STICTION IN MICROFLUIDIC ENVIRONMENTS

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ABSTRACT

Although much insight has been gained into the problem of stiction for MEMS operating in air, no systematic investigation of the phenomenon in microfluidic environments has been performed. With the increased interest in BioMEMS and microfluidic applications, the characterization of microstructure adhesion in fluids becomes important. The adhesion characteristics of oxide-terminated and SAM-coated polycrystalline Si (polysilicon) cantilever beams in various solvents are investigated. It is found that surfaces behave quite differently in microfluidic environments, when compared to their behavior in air. Oxide-terminated surfaces are found to exhibit much reduced adhesion in water, in comparison to air. In contrast, hydrophobic SAM-coated surfaces experience strong adhesion in water, a behavior opposite to what is observed in air. It is also observed that oxide-terminated surfaces exhibit greater adhesion in hydrocarbons, compared to SAM-coated surfaces, while surfaces show no adhesion in isopropyl alcohol regardless of surface termination.

INTRODUCTION

One of the biggest problems that plagues MEMS is the occurrence of stiction [1], the adhesion that takes place when surfaces of MEMS come into contact. One method that has been suggested to reduce adhesion consists of coating the microstructure surfaces with self-assembled monolayer (SAM) films [2-4]. These monolayer coatings help overcome adhesion by making the microstructure surfaces hydrophobic. This hydrophobicity prevents suspended surfaces from being attracted to each other or to the substrate due to surface tension forces when they are brought out of the liquid phase associated with the release step. It also reduces adhesion during device operation.

Although the performance of oxidized and SAM-coated microstructures operating in air has been the subject of much analysis, little has been done to systematically study what occurs when these films are subjected to fluidic environments. This may be crucial to the BioMEMS and microfluidic technologies, which involve valves, pumps, and diverse fluidic environments such as blood samples. In these instances, SAM coatings have been investigated as a means to control the movement of liquids in microfluidic devices [5, 6]. By rendering capillaries in microfluidic devices hydrophobic or hydrophilic, the flow of liquid can be manipulated. It is in regards to these applications that adhesion in microfluidic environments has been investigated in this paper.

EXPERIMENTAL DETAILS

Release and Coating Procedures:

The structures that were investigated in this paper consisted of arrays of polysilicon cantilever beams, so-called cantilever beam arrays (CBA), ranging in length from 150 to 1700 μm in 50 μm increments. All beams were 18 μm wide, with a thickness of 2.5 μm and suspended approximately 2 μm from the substrate surface (Fig. 1). These structures were fabricated using the Sandia SUMMIT IVTM process. Four surface treatments and four solvents were used in this study. The surface treatments were chemically

grown silicon oxide, and three organic monolayer coatings derived from the following precursors: dichlorodimethylsilane, $(\text{CH}_3)_2\text{SiCl}_2$ (DDMS) (Alfa Aesar, 99+%), octadecyltrichlorosilane, $\text{C}_{18}\text{H}_{37}\text{SiCl}_3$ (OTS) (Aldrich Chemical Co., 90+%), and 1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane, $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCl}_3$ (FDTS) (Lancaster Synthesis Inc, 96%). The precursor OTS was deposited through liquid means, while DDMS and FDTS were deposited from both liquid and vapor phases. Coatings were deposited using both methods in order to determine if deposition method affected adhesion behavior. The solvents were DI H_2O (18 $\Omega\text{-cm}$), isopropyl alcohol (IPA), anhydrous iso-octane, and hexadecane (HD) (Aldrich Chemical Co.). These solvents were chosen because of the similarities to fluids that may be used in micro-fluidic applications and also to explore the effect of polar versus nonpolar solvents, and short-chained versus long-chained hydrocarbons.

Each release/coating cycle consisted of two dies containing cantilever beam array (CBA) structures and a Si(100) piece. The processing began by releasing the structures in a 1:1 (v/v) HF (49 wt%)/HCl (36 wt%) solution and oxidizing the surface in a piranha solution (2:1 (v/v) sulfuric acid/hydrogen peroxide (30 wt%)). After oxidation, the chips were placed in a series of DI H_2O rinses until the pH remained neutral in the last DI H_2O rinse.

For chips undergoing the oxide surface treatment only, one die and the Si(100) piece were pulled directly from the water rinse, and left to dry through evaporation. These samples were used as control samples to ensure process robustness. The other chip was removed from the water rinse and placed in a vial of the desired solvent through a series of intermediate rinse steps.

For chips undergoing liquid monolayer coatings, bulk water was removed through a series of solvent rinses before they were placed in the coating solution with the appropriate precursor. The intermediate rinses consisted of methanol, followed by IPA, and iso-octane. Iso-octane was used as the solvent for the SAMs solution, with precursor concentrations of 1 mM for DDMS, 0.5 mM for OTS, and 1 mM for FDTS in a pre-conditioned (with the particular precursor) glass container. The chips were left in the covered container until the contact angle measured on the Si(100) piece was within the expected range for the particular precursor used in the coating [7, 8]. Once the expected contact angles were reached, the chips were stepped back through the iso-octane rinses. The series of rinses used for each environment can be seen in Table 1. The other chip and the Si(100) piece followed the standard coating process by continuing through the IPA rinses, the methanol rinse, and by finishing in a DI H_2O rinse. Once pulled from the water rinse, these chips were dry.

For chips undergoing DDMS and FDTS monolayer coatings deposited in the vapor phase (V-DDMS and V-FDTS), the chips were placed in a methanol rinse after the DI water rinses, and were then placed in vials of methanol. The chips were kept in methanol for at least 24 hours and then dried using a Tousimis model 815 "Autosamdri" supercritical carbon dioxide dryer. The samples were then plasma-cleaned and coated with either DDMS or FDTS in the vapor phase as described elsewhere [8]. Once coated, the chips were placed in IPA to wet the surfaces, transferred to a rinse of the desired solvent, and then placed in a vial of the solvent until tested.

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Table 1: The series of rinses used for bringing SAM-coated dies into a given environment.

Desired Environment	Rinse 1	Rinse 2	Rinse 3	Rinse 4	Final Step
Air	Iso-octane	IPA	Methanol	Water	Air
Water	Iso-octane	IPA	Water	--	Water Vial
IPA	Iso-octane	IPA	--	--	IPA vial
Iso-octane	Iso-octane	--	--	--	Iso-octane vial
Hexadecane	Iso-octane	Hexadecane	--	--	Hexadecane vial

Probing Techniques in Solution

Chips were kept in vials of solvent for at least 24 hours before testing. This was to ensure that the sample surface had come to equilibrium with the fluid. A 4.25" diameter glass dish with an approximate 9/16" sidewall was used to hold the chips during testing. The dish was placed in a UVO cleaner to remove any undesirable contaminants from the surface. The dish was then placed under a Mitutoyo Finescope 60 microscope with a Nomarski style differential interference contrast (DIC) prism, and viewed with a Mitutoyo M Plan Apo 10x objective. The dish was filled with the desired solvent, and the chip was placed in the dish while maintaining the liquid meniscus. Before any testing, all beams were insured to be free from the surface. Signatone SE-SMS probe tips were used to probe the beams. A color change determined which beams were adhered to the surface, as seen in Fig. 1(a). To insure that the coatings were not altered by storage in the various fluids, the testing was performed within 5 days of film formation.

Figure 1. (a) Differential Interference Contrast (DIC) image of DDMS-coated beams in iso-octane after probing manually. Light beams are adhered to the substrate. The beam at the far right is 950 μm , while that at the far left measures 1700 μm . (b) Side view schematic of a cantilever beam.

Manual Actuation and Analysis

Beams were probed systematically at the very tip of the beam. Any beams that remained adhered after immediate probing were recorded. A second pass was then performed on all beams that remained free-standing. These beams were brought into contact with the substrate and held there for thirty seconds. Adhered beams were recorded. Finally, the procedure was

repeated a third time, but for a probing time of one minute on any remaining free-standing beams. In this last cycle, rarely were additional beams adhered. Once testing was complete, the chip was returned to its vial and the dish was rinsed.

Using the adhered beam data from the cantilever beam probing, the average detachment length, l_d , was calculated based on the probability that a beam of length, l , was adhered to the substrate [9]. From this, the apparent work of adhesion was then obtained [7].

AC Electrostatic Actuation

Similar to the method described under the manual probing, an electrostatic method was employed to test cantilever beams in various environments. This electrostatic probing method was modified from a version used by Sounart and Michalske [10]. Two Signatone SE-10T probe tips were used to actuate the cantilever beam array by applying an AC square wave signal between the actuation pad and the ground plane, see Fig. 1(b) [11]. Voltages and frequencies were varied to avoid electrolysis. Adhered beams were recorded after an immediate voltage was applied and released, after 30 seconds of sustained applied AC voltage, after 1 minute of sustained applied AC voltage, and finally after 5 minutes of sustained applied AC voltage. The adhered beam data were then used to determine the work of adhesion, as done for manual actuation.

RESULTS

Results of Manual Probing

The work of adhesion data for actuation in air and water can be seen in Table 2. When water was used as the fluidic environment, cantilever beams displayed behavior opposite of that observed in air. While in air, beams with only an oxide treatment adhered to the substrate for beams less than 250 μm , corresponding to values for the work of adhesion of 1020 $\mu\text{J}/\text{m}^2$, oxide beams showed no tendency to adhere in water. In fact, the longest beams (1700 μm) were routinely free-standing in water even when held in contact with the substrate for a prolonged period, which yielded values for the apparent work of adhesion of $<0.5 \mu\text{J}/\text{m}^2$. However, SAM-coated beams adhered strongly to the substrate in water, while displaying much longer detached beams in air.

Independent of surface treatment, beams remained free in IPA despite contact with the substrate for a prolonged period, corresponding to values for the work of adhesion of $<0.5 \mu\text{J}/\text{m}^2$.

For actuation in iso-octane and hexadecane, although SAM-coated beams would stick to the substrate, there was not a strong attraction to the surface. In some cases, beams could be probed with a probe tip to the free position after being adhered to the substrate. However, in the case of oxide-terminated beams, they were strongly adhered to the substrate. These beams were more difficult to probe to a free position than beams with SAM coatings. Values for the work of adhesion for the various surface treatments in iso-octane and hexadecane can be seen in Tables 3 and 4.

Table 2: Detachment lengths and work of adhesion data for various surface treatments in air, water, and IPA, using manual actuation. Water and hexadecane contact angles are also listed. The relative humidity of the ambient environment was $50 \pm 10\%$.

Surface Treatment	Contact Angle in Water	Contact Angle in Hexadecane	Detachment length, l_d (μm)			Work of Adhesion ($\mu\text{J}/\text{m}^2$)		
			Air	Water	IPA	Air	Water	IPA
Oxide	$<30^\circ$	$<20^\circ$	250	1700	1700	1020	<0.5	<0.5
DDMS	103°	38°	516	150	1700	56	>7870	<0.5
V-DDMS	103°	38°	531	150	1700	50	>7870	<0.5
OTS	110°	38°	680	150	1700	19	>7870	<0.5
FDTS	115°	68°	667	150	1700	20	>7870	<0.5
V-FDTS	115°	68°	1000	150	1700	4	>7870	<0.5

Results of AC Electrostatic Actuation

Electrostatic actuation was not performed on beams in water since they were either completely free, as in the case of oxide-terminated beams, or all strongly adhered, as in the case of SAM-coated beams (Table 2). Because all beams despite surface treatment were free-standing in IPA, beams were not electrostatically actuated in this environment either.

As mentioned in the experimental section, estimates of the voltages and frequencies were obtained for the actuation in iso-octane and hexadecane. In this paper, we present results using 94 V actuation voltage and frequencies above 10 Hz. It was found that 94 V was enough to insure good contact between the beams and the substrate, and beams actuated at voltages greater than 94 V became electrostatically shorted to the actuation pad under them. Frequencies lower than 10 Hz caused electrolysis in the fluid. Results of the electrostatic actuation in iso-octane can be found in Table 3, along with the results from manual probing as a comparison. Although prolonged actuations of 1 and 5 minutes were performed, the results did not differ from those found at 0.5 minutes. Therefore, one value is reported for each combination of voltage and frequency.

The results for actuation in hexadecane of the monolayer-coated beams can be seen in Table 4. It can be observed that the values of the work of adhesion of the SAM-coated beams are at least one order of magnitude less than the values for oxide-terminated beams. Results for prolonged probings of 1 minute and 5 minutes did not differ from the results for 0.5 minutes. Therefore, one value is displayed for these coatings in hexadecane.

DISCUSSION

The oxide-terminated beams are found free-standing in water, for any beam length. Because oxide-terminated beams are hydrophilic, the surfaces can more effectively form hydrogen bonds with the surrounding water than with each other. As a result, these surfaces interact weakly with each other in favor of forming the hydrogen bonds with the surrounding water [12].

In contrast, SAM-coated beams are found to strongly adhere to the substrate in water. This behavior can be attributed to hydrophobic interaction [12]. Because of this interaction, when the hydrophobic surfaces of the SAM-coated beams and the substrate come together, they squeeze out water molecules between the surfaces in favor of forming vapor cavities. This lowers the free energy of the system since the ejected water molecules are able to form hydrogen bonds in the bulk, resulting in adhered surfaces.

Independent of surface treatment, none of the beams are adhered to the substrate in IPA. It is observed that the contact angle of isopropyl alcohol measures less than 20° for all the

surface treatments. Because IPA completely wets all of the surfaces, it is not energetically favorable for vapor to condense at contact sites as expected in the case for SAM-coated surfaces in water. Results are consistent with this argument.

For oxide-terminated beams in both iso-octane and hexadecane, it can be observed that the standard deviation is quite large compared to the values of the work of adhesion. During actuation, the detachment lengths never varied more than $150 \mu\text{m}$ per array of beams. However, since the detachment lengths were rather small in these fluids, ranging between 200 and $400 \mu\text{m}$, Δl_d of $50 \mu\text{m}$ has a significant impact on the standard deviation of the work of adhesion due to $\Delta l_d/l_d^5$ scaling. For large detachment lengths as seen with the SAM-coated beams in these fluids, l_d^{-5} causes the standard deviation of the work of adhesion to become small, compared to that of the oxide-terminated beams.

With the highest values for contact angles in both water and hexadecane, it would be expected that beams coated with FDTS would be adhere at shortest beam lengths in iso-octane and hexadecane, and would therefore have the greatest values for the apparent work of adhesion. Although this is observed for vapor FDTS-coated samples, it is not observed for liquid-deposited FDTS samples. Differences between the vapor-deposited and liquid-deposited FDTS coating quality may arise from the particle generation inherent in the liquid deposition method (vapor-deposited coatings usually exhibit less particles). A rougher surface due to more particles may actually decrease the work of adhesion since less surface area will be contacting when compared to a smooth surface. As a result, one might expect lower values for the work of adhesion for liquid-deposited FDTS-coated beams, than those with vapor-deposited FDTS. This is consistent with the experimental observation.

It would also be expected that beams coated with DDMS and OTS would have comparable values for the detachment lengths and apparent work of adhesion since both precursors yield films with similar contact angle values (and both have lower contact angles than FDTS). This is consistent with results, with both liquid- and vapor-deposited DDMS samples. Although deposition method makes a difference in the values of work of adhesion for FDTS-coated samples, no such difference is observed for the two methods of deposition for DDMS. This can be attributed to the fact that the liquid method of DDMS deposition yields few particles for this precursor [4].

Although it was observed that some of the detachment lengths from manual actuation after electrostatic actuation were lower than the lengths found before actuation, corresponding to higher works of adhesion for the manual actuation, these differences were small and may be due to slight rearrangement of the coating molecules on the surfaces due to electrostatics. After electrostatic actuation, the ground pad and actuation pad were visibly changed where the probe tips touched the pad. It

Table 3: Work of adhesion of various surface treatments in iso-octane after manual and electrostatic actuation. A “V” stands for vapor-deposited coating, while those coatings without a “V” imply deposition in the liquid phase.

Testing Conditions	Work of adhesion in iso-octane ($\mu\text{J}/\text{m}^2$)					
	Oxide	DDMS	V-DDMS	OTS	FDTs	V-FDTs
manual (original)	492 ± 331	7 ± 1	2 ± 0.7	5 ± 1	9 ± 3	397 ± 146
94v, 10Hz	185 ± 147	6 ± 1	1 ± 0.5	4 ± 1	5 ± 1	44 ± 79
94v, 100Hz	790 ± 688	5 ± 1	1 ± 0.4	5 ± 1	8 ± 2	44 ± 79
94v, 1kHz	185 ± 147	4 ± 1	1 ± 0.4	5 ± 1	5 ± 1	44 ± 79
manual (repeat)	395 ± 144	7 ± 1	2 ± 0.9	5 ± 1	13 ± 0	322 ± 112

Table 4: Work of adhesion of various surface treatments in hexadecane after manual and electrostatic actuation. A “V” stands for vapor-deposited coating, while those coatings without a “V” imply deposition in the liquid phase.

Testing Conditions	Work of adhesion in hexadecane ($\mu\text{J}/\text{m}^2$)					
	Oxide	DDMS	V-DDMS	OTS	FDTs	V-FDTs
manual (original)	2490 ± 0	4 ± 0	2 ± 0.6	2 ± 0.4	4 ± 0.4	221 ± 70
94v, 10Hz	2490 ± 0	3 ± 1	2 ± 0.5	1 ± 0.1	1 ± 0.4	184 ± 56
94v, 100Hz	2490 ± 0	3 ± 1	2 ± 0.3	1 ± 0.1	1 ± 0.4	184 ± 56
94v, 1kHz	2490 ± 0	3 ± 1	2 ± 0.3	1 ± 0.2	1 ± 0.3	184 ± 56
manual (repeat)	2490 ± 0	10 ± 2	2 ± 0.4	3 ± 1	4 ± 0.4	266 ± 152

appeared that particles were accumulated where the probe tip has been. In manual actuation, no visible damage was seen at the end of the beams where the probe tip was placed.

CONCLUSIONS

It has been shown that the behavior of modified surfaces in microfluidic environments differs greatly than that observed in air for the same treatments. For oxide-terminated surfaces, the apparent work of adhesion is $<0.5 \mu\text{J}/\text{m}^2$ in water, but as much as $1020 \mu\text{J}/\text{m}^2$ in air. For SAM-coated surfaces, the apparent work of adhesion is smallest in air, ranging from $19\text{--}56 \mu\text{J}/\text{m}^2$, depending on the precursor, while it is the greatest in water, $>7870 \mu\text{J}/\text{m}^2$. In IPA, beams undergoing any of the surface treatments are free-standing. In iso-octane and hexadecane, oxide-terminated beams yield the largest values for work of adhesion when compared to any of the SAM-coated beams. DDMS- and OTS-coated beams yield similar works of adhesion in both of these environments while vapor-deposited FDTs-coated beams yield higher works of adhesion, compared to DDMS and OTS, but lower works of adhesion when compared to oxide-terminated beams. Liquid-deposited FDTs-coated beams yield values for the work of adhesion comparable to DDMS- and OTS-coated beams, and lower than vapor-deposited FDTs-coated beams in these fluidic environments. This is attributed to the presence of particles on liquid-deposited FDTs films. Finally, two methods of actuation for the cantilever beams are demonstrated for determining detachment lengths, and therefore the apparent work of adhesion in fluid, with similar results for both methods.

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