

# Self-assembled monolayers as anti-stiction coatings for MEMS: characteristics and recent developments

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## Abstract

Despite significant advances in surface micromachining technology, stiction remains a key problem, severely limiting the realization and reliability of many micro-electro-mechanical systems (MEMS) devices. In this article, we focus on self-assembled monolayers as release and anti-stiction coatings for MEMS. Their formation mechanism, the microstructure coating process, and the characteristics of the coated microstructures are described, followed by a discussion of the current limitations, areas for improvements and recent progress for this coating technology. © 2000 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

The inherent mechanical nature of MEMS devices brings about a new level of complexity to their production and reliability compared to standard integrated circuits. Strong adhesion, friction and wear are major problems limiting both the production yield and the useful lifetime of many of these devices [1–9]. The traditional high yields experienced in the IC industry extend to MEMS production only up to the point of microstructure release. From there on, virtually every type of micromechanical device is susceptible to stiction.

Stiction is present during the release process when the surface tension of the draining rinse liquid draws the microstructure into contact with the underlying substrate (release stiction). Stiction also occurs later in use, when intentionally or accidentally parts come into contact (in-use stiction). Strong adhesion is generally caused by capillary, electrostatic and van der Waals forces, and in some cases by “chemical” forces such as hydrogen bonding and solid bridging. Treatments are needed that render the surfaces hydrophobic to eliminate capillary forces, stable both under ambient and elevated temperatures, hard and wear resistant, and electrically conductive to minimize charge trapping. (van der Waals attraction, which originates in the

polarizability of materials and as such cannot be eliminated, is greatly reduced by roughening the surfaces.) The fabrication processes pose stringent constraints on any such treatment [7]. The easiest approach is to treat the surfaces during or right after the microstructure release since this would have the least impact on the overall fabrication process. However, in this case, the coating process must be *conformal* (rather than line-of-sight) to insure uniform deposition on all sides, including underneath suspended devices. Several approaches have been investigated to alleviate release and in-use stiction. These methods have been more extensively reviewed in Refs. [1–7]. With the exception of SAM coating, none of these processes address both of these problems simultaneously.

## 2. Self-assembled monolayer coating

We have demonstrated that self-assembled monolayer coatings can achieve the following characteristics [10–16] when properly integrated into microstructure release process: (a) eliminate release stiction by effectively reversing the shape of the water meniscus that forms underneath microstructures during the drying process. This effect can be quantified by measuring water contact angle on these surfaces. Water contact angle increases from  $< 30^\circ$  on  $\text{SiO}_2$  surfaces, to  $\geq 110^\circ$  on SAM-coated surfaces (see Fig. 1); (b) reduce in-use stiction by three to four orders of

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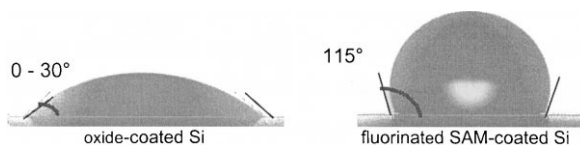


Fig. 1. Water contact angles on oxide- and FDTS-coated Si surfaces.

magnitude with respect to the conventional oxidized release process; (c) eliminate the need for large input signals (or mechanical probing) in the start-up phase in microengines; (d) reduce friction in microengines (static friction value of 0.08 vs. 2.3 for oxide-coated surfaces); (e) reduce wear significantly (over 40 million operation cycles have been achieved in touch-mode electrostatic actuators); and (f) survive packaging environments (thermally stable to 400°C in various, including oxygen containing, environments).

### 3. SAM film formation

Two SAM coating processes have been developed and demonstrated for MEMS applications. One is based on octadecyltrichlorosilane ( $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ , OTS), and the other on 1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane ( $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCl}_3$ , FDTS) precursor molecules. The SAM coating, or silanization, of silicon with a  $\text{RSiCl}_3$  precursor begins with the hydrolysis of the polar head-group that converts the Si–Cl bonds to Si–OH (silanol) groups [17,18]. Next, these groups, which are strongly attracted to the hydrophilic surface of oxidized silicon, condense and react with silanols on other precursor molecules and silanols on the surface to produce covalent siloxane bonds, Si–O–Si. After monolayer formation, the solid–vapor interface consists of the alkyl or perfluoroalkyl tail group of the precursor molecule (Fig. 2). The condensation of a monolayer takes of order of several minutes up to several hours (depending on SAM solution concentration). The complete polymerization of the silanols into a covalent siloxane network on the other hand requires aging of the surfaces in air for a few days or baking at 100–120°C for a few hours.

Although the coating process requires some amount of water to hydrolyze the Si–Cl headgroups (converting them to Si–OH), bulk or too much water initiates bulk polymerization of the trichlorosilane groups. Bulk polymerization often manifests itself as particulates on the wafer. To minimize this problem, the solvents used for SAM coating with  $\text{RSiCl}_3$  precursors must be anhydrous. (When preparing OTS coatings for research purposes, a long alkane such as hexadecane is often mixed with 30 vol.% of a co-solvent such as carbon tetrachloride or chloroform to better solubilize the polar headgroup [17–19]. For large-scale production, however, it is mandatory to avoid using chlorinated solvents for environmental and health reasons; this can be accomplished by using pure toluene as a solvent.)

### 4. Microstructure coating process

The SAM coated surfaces are extremely hydrophobic (water contact angles  $> 90^\circ$ ). The monolayers themselves are molecularly thin (OTS thickness  $\sim 2.8$  nm, FDTS  $\sim 1.4$  nm). As such, they are not expected to affect significantly the bulk materials properties. Furthermore, when deposited from solution, they are expected to produce a uniform conformal coating. These features make SAMs very attractive for MEMS applications.

The release and coating processes for OTS and FDTS films are described in detail elsewhere [10–12]. Briefly, all steps of the SAM coating process are wet chemistry based. Upon etching of the sacrificial layer in HF, de-ionized water is used to thoroughly “displace” the HF. This and all subsequent displacements are done by pouring the new solution (DI water in this case) while aspirating the old solution. The reason for displacement is that the structures must remain in liquid until they are properly coated with SAMs. Otherwise, they get pulled down and stick by capillary forces (i.e., release stiction). Furthermore, the dies must be swirled to make sure the old solution is not trapped underneath the structures, and hence is not carried over to the next step. In the next step, water is displaced with  $\text{H}_2\text{O}_2$  to reoxidize the surface, since the SAM molecules only react with Si–OH bonds on the surface. Then,  $\text{H}_2\text{O}_2$  is displaced with water.

Now, before entering the SAM solution, bulk water must be eliminated. To this end, iso-propanol is used to displace the water. Next, the dies are picked up from IPA and moved to a bath of iso-octane. During this transfer, the operator must take great care to ensure that enough liquid is trapped on top of the die such that the meniscus remains above the structures. Otherwise, dewetting of the structures results in release stiction. Then, the microstructures enter the SAM solution. (In the FDTS coating process, this step actually takes place inside a dry box, although our more recent results show that this precaution may not be necessary.) After the SAM film formation is completed, the above steps are repeated in reverse. In other words, the structures are transferred into pure iso-octane and, in case of the FDTS process, are taken out of the dry box. Then, the structures are moved to isopropanol, which is then displaced with water. At this stage, the structures are pulled out of water whereby they emerge dry and unstuck. Upon actuation, the microstructure surfaces exhibit significantly lower levels of in-use stiction, friction and wear.

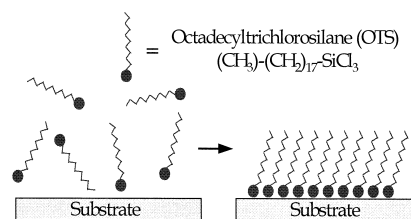


Fig. 2. Schematics of SAM formation process.

Furthermore, they survive a wide range of packaging environments and withstand temperatures up to 400°C even in oxygen-containing environments, in the case of FDTS (OTS withstands up to those temperatures only in oxygen-free atmosphere).

### 5. Characteristics of SAM-coated microstructures

The SAM-coated microstructures have been characterized in several ways. Cantilever beam arrays has been used to determine the success of the coating for releasing microstructures. Beams 1 mm and longer (and 2  $\mu\text{m}$  above the surface) have been successfully released without the need for additional drying techniques. Furthermore, the CBA technique [20] has been used to measure the work of adhesion [10–12]. The exact values depend on the surface topography, e.g., surface roughness. On a polysilicon surface with rms roughness of about 3 nm, the average work of adhesion was found to be about 23 and 5  $\mu\text{J}/\text{m}^2$  for OTS and FDTS coated beams, respectively (cf., 56  $\text{mJ}/\text{m}^2$  for oxide-coated surfaces).

A lateral friction test structure [21,22] was used to examine the friction and wear characteristics of SAM coated surfaces. The static coefficient of friction was found to decrease from 2.0 for  $\text{SiO}_2$  to 0.1 for SAM-coated microstructures [14]. These values remained unchanged after 1 million impacts at an apparent contact pressure of 26 kPa.

A side wall friction test structure was used to study the tribological properties of SAM coated side walls [14,23]. Kinetic coefficient of 0.02 was obtained on FDTS coated side walls under an apparent contact pressure of 84 MPa. After 2100 cycles, friction coefficient increased to 0.27, suggesting SAMs wear. After  $3.7 \times 10^5$  cycles, stick–slip behavior was observed.

The effect of SAM coating on the reliability of touch-mode electrostatic actuators has also been examined [15,16]. It was found that the SAM treatment desensitizes the actuator to environmental conditions, in particular to humidity. On the other hand, OTS coated actuators showed enhanced in-use stiction as compared to non-coated devices. It was argued that the permanent stiction in these OTS-coated devices is caused by surface charging associated with the higher resistivity of the layer and/or by surface interactions taking place between the hydrophobic layers. The performance of FTDS-coated actuators was found to be far superior to that of OTS, likely because of their lower resistivity. Over 40 million actuation cycles were achieved for FDTS-coated surfaces in room air.

### 6. Manufacturability

Although much progress has been made, by us and others, towards making this release/coating process a viable manufacturing process, research to date has inade-

quately (if at all) addressed two crucial issues. One is reproducibility. According to our experience, the issue here is almost one of “portability” of the process between different laboratories since it appears that some of the groups that have received training from us on the SAM coating process have consistently reported high release yields, whereas others have failed. This is perhaps not surprising, given the large number of process variables, which makes the process susceptible to operator errors in many of its critical steps. Process automation and sensing for real time process monitoring are highly desirable features that future research should address. The other issue is scaling up the process from single dies to whole wafers and eventually multi-wafer cassettes. Much of the work up to this stage has consisted of releasing dies  $1 \times 1 \text{ cm}^2$ . Scaling up the release and coating process to full-wafer level and eventually to multi-wafer cassettes is quite a challenging task. The scaled-up process should include proper displacement of solvents from one stage to next without allowing the wafer to dry and without excessive use of solvents and the associated production of chemical waste.

### 7. Recent progress

One effort to reduce the amount of chemical waste from the OTS process is based on a solvent “fill/drain” approach instead of an aspiration approach. A schematic of an apparatus designed to accomplish this is shown in Fig. 3. Basically, this device consists of a Teflon FEP separatory funnel modified by cutting the top such that the rounded portion is removed. Also, a Teflon ETFE plug is machined to fit inside the modified funnel so as to leave sufficient volume above the cone for process liquids. The plug reduces the amount of solvents needed, by reducing the stagnant volume of the funnel. Slots are cut into the Teflon plug to facilitate transfer of sample dies.

Since all the parts of the apparatus are made of some form of Teflon, the *entire* OTS process (sacrificial layer etch to final water rinse) can occur within the funnel, i.e., there is no need to transfer the sample while maintaining a meniscus. In order to displace one liquid with the next, the

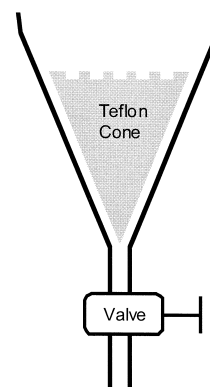


Fig. 3. Schematic diagram of the “fill/drain” apparatus.

contents of the funnel are drained out (via the valve) until the liquid level is slightly above the sample die. Then the new solvent is poured into the top opening, mixed, and the funnel contents are drained out again. This process is repeated until the old solvent is completely displaced. When properly performed, a single fill/drain cycle results in approximately one order of magnitude dilution of the old solvent with the new solvent. For example, to completely displace the concentrated HF etch solution (pH ~ 0) with deionized water (pH ~ 7) will take seven cycles, at about 50 ml solvent per cycle for a total of 350 ml for the displacement.

Process run data indicate that the use of an apparatus like the one shown in Fig. 3 can reduce the total volume of chemical waste from some 6 liters (generated by the aspiration process, described in Section 4) to about 1.8 liters. It should also be noted that much of this total volume is aqueous waste, and can be disposed of much more easily than organic waste. Additionally, due to the reduced handling of the sample dies, and the improved ability to displace solvents, the “fill/drain” approach may simplify the scale-up of the OTS process to the wafer level.

## 8. Future directions

The results on the side-wall friction testers show that SAMs do wear off under high load, and hence, a wear-resistant conformal anti-stiction coating remains highly desirable. Furthermore, in light of the results on the electrostatic actuators, the ability to tailor the electrical properties of SAM appears to be very important.

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