscopy, we investigated the adhesion-promoting ability of chromium. An intermediate layer of chromium can overcome the low adhesion between metal films and silicon dioxide. For the first time, we quantitatively studied this experimentally well known fact. We compared the adhesion between chromium and different substrates such as gold, silver, mica, and silicon dioxide and, beyond that, the adhesion between silicon dioxide and the same substrates. To avoid additional effects due to water, we chose ethanol as a nonpolar solvent. Taking the interfacial energies of the surfaces with the liquid into account eliminates the direct influence of the fluid medium on the adhesion of the solid material. The results we obtained corroborate the experimental fact of higher adhesion of chromium with the chosen substrates, as well as substantiate the value of chromium as an adhesion promoter. The adhesion of chromium-coated probes on gold, silicon dioxide, and mica is higher than the adhesion of silicon dioxide probes on the same substrates.

Keywords: Adhesion promoter; Force spectroscopy; Surface energy; Atomic force microscopy

Received 11 June 2002; in final form 13 November 2002.

We thank the “Bundesministerium für Bildung und Forschung” (Project Number 03C0291C/5) for financial support. In addition we are indebted to Dr. G. Papastavrou and Dr. H. Riegler for discussions and C. Jones for language corrections. The authors also acknowledge A. Heilig for help in the lab.

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INTRODUCTION

Gold coatings are widely used because of their relative inertness to many gases and liquids [1]. They do not form an oxide layer, and their contamination from the atmosphere is low [2]. These properties make gold an ideal coating for surfaces that must be protected against aggressive chemical solvents. Furthermore, gold is used for the convenient and consistent fabrication of electrodes [3–7] and electrochemical devices [8, 9]. Additionally, gold has a strong specific interaction with sulphur [10] that allows the formation of alkanethiol monolayers with a variety of functional groups [2, 8, 10–15]. This is one of the reasons for the extensive application in chemical force microscopy (CFM) [16–19]. For all of these applications an adhesion-promoting sublayer was used, because the adhesion of gold to the substrates is low [20] (e.g. the adhesion of gold to SiO_2 [21]). Organic monolayers [22–24], titanium, or chromium [25] have been used to promote adhesion of gold. Chromium is used most commonly as an adhesion promoter [2, 8, 10–15]; however, up to the present time there has been no quantitative work (only semiquantitative work [24]) that supports this experimental fact about the adhesion properties of chromium.

With the work presented here, we wish to give more evidence for the well known fact that chromium promotes adhesion, with quantitative force measurements performed with an atomic force microscope (AFM) on relevant substrates.

MATERIALS AND METHODS

For the force measurements we used a standard scanning force microscope (D3000, Digital Instruments, Santa Barbara, California USA). All samples were placed at the same time in a homemade fluid cell, made completely from Teflon, and then immersed in ethanol (p.a.) (Riedel-deHaën, Seelze, Germany) Ethanol was chosen as an organic measuring solvent to avoid electrostatic interactions as well as hydrophobic interactions. Only van der Waals and hydrogen-bonding interactions should contribute [26–30] to the interaction energies and, therefore, to the adhesion.

Rectangular SiO_2 contact AFM-cantilevers (MikroMasch, Silicon-MDT Ltd., Moscow, Russia) were coated by thermal evaporation with a $d = 6$ nm thick chromium layer on both sides and afterwards directly immersed in ethanol to avoid contamination. The thickness of the chromium layer was chosen to represent a typical thickness of an adhesion-promoting sublayer. The spring constant was ascertained

using the calibration method of Sader [31]. The tip radius was estimated using an ultrasharp silicon calibration grid (tip characterisation grating TGT01, pitch $2.12\ \mu\text{m}$, height $\Delta z = 0.7\ \mu\text{m}$) and the deconvolution program (deconvo1.1) from MikroMasch. We verified these results from the TGT01 grid using the pictures obtained from imaging the grid. The section analysis of these images (not shown) enables us to estimate the tip radius. The known radius of curvature of the surface features allows reconstruction of the tip radius by means of a deconvolution algorithm.

We used polished silicon wafers (Wacker Siltronic AG, Burghausen, Germany) that were cleaned with the RCA cleaning process (SC-1; Radio Corporation of America, Princeton, New Jersey, USA). The RCA-SC-1 method introduced by Kern [32, 33], involves a H_2O_2 /ammonia/ H_2O mixture (1:1:5) used at temperatures between $T = 75\text{--}80^\circ\text{C}$. In addition, we used freshly cleaved mica and ultraflat template stripped silver and gold surfaces. The latter two were produced by the procedure described by Stamou *et al.* [34], which is a modification of the method of Hegner *et al.* [35] and Wagner *et al.* [36]. The use of flat surfaces is important to eliminate surface roughness effects. Rough surfaces change the contact area between the tip and the surface, leading to incomparable measurements; even in the same measurement one obtains a broader distribution of the adhesion forces due to drift.

To check the reliability of our data, a comparison of different radii is suitable because the adhesion energies should be the same for equivalent systems and independent of the tip radius. Therefore, we coated a second tip with a different tip radius. To increase the tip radius of the commercially available silicon tips, we used a method introduced and described by Hüttl *et al.* [37] and Hüttl [38].

RESULTS AND DISCUSSION

The adhesion forces were obtained from the deflection displacement curves after calibrating the cantilevers (Figure 1). Using the TGT01 grating, we can calculate the radii of the tips. The uncoated tip had a radius of $R_{\text{uncoated}} = (17 \pm 2)\ \text{nm}$, the chromium-coated tip had a radius of $R_{\text{coated}} = (21 \pm 2)\ \text{nm}$. An oxidised coated tip with $R_{\text{coated}_{\text{ox}}} = (50 \pm 5)\ \text{nm}$ was used for control experiments.

The adhesion forces of the different tips cannot be reliably compared with each other due to the different radii of the probes used. The investigation of the tip radius allowed us to convert the forces to an adhesion energy. The theory of Derjaguin, Muller, and Toporov (DMT

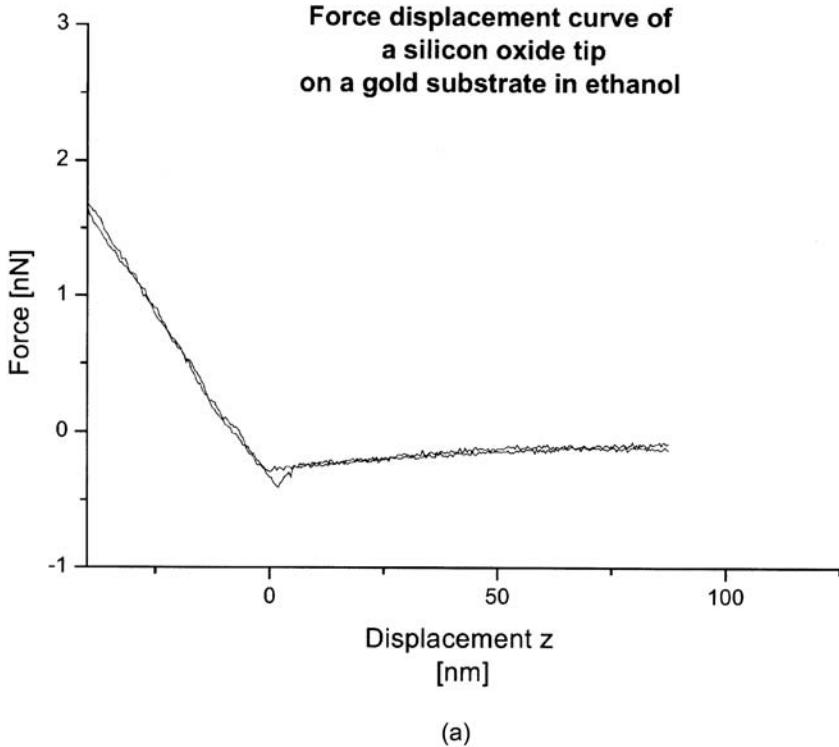
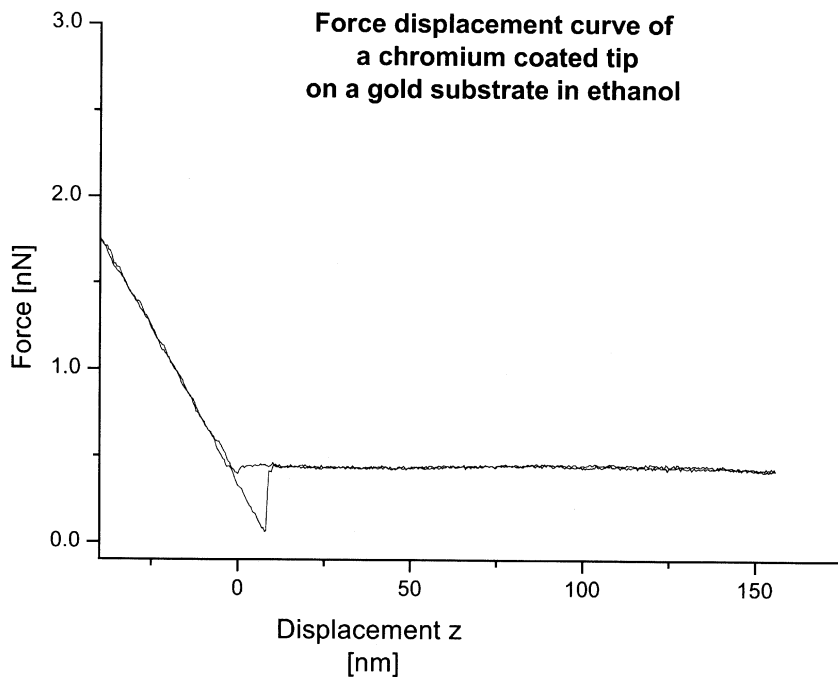


FIGURE 1 (a) Representative force-distance curve of an unmodified silicon dioxide probe. (b) Force-distance curve of a chromium-coated probe. (c) Chromium-coated probe with increased tip radius. The curves represent the deflection during the approach of the surface and the retraction of the probe from the surface. All measurements were performed in ethanol on an ultraflat gold substrate. The difference in the adhesion forces for the three different tips is obvious. (Continues).

theory [39]), which is suitable for small tip radii and low adhesion, can accomplish the conversion [40];

$$F_{\text{adh}} = 2\pi R_{\text{tip}} W_{132}. \quad (1)$$

Equation (1) relates the adhesion force, F_{adh} , to the tip radius, R_{tip} , and to the adhesion energy, W_{132} . R_{tip} is the radius of an approximating sphere for the very end of the probe and W_{132} is the work done when separating medium 1 from medium 2 in medium 3 [41]. The energy is a characteristic value for each system depending on the components involved in the adhesion. The adhesion energy, W_{ad} , is



(b)

FIGURE 1 Continued.

composed of the individual interfacial energy contributions, γ_{ii} , and equals W_{132} :

$$W_{ad} = \gamma_{tip-solvent} + \gamma_{substrate-solvent} - \gamma_{tip-substrate}. \quad (2)$$

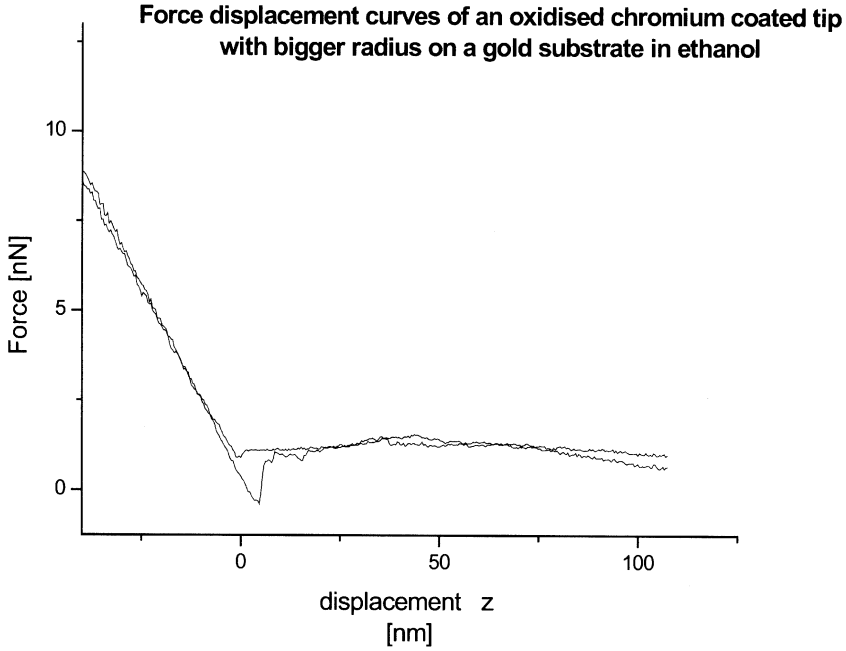
In the case of a symmetric system, the tip and the substrate are of the same material, and according to Israelachvili [41], Equation (2) may be written as

$$W_{ad} = 2\gamma_{substrate-solvent}. \quad (3)$$

The interfacial energy of the solvent-substrate interaction can be determined with Equation (3).

In Table 1 the normalised forces for a noncoated silicon oxide tip and a chromium-coated tip on Au, Ag, silica, and mica surfaces are shown. The measurements were for each series performed with the same tip.

Though all obtained values except that of silica are equal within error, a tendency can be clearly seen (Figure 2): the mean values are

**FIGURE 1** Continued.

well separated and the mean half width of the measurements do not overlap. This trend indicates that most of the measured data are well separated. Hence, for all substrates the adhesion energy is increased while using the chromium-modified probe. This fact corresponds with the ability of chromium to increase the adhesion forces and to act as a promoter in ethanol. Using a second tip with a different tip radius is highly necessary to obtain an idea of the relevance of our measurements.

TABLE 1 Work of Adhesion on Different Substrates in Ethanol

	$(F/R)_{\text{gold}}[\text{mN/m}]$	$(F/R)_{\text{silver}}[\text{mN/m}]$	$(F/R)_{\text{silica}}[\text{mN/m}]$	$(F/R)_{\text{mica}}[\text{mN/m}]$
Si-tip	11.77 ± 3.8	11.18 ± 3.1	10 ± 4.1	14.12 ± 4.4
Cr-tip	18.10 ± 3.6	13.81 ± 3.0	21.43 ± 3.8	20.48 ± 4.2

The errors are calculated using $\Delta \frac{F}{R} = \frac{\Delta F}{R} + \frac{F}{R^2} \Delta R$.

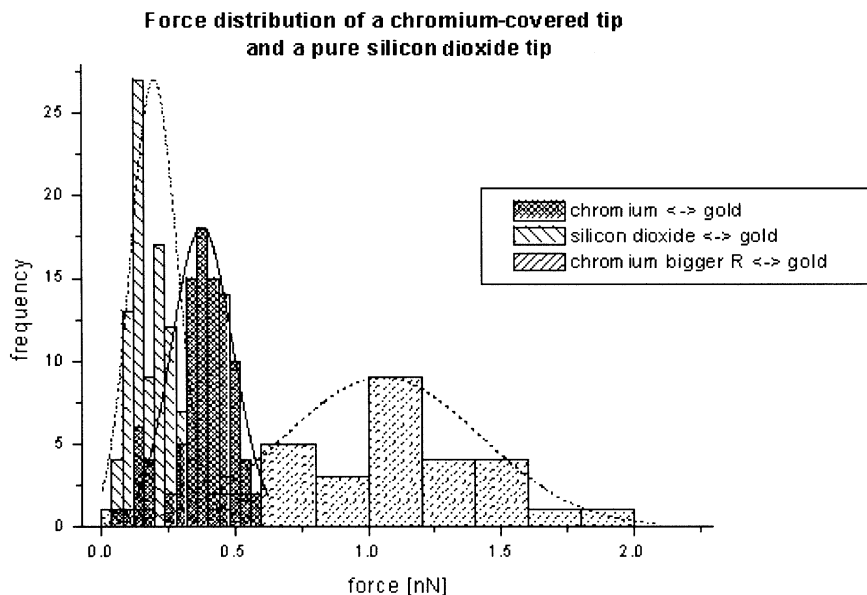


FIGURE 2 Histogram of the adhesion forces on a gold-coated substrate with a silicon dioxide tip (under dashed dotted line), a chromium-coated tip (under solid line) and an oxidised chromium-coated tip with a bigger radius (under dashed line). The lines represent a Gaussian fit to the distribution of the force data. All measurements were performed in ethanol on an ultraflat gold substrate.

Instead of using colloidal particles attached to the tip, we increased the tip radius by oxidation of the silicon dioxide probe. In Table 2 the results for the series of measurements on Au, Ag, silica, and mica surfaces are listed. To compare these results we use the knowledge that the energies should be the same for the individual substrate-tip systems. Using Equation (1), we are able to estimate a tip radius using the given (measured) force (Table 2) and the calculated energies obtained from the measurement with the small tip radius.

TABLE 2 Measured Forces with an Oxidised and Chromium-coated Tip on Au, Ag, Silica, and Mica surfaces

Cr-tip (ox.)	F_{gold} [nN]	F_{silver} [nN]	F_{silica} [nN]	F_{mica} [nN]
Measured	1.05 ± 0.37	1.22 ± 0.31	1.41 ± 0.33	1.28 ± 0.36

This enables us to calculate an expected tip size that would correspond with the energy. This calculated radius be equal to the measured tip radius. Because the oxidised probe has the highest uncertainty when determining the radius of the probe, we calculated the tip size using the energy measurement. Especially because the tips were already used for the force measurements and to evaluate the tip radius on the calibration grating.

From the broad distribution of the force measurement (Figure 2) one can additionally conclude that the oxidised tips are rougher. Table 3 illustrates the calculated tip sizes which have the same dimensions as the radius we obtained from measuring the reference grid. Only the measurement on the silver surface does not provide a value consistent with the experimentally found radius within error. The errors are calculated by taking the force measurement deviations and the error of the adhesion energy from the first measurement into account. The increased size of the tip radii is most likely due to an asymmetric shape of the probe.

However, up to this point we only considered the adhesion energy that is strongly influenced by the surrounding medium. What we now know is that chromium has a higher adhesion with silicon dioxide, mica, and gold in ethanol than silicon dioxide with the same substrates (silver surfaces are no longer considered because of the deviations being bigger than the error of the adhesion energy for the two tip radii).

The measurement of the silicon dioxide tip on the silicon dioxide substrate enables us to obtain the interfacial energy of silicon dioxide in ethanol *via* Equation (3): $\gamma_{\text{silicon-ox-EtOH}} = (0.8 \pm 0.3) \frac{\text{mN}}{\text{m}}$. The interfacial energy of gold in ethanol can be found in the literature: $\gamma_{\text{Au-EtOH}} \approx 0.2 \frac{\text{mN}}{\text{m}}$ [42]. The $\gamma_{\text{Cr-EtOH}}$ was determined in an independent measurement of a chromium-coated tip *versus* a chromium-coated substrate. Using Equation (2) and the interfacial energies of the substrates in ethanol, we calculated the surface energy for the

TABLE 3 Measured Tip Radius Using the TGT01 Grating and Calculated Tip Geometry for the Measured Force Values

Cr-tip (ox.)	R_{gold} [nm]	R_{silver} [nm]	R_{silica} [nm]	R_{mica} [nm]
Measured	50 ± 5	50 ± 5	50 ± 5	50 ± 5
Calculated	58 ± 21	88 ± 15	66 ± 14	63 ± 17

Errors are calculated using $\Delta R = \frac{\Delta F}{E} + \frac{F}{E^2} \Delta E$.

TABLE 4 Interfacial Energies of Chromium, Gold, and Silicon Dioxide in Ethanol and the Resulting Interfacial Energies for the Tip-Substrate Interaction

	Cr-EtOH	SiO ₂ -EtOH	Au-EtOH	Cr-Au	Cr-SiO ₂	Au-SiO ₂
γ [mN/m]	0.4	0.8	0.2	2.2	2.2	0.9

pure tip-sample interaction. In Table 4 the values for the surface energies are summarised.

A question we should address is: Can the results of these measurements be reliably applied to the situation we face coating surfaces in a vacuum?

When the coated samples are taken out of the vacuum chamber, a thin oxide layer forms on the chromium, producing a stable and passive interface as on aluminium [43, 44]. What is the situation throughout consecutive coating in a vacuum? The pressures normally used for evaporation of metals rarely fall below 10^{-6} mbar [34, 45–47]. The usage of these pressures results in the contamination of the freshly formed metal surfaces from the gas still in the coating chamber. The time of the formation of an added layer for a given pressure can be estimated with

$$t_{\text{mono}} = \frac{3.6 \cdot 10^{-6}}{p}, \quad (4)$$

where p is the pressure in mbar and t is the time in seconds [48]. For typical coating pressures we obtain $t_{\text{mono}} \sim 4$ s to form an added layer that will most probably result in the oxidation of the chromium due to the remaining oxygen in the vacuum chamber [44]. Due to the inertness of the layer, the two chromium surfaces will be quite similar to each other, so our results can be taken as a description of chromium's ability to promote adhesion.

CONCLUSION

In summary, we can state that we could verify the fact that the adhesion of chromium with gold, mica, and fused silicon is higher than the adhesion of a silicon surface with these substrates.

Force measurements allow us to calculate adhesion energies for the investigated substrates in ethanol, which should be of general interest. In addition, we obtained the interfacial energies of the different

substrates in ethanol. On the basis of these interfacial energies of the substrates in ethanol we could estimate the tip-substrate interaction in a vacuum.

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