HYDROPHOBIC SURFACE COATINGS ON TOOLS USED FOR HANDLING OF MICRO-PARTICLES

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ABSTRACT

After a brief discussion on the main forces involved between particles in the micro-world, possible surface coatings for manipulating tools for micro-particles are investigated. To this end, silicon nitride and silicon atomic force microscopy tips were made hydrophobic through sputter coating with gold, chemical vapor deposition of hexafluoropropene (HFP), and silanization with octadecyltrichlorosilane (OTS). The performance of the coatings was assessed by examining water droplets of a fixed volume deposited on the coatings, by quantifying their adhesion to test samples at different humidities, by evaluating their homogeneity in the scanning electron microscope (SEM), and by evaluating their abrasion characteristics. The coatings that qualified best were also prepared on micro-pipettes used for vacuum gripping of 50 μm sized glass beads. The performance of the coated micro-pipettes in pick and place experiments of above objects was much improved when compared to uncoated micro-pipettes.

KEYWORDS

pick and place, manipulation, adhesion, humidity, capillary condensation, hydrophobic coatings

INTRODUCTION

Below a particle size of several 100 μm the gravitational force no longer dominates the interaction between particles. At these particle sizes, attractive forces due to electrostatic or van der Waals interaction and to capillary condensation will cause the small, handled objects to stick to the manipulating tool. This impedes the manipulation of micro-objects and makes exact positioning almost impossible. The manipulating tool might still be able to pick up a micro-object but can no longer release it at an exact position, if at all. Especially when working at ambient conditions, the water vapor always present in humid air will condense in the small contact sites between the tool and the small object, causing the dominant contribution to the adhesive forces (this strong adhesive force is also responsible for such effects as the adhesion of powders or partially wet sand). The strength of this interaction will depend on the relative humidity and also on the surface properties of the tool and particles involved. If the ambient conditions cannot be controlled, the surface properties of the tool are the only means to influence the adhesion component caused by capillary condensation. If, for example, the tool were coated with a strongly hydrophobic material, the effect of capillary condensation could be suppressed. The ideal candidate for such surface coatings, should be sufficiently hydrophobic (to suppress capillary condensation), resistant to abrasion (to guarantee a stable tool), homogeneous (to ensure an even coating), and easily applied (to facilitate preparation).

FORCES INVOLVED IN THE MICRO-WORLD

Three main types of adhesive forces apply to the micro-world: van der Waals, electrostatic, and forces do to capillary condensation of water. In the following the forces are described for two very smooth, solid glass spheres of radius R .

Van der Waals Force [1]

$$F_{vdW} = \frac{AR}{12D^2} \qquad (1)$$

where A is the Hamaker constant ($6 \cdot 10^{-20}$ J for glass) and D the surface roughness (defined as 0.2 nm in this example).

Electrostatic or Coulomb Force

$$F_C = \frac{\pi R^2 \sigma^2}{\varepsilon_0 \varepsilon} \qquad (2)$$

where σ is the surface charge density (which will depend on the environment, but might range from 10^{-3} Cm^{-2} for very dry conditions (case 2 in Fig.1) to 10^{-6} Cm^{-2} for humid conditions (case 2 in Fig.1)), ε_0 the permitivity of vacuum, and ε is the dielectric constant of the media between the particles (i.e. 80 for the water meniscus).

Force due to Capillary Condensation [1]

$$F_{CC} = 2\pi R(\gamma_L \cos\theta + \gamma_{SL}) \qquad (3)$$

where γ_L is the surface tension of water, θ the contact angle of the water on the glass spheres, and γ_{SL} the surface energy of the glass spheres. Because $\gamma_L = 72 \cdot 10^{-3}$ Jm^{-2} is relatively large and $\cos\theta \approx 1$ for hydrophilic surfaces such as glass equation (3) can be simplified to

$$F_{CC} = 2\pi R \gamma_L \qquad (4)$$

Gravitational Force

When trying to pick up one glass sphere with the other, the force opposing the above adhesive forces is the gravitational force:

$$F_G = \frac{4}{3}\pi R^3 \rho g \qquad (5)$$

where ρ is the density (i.e. $3 \cdot 10^3$ kgm^{-3} for glass) and g the gravitational acceleration of earth.

Fig.1 shows the magnitude of all forces involved as a function of the sphere radius R. The shaded rectangle highlights the particle sizes of interest in this paper.

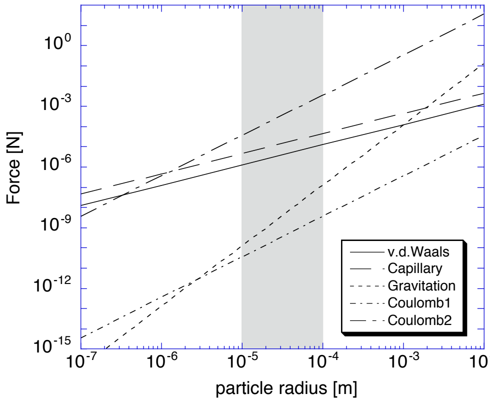

FIGURE 1: Adhesive forces involved in the microworld compared to gravitation calculated for two glass spheres

If the surface charge of the particles is not to high, the force originating through capillary condensation of water is dominant. Thus, when working at ambient conditions, where the relative humidity is often around 50%, decreasing the water meniscus between the particle to be handled and the handling tool will improve actually letting go of the particles at the desired location. The best way to decrease these capillary forces is by coating the handling tools with hydrophobic layers, thereby increasing θ and decreasing F_{CC}.

HYDROPHOBIC COATINGS

Sputtered Gold Coatings. A Balzers MED 010 magnetron sputter source (Balzers, Liechtenstein) with a film thickness monitor was used to coat silicon nitride (SiN) and silicon Si atomic force microscopy (AFM) cantilevers (from Digital Instruments, USA and Nanosensors, Germany respectively) and glass coverslips with 5 nm of chromium and subsequently 5 nm of gold. The intermittent chromium layer is needed to ensure proper adherence of the gold to the SiN, Si, and glass surfaces.

Chemical Vapor Deposited HFP Coatings. A home-built plasma coating unit was used to first clean the surfaces of the AFM cantilevers and glass coverslips and pipettes in an air plasma for 1 min and subsequently exposing the surfaces to a HFP plasma for 1 min to deposit a Teflon-like layer consisting of a mesh of carbon and fluorine. The layer is approximately 7 nm thick (see [2,3] for details).

Silanized OTS Coatings. Only the AFM cantilevers and the glass coverslips were silanized for reasons explained further down. Prior to silanization the cantilevers and coverslips were exposed for 30 min to UV-light (254 nm) of a Penray Mercury lamp (Ultra-Violet Products, USA) to clean and activate the surfaces. Silanization was accomplished by immersing the cantilevers and coverslips into a 0.7 mM solution of OTS in hexadecan and chloroform (7:3) for 2 hours and thorough rinsing with chloroform afterwards.

Cleaned Surfaces. As a control the SiN and Si cantilevers, the glass coverslips, and the glass pipettes were only cleaned by washing in ethanol and subsequent UV irradiation for 30 min. This procedure ensured that no contaminants were on the surface that could impede the reproducibility of test done with uncoated surfaces.

Characterization of the Coatings

Size of Water Droplets. The hydrophobicity of the different coatings was assessed by examining the size of 10 μl water droplets (Ultra High Quality water at 18.2 MΩ cm^{-1} resistivity) placed on the coated glass coverslips [4]. The droplets were viewed perpendicular to the surface with a video camera and the area enclosed by the droplet's circumference was measured with NIH image software [5].

The results of these measurements are shown in table 1. Only on the cleaned coverslips do the water droplets spread freely, having a contact angle close to zero, i.e. glass is highly hydrophilic. These droplets are also not circular, thus no radius was calculated. On all coated coverslips the water droplets do not spread having contact angles above 90°. The gold coated and HFP treated coverslips are equally hydrophobic, whereas the silanized coverslips are a bit more so.

TABLE 1: Size of 10 µl H_2O droplets on glass coverslips

	cleaned	Cr/Au coated	HFP treated	silanized
area [mm^2]	32±5	11.4±0.3	11.4±1.0	9.1±0.3
radius [mm]	n.a.	1.90±0.05	1.9±0.2	1.70±0.06

Adhesion Measurements. To study the adhesion of the coatings, the cleaned, gold coated, HFP treated, and silanized SiN cantilevers were used to measure their adhesion to hydrophilic (freshly cleaved mica, Provac, Liechtenstein) and hydrophobic (freshly cleaved highly oriented pyrolytic graphite (HOPG), Agar Scientific, United Kingdom) test samples at increasing humidity. To this end the tip on the cantilever end was brought into contact with the sample surface, withdrawn from it, and the force needed to disengage the cantilever from the surface recorded. This routine was done for 10 cantilevers of each coating type and 10 cleaned cantilevers. 5 of each surface type were used with the hydrophilic and hydrophobic test samples respectively. For each humidity value/test surface/tip coating combination an average was calculated.

Fig. 2 a) and b) show the results of these measurements on mica and HOPG respectively. The adhesion values were normalized to the value at 8% relative humidity, because the forces measured were based on the nominal spiring constant of the cantilevers, which can really only be applied to uncoated cantilevers. For the behavior on mica, a strong increase in adhesion for increasing humidity can be seen for the cleaned, uncoated cantilevers. Because both tip and sample are hydrophilic, this is expected and once more shows the strong influence of capillary condensation to the adhesion. Both gold coated and HFP treated tips show a slight decrease in adhesion with increasing humidity, proving the potential of these coatings to minimize capillary condensation. The tips silanized with OTS show no apparent relation between adhesion and humidity.

On HOPG the gold coated and HFP treated tips' adhesion stays more or less constant with increasing humidity, because neither the sample nor the tip is prone to water condensation on its surface.

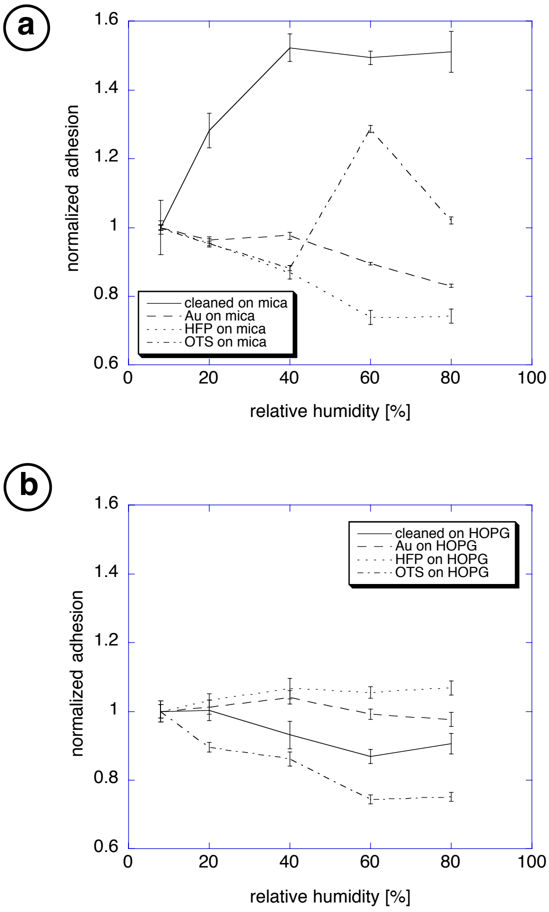

FIGURE 2: Normalized adhesion values of coated and cleaned AFM tips on a) a hydrophilic sample (mica) and b) a hydrophobic sample (HOPG). Error bars show the standard deviation.

The uncoated and silanized tips both show a slight decrease in adhesion with increasing humidity, which would actually indicate both these coatings are hydrophilic, which is expected for the uncoated tips but seems strange for the silanized tips. A possible explanation for this behavior is offered in the next section.

Homogeneity of Coatings.

To judge the homogeneity of the coatings, a few of the differently treated tips were viewed in a Hitachi S900 high resolution, in-lens SEM. Typical results from these images are shown in Fig.3. The gold and HFP coatings seem relatively homogenous, whereas the OTS coating often has a patchy appearance. This behavior has more extensively been investigated by Flinn et al. [6], who show that the OTS layers can be patchy and not strongly bound to the underlying surface. This would also explain why the adhesion experiments with OTS coated tips show no clear characteristic. From the four tip types imaged, only gold coated tips are conductive. The charge build up on the non-conducting tips is also responsible for the shading effects during imaging in the SEM (especially visible in Fig. 3 c) and d)).

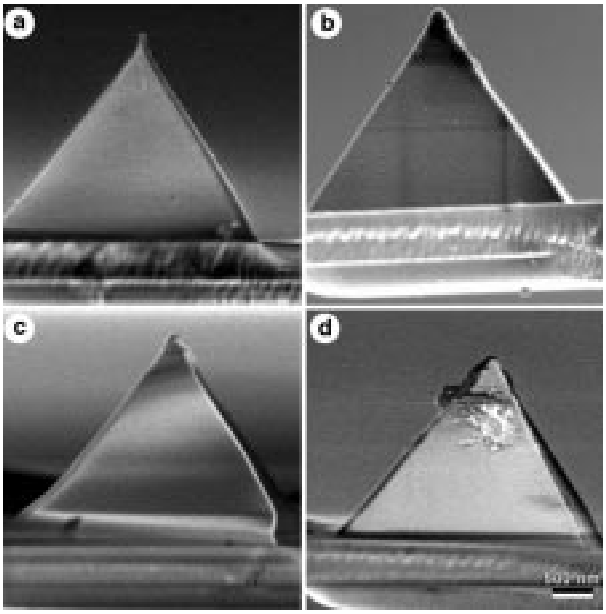

FIGURE 3: SEM images of a) cleaned, b) gold coated, c) HFP treated, and d) OTS silanized AFM SiN tips.

Abrasion Characteristics of the Coatings. The stability of the coatings was evaluated by scanning over the exposed pits of a CD with gold coated and HFP treated Si cantilevers in the tapping mode in a Nanoscope AFM in (Digital Instruments, USA).

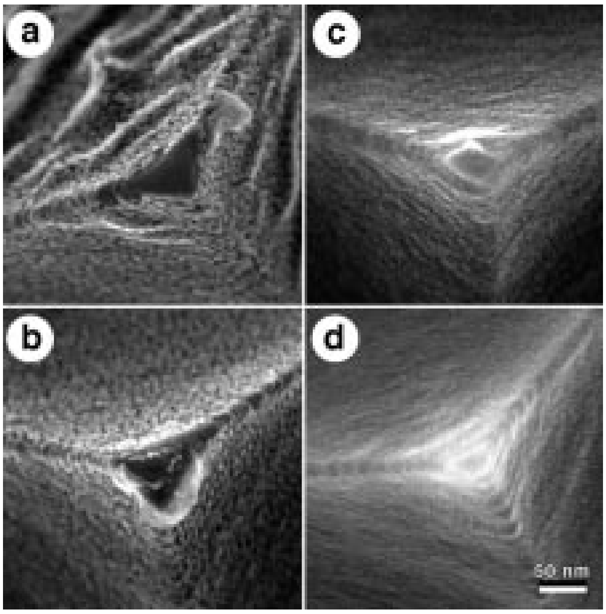

FIGURE 4: SEM top view images of a) and b) gold coated and c) and d) HFP treated Si tips.

The forces during imaging are in the few tens of nN range. The tips used for scanning were then imaged in the SEM. Fig. 4 shows two examples for each of the two coatings. The gold coating was clearly removed from the apex of the tip, whereas the Teflon-like coating seems to have stayed intact.

Consequences of Coating Characterization

Even though the OTS silanized surfaces show a distinct hydrophobic behavior on the macroscopic scale (water droplet size), the layer is inhomogenous on a microscopic scale (as concluded from the adhesion experiments and the SEM images). Furthermore, it is also the most tedious procedure and was thus excluded as a possible candidate for hydrophobic coatings.

The gold coating and the HFP treatment of glass and glass-like surfaces (i.e. SiN and Si cantilevers) almost fulfill all the criteria listed in the introduction. They are hydrophobic, homogenous, and easily applied. Gold coatings, however, are not as resistant to abrasion as the Teflon-like coatings obtained through HFP treatment. On the other hand gold coatings are conductive and thus offer means to control the electrical charge on the tool which would help to tackle Coulomb forces in situations where these become dominant. For these reasons, only gold coating and HFP treatment were applied to the glass pipettes used for vacuum gripping of 50 μm glass beads.

PICK AND PLACE TRIALS

System Setup

The soda glass pipettes (Fig. 5) are drawn in a D7410 pipette puller (Bachhofer, Germany) from glass capillaries with an O.D. and I.D. of 1.5 mm and 0.9 mm respectively (see [7] for details).

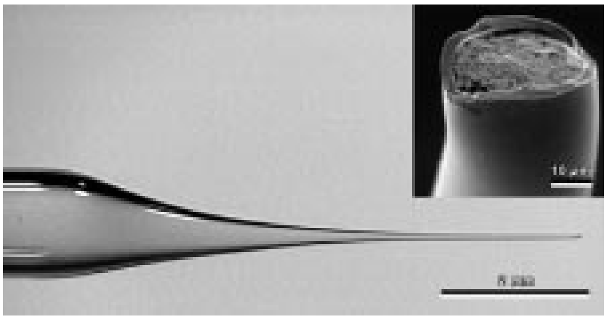

FIGURE 5: Glass pipette used as vacuum gripping tool. Inset shows gold coated apex of the pipette.

The overall shape, length, and orifice diameter of the pipette can be controlled by choosing the appropriate heating temperature, pulling velocity, and by cutting the pipettes after pulling. In this case for all pipettes used the length of tapered end was 4-5 mm and the orifice was approximately 40 µm. The size of the opening has to correspond to the size of the manipulated objects. With the orifice size chosen here, we are able to manipulate micro diamonds 100-120 µm in size as well as the 50 µm glass beads. The region of optimal orifice size is discussed in detail elsewhere [7]. The pipettes are then used in our NanoRobot, a 5 D.O.F. platform (x, y, z, rotation about the z-axis, and tilt of the x-y-plane) over which the pipette is fixed at 45°. A flexible tube connects the pipette to the vacuum system. A binocular allows to view the platform and the vacuum gripper from above. The complete system is described in detail elsewhere [7, 8, 9]. A 10 mm by 10 mm piece of silicon wafer is fixed to the platform and used as the substrate for the 50 µm glass spheres. To control the humidity, the work space is enclosed in a plastic bag into which air with controlled humidity can be streamed.

Pick and Place Sequence

The manipulation sequence for the micro objects (glass beads) was the following: The pipette was approached towards an object from above, the vacuum was applied to the pipette, the object was lifted from the surface and moved to the desired location, the vacuum in the pipette was turned off, the object still held by the pipette was brought into contact with the surface, and finally the pipette was moved away from the object. If all steps in this sequence were accomplished, the trial was declared successful. This routine was repeated 40 times for cleaned, gold coated, and HFP treated pipettes at 30% and 65% relative humidity respectively.

Results

Fig. 6 shows the results obtained from the pick and place trials.

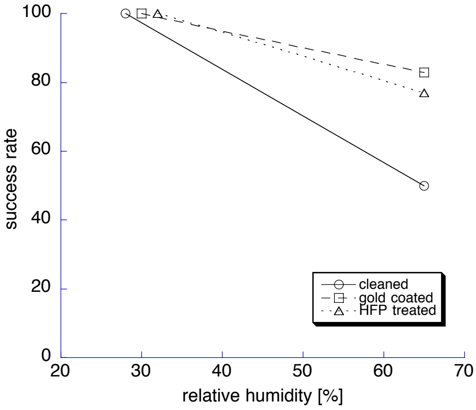

FIGURE 6: Pick and place trial results using cleaned and coated pipettes

low humidity values uncoated and coated pipettes perform equally well at 100% success rate. At higher humidities the success rate for uncoated tips decreases sharply to 50%, whereas gold coated and HFP treated tips still have a success rate around 80%.

Finally in Fig. 7 a structure made with a HFP treated vacuum gripper is shown. The time it took to make these three structures was 30 min.

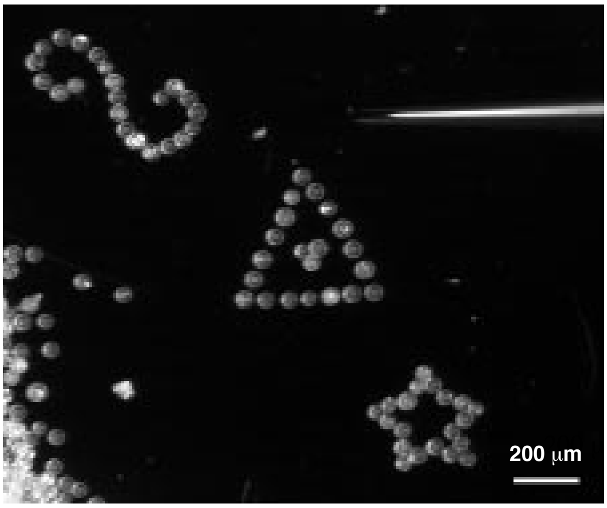

FIGURE 7: Structures made from 50 µm glass beads with a HFP treated vacuum gripper (top right).

CONCLUSIONS

With the sputtered gold coatings and the Teflon-like layers obtained through HFP plasma treatment we were able to successfully reduce the adhesion between two surfaces caused by capillary condensation of water in humid air. Pick and place trials at ambient conditions (humid air) were much improved by using our vacuum gripper with these coatings. In principle, the coatings should improve any micro-handling tool. When comparing the two coating types, the Teflon-like coatings seem superior to gold coatings in their abrasion properties, whereas the gold coatings, by being conductive, offer the possibility to control the electrostatic forces which can be another mayor source to the interaction between surfaces in the micro-world.

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