Surface processes in MEMS technology

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Manuscript received in final form 9 October 1997

Abstract

This review focuses on the problem of adhesion in microelectromechanical systems and on the application of the principles and techniques of surface science to understand and manipulate, at the atomic level, the interfacial forces which are responsible for strong adhesion in microdevices. Various approaches developed for reducing both release and in-use adhesion are discussed. They include surface roughening and chemical passivation. Results of ultrahigh vacuum studies on well-characterized surfaces are compared to experiments on test structures, such as cantilever beam arrays, which are specifically designed to study the surface properties of real micromechanical devices under normal operating conditions. Copyright © 1998 Elsevier Science B.V.

1. MEMS technology

There is a growing interest in developing technologies which use silicon and other electronic materials as mechanical materials. Using standard processes of the integrated circuit industry, researchers have successfully fabricated miniature mechanical components (micromachines) such as membranes, gears, motors, pumps and valves [1–3]. The integration of miniaturized mechanical components with micro-electronic components has spawned a new technology, known as microelectromechanical systems (MEMS). It promises to extend the benefits of microelectronic fabrication to sensing and actuating functions. A number of fabrication techniques have been developed for this technology and have been reviewed elsewhere [4–6]. In this review, I focus on surface micromachining technology and adhesion problems in surface-micromachined polycrystalline silicon (polysilicon) structures, although many of the principles discussed will also apply to single crystal silicon microstructures.

1.1. Surface micromachining

Surface micromachining, defined as the fabrication of micromechanical structures from deposited thin films, is one of the core technological processes underlying MEMS [5,6]. Surface microstructures
have lateral dimensions 50–500 µm, with thicknesses 0.1–2.5 µm, and are offset 0.1–2 µm from the substrate. The basic steps in a surface micromachining process are illustrated in Fig. 1. First, the substrate is typically coated with an isolation layer (Fig. 1(a)) that protects it during subsequent etching steps. A sacrificial layer is then deposited on the substrate and patterned. For simplicity, Fig. 1(b) shows that the opening of the sacrificial layer is terminated on the isolation layer. The microstructural thin film is then deposited and etched (Fig. 1(c)). Finally, selective etching of the sacrificial layer creates the free-standing micromechanical structures such as the cantilever beam shown in cross section in Fig. 1(d). The technique can be extended to make multiple layer microstructures.
Table 1
Mechanical properties of selected materials (from Ref. [7]. © 1982 IEEE)

<table>
<thead>
<tr>
<th>Material</th>
<th>Yield strength (10^{10}) dyn/cm²</th>
<th>Knoop hardness (kg/mm²)</th>
<th>Young’s modulus (10^{12}) dyn/cm²</th>
<th>Density (g/cm³)</th>
<th>Thermal conductivity (W/cm°C)</th>
<th>Thermal expansion (10^{-6} / ^°C)</th>
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<tbody>
<tr>
<td>Diamond</td>
<td>53</td>
<td>7000</td>
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<tr>
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<td>3.3</td>
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<td>SiO₂ (fibers)</td>
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<td>820</td>
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<td>Steel (max. strength)</td>
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<td>2.1</td>
<td>7.9</td>
<td>0.97</td>
<td>12</td>
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<tr>
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<td>19.3</td>
<td>1.78</td>
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<td>Stainless steel</td>
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</tr>
</tbody>
</table>

* Single crystal.

Polysilicon microstructures are an important example of structures fabricated by a surface micromachining process. The mechanical properties of silicon, listed in Table 1, make it an excellent material for micromachining [7]. With polysilicon as the structural material, the sacrificial layer is an oxide film, the isolation layer is typically silicon nitride, and the structural layer is polysilicon deposited by low-pressure chemical vapor deposition (LPCVD). The oxide film is etched by hydrofluoric acid (HF), which etches silicon nitride relatively slowly and has a negligible effect on polysilicon. Although the basic idea behind surface micromachining dates back to the 1960s [8], only recently has it become the focus of rapidly growing research and commercial applications. Surface micromachining has rapidly expanded owing, in part, to the mature infrastructure for depositing, patterning, and etching thin films borrowed from silicon integrated circuit technology. Another reason for this rapid expansion has been the potential of integrated microsystems, which incorporate surface micromachined sensors or actuators together with integrated electronics on the same substrate [9]. Early applications of this technology include the digital mirrors display, which has on the order of \(10^6\) aluminum thin-film micromirrors (Fig. 2) fabricated on top of a CMOS static random access memory integrated circuit [10,11]. Other applications include integrated accelerometers for such tasks as air-bag deployment [12,13]. Microsensor applications are not limited to inertial sensors; chemical sensing, achieved by appropriately coating the surface of microstructures, is also an active area of research [3]. The commercial potential of MEMS technology has been reviewed recently by Bryzek [14].

1.2. Adhesion and friction

Given the large surface area-to-volume ratio of surface microstructures, they are particularly vulnerable to adhesion to the substrate or adjacent microstructures during the release process or later,
during use [15–17]. This phenomenon is more generally called *stiction* since in these microdevices one is often dealing with a restoring force that has a tangential as well as a vertical component. Since microactuators have surfaces in normal or sliding contact, friction and wear are also important issues [18]. Surface modifications are needed to reduce adhesion and friction in micromechanical structures. MEMS fabrication processes pose stringent constraints on surface coatings. The coatings must be compatible not only with the surface microstructure fabrication and release process (vide infra), but also with the back-end processes of wafer dicing, die attachment, and final hermetic encapsulation. Major consideration must be given to the temperatures required for die attachment and hermetic encapsulation typically in the range 350–425°C. The final ambient in the package can be an inert gas or vacuum.

These examples point to the importance of understanding the surface properties of the materials used in MEMS technology, and of manipulating, at the atomic level, the interfacial forces which are responsible for stiction in microdevices. Although engineers have worked around the problem of stiction for some time with mixed success, systematic and fundamental studies have begun relatively recently. Research has progressed enough, however, that one feels confident that good solutions are at hand. At the same time, interesting new scientific and technological problems have been uncovered, which undoubtedly warrant further research. The goal of the present review is twofold. First, I review various recent advances in surface processes for reducing release-related and in-use adhesion in MEMS. Second, I review various ultrahigh vacuum studies which aim to understand the successes and limitations of those technological advances in light of the results of experiments performed on well-characterized surfaces.
2. Polysilicon surface treatments for adhesion reduction

2.1. Background

The adhesion of the microstructure to adjacent surfaces can occur either during the final steps of the micromachining process (release adhesion) or after packaging of the device, due to overrange input signals or electromechanical instability (in-use adhesion) [15–17]. The distinction between the two classes is useful, since the causes and strategies for eliminating or minimizing adhesion differ between them.

In surface micromachining, microstructures are fabricated on a silicon substrate by deposition and selective etching of multiple layers of structural and sacrificial films [5,6]. Polysilicon is the most commonly used structural material, and phosphosilicate glass (PSG) or low-temperature silicon oxide (LTO) are chosen for the sacrificial spacer layer. The final step in the surface micromachining process is the removal of the sacrificial layer. It requires wet etching in hydrofluoric acid, since HF attacks PSG or LTO much more rapidly than it attacks polysilicon. After the etch is complete, the structure is rinsed in deionized water to remove the etchant and etch products. Either during the water rinse or upon subsequent exposure to air, a layer of oxide is formed on the surface of silicon, with hydroxyl groups residing on the surface and in the oxide film. The oxide layer is typically 5–30 Å thick and has a high surface energy due to the hydroxyl groups [19]. Such hydrophilic surfaces exhibit strong capillary forces as the microstructures are pulled out of water or as they come in contact with air.

2.1.1. Release adhesion

Let us consider the situation where the microstructures are pulled out of water (release stiction). Underneath the microstructures, the liquid meniscus creates a Laplace pressure given by

\[ P_L = \gamma_l \left( \frac{1}{r_1} + \frac{1}{r_2} \right). \]

The liquid surface tension is denoted by \( \gamma_l \), and the two radii of curvature of the liquid surface are denoted by \( r_1 \) (parallel to the surface normal of the substrate) and \( r_2 \) (in the plane of the substrate) [20,21]. In micromechanical structures, lateral dimensions are typically much larger than the vertical spacings, \( r_2 \gg r_1 \). Thus, Eq. (1) reduces to

\[ P_L = \frac{2\gamma_l \cos \theta}{d}, \]

where \( \theta \) is the contact angle of the liquid on the solid surface, and \( d \) is the separation distance between the two surfaces, equal to \( 2r_1 \cos \theta \). On hydrophilic surfaces, such as the native oxide of silicon, where \( \theta < 25^\circ \), the meniscus shape will be concave underneath a structure (Fig. 3(a)). The attractive capillary force is sufficiently strong to pull the compliant structures into contact (Fig. 3(b)). Hence, the microstructures adhere to the substrate or to the adjacent surfaces following the drying process.

A number of drying techniques have been developed recently, such as freeze–sublimation [22] and supercritical carbon dioxide drying [23], that completely avoid the formation of a liquid meniscus between microstructure surfaces. These new drying techniques have largely eliminated release-related adhesion and have made possible the successful release of extremely compliant microstructures [24]. However, none of these techniques addresses the problem of in-use adhesion which is discussed below.
2.1.2. In-use adhesion

Given the dimensions of micromechanical devices, many concepts based on the macroscopic engineering world must be discarded. As an illustration, a ball bearing 1 cm in diameter would experience an adhesion force to a dirty surface several orders of magnitude smaller than the force of gravity. By contrast, a bearing 1 μm in diameter experiences an adhesion force more than a million times greater than the force of gravity, because the adhesion force falls linearly with size whereas the gravitational force falls with the size cubed [25]. This means that compliant micron-sized structures adhere to their neighbors or to the surrounding surfaces, and unless adhesion is reduced, miniature machines cannot work because their parts spontaneously jump together (in-use stiction).

The causes of strong in-use adhesion can be traced to the interfacial forces existing at the dimensions of microstructures. These include capillary, electrostatic, and van der Waals forces [15–17]. In Fig. 4, an estimate is provided for each of these interactions across a 1 μm² area of two perfectly flat and parallel surfaces of silicon. For capillary force, 45% relative humidity is assumed. For electrostatic attraction, 1 V potential difference is assumed since the work function difference for silicon yields at most 1 V potential difference in equilibrium. Given the dimensions of most microdevices, gravity and other body forces are weaker by many orders of magnitude than the forces mentioned above, and do not play a significant role. In comparison, the restoring pull-off force varies between 10 and 10⁻³ μN for spring-suspended microstructures that are deflected by 1 μm. The cause of strong adhesion is the attractive forces present at these dimensions, which are significantly greater than the available restoring forces in many microdevices.

It can be seen from Fig. 4 that capillary forces dominate at close separation range, and are thus the major contributor to the attractive forces present between two hydrophilic surfaces such as silicon with their native oxide layers. In addition, it should be noted that the magnitudes of both van der Waals and electrostatic forces become significant when the two surfaces are near contact. Therefore, all these forces must be manipulated if the adhesion force is to be reduced below the spring restoring force. An
effective treatment for these microstructures must provide a stable hydrophobic surface in order to avoid the formation of water layers on the surface, thereby eliminating capillary forces altogether. The removal of the hydrophilic hydroxyl groups from the surface will also eliminate the possibility for hydrogen bonding as the two surfaces come in contact. To minimize electrostatic attraction, the two surfaces should be conductive, allowing charge dissipation to occur effectively. Finally, a reduction in the effective contact area is necessary to further reduce the overall adhesion forces in microdevices.

The polycrystalline silicon surfaces used in micromechanical devices are often rough. This affects, in some cases quite significantly (vide infra), the magnitudes of the adhesion forces. Several models have been proposed to predict the effect of roughness on adhesion between two surfaces. These treatments have considered Hertzian, Johnson–Kendal–Roberts, and Deryagin–Muller–Taporov contacts, and have been reviewed and extended most recently by Maugis [26]. In general, these theories predict adhesive forces by taking into account the repulsive forces due to elastic deformation, the attractive forces due to surface interactions in and/or near the region of contact, and by assuming a Gaussian asperity-height profile. In some cases, usually dealing with soft materials, these theories have been used successfully to predict the measured pull-off forces of bodies in contact [27,28], which experimental observations show can often decrease by several orders of magnitude when surface roughness is present [28,29]. However,
the polysilicon structural material used in many micromachined devices is extremely stiff and exhibits essentially no deformation upon contact. Furthermore, since these devices often operate at or near zero applied load, there may well be only very few actual contact points, and the interactions between parts of the surfaces nearly in contact may be comparable to or even larger than the interactions at the actual contact points. Since existing theories neglect the interactions between parts of the surfaces which are close to contact, but not in contact with each other, they may not reliably predict the adhesion properties of polysilicon microstructures. Further investigations and modeling of surface roughness under these extreme situations would be highly desirable.

2.2. Test microstructures: the cantilever beam array technique

A number of experimental techniques have been developed specifically to examine the surface-surface interactions involved in silicon microstructures. Here, I review the cantilever beam array technique, which has been widely used to quantify adhesion between two microstructures, and has been used in conjunction with traditional surface science tools to study the effect of various surface passivating treatments. For a review of the principles and operation of other test microstructures, see Refs. [15–17].

To investigate adhesion properties of microstructures, Mastrangelo and Hsu [30] have developed a technique which enables measurement of the work of adhesion between surfaces, defined as the energy needed to separate unit areas of two adhering surfaces. The technique utilizes an array of micromachined beams, referred to as a cantilever beam array (CBA), anchored to the substrate at one end and with different lengths parallel to the surface. A SEM picture of a CBA is shown in Fig. 5(a), and a schematic side-view of a single cantilever beam is shown in Fig. 5(b).

To measure the work of adhesion, the beams are brought into contact with the underlying substrate; in practice this may be achieved in a number of ways (vide infra). Once the beams make contact with the underlying substrate, the applied actuation force is removed, and the beams will begin to peel themselves off the surface. For beams shorter than a characteristic length, their stiffness will be sufficient to free them completely from the underlying surface. Beams longer than this characteristic length, however, will remain adhered to the surface. Thus, the value of this characteristic length, termed the detachment length, $l_d$, is measured as the beam length at which the beams exhibit a transition from adhered to free standing. Based on this definition, the beams at the transition region are adhered to the substrate only at their tips, and by balancing the elastic energy stored within the beam and the beam-substrate interfacial energy, the work of adhesion, $W$, between the two surfaces can be calculated using the following equation [30]:

$$W = \frac{3 E h^3 t}{8 l_d^3},$$  

where $E$ is Young's modulus ($\sim$170 GPa for polysilicon), $h$ is the spacing between the beam and the substrate, and $t$ is the thickness of the polysilicon beams. The equation takes into account the shear deformation of the tip of the beam. If the two contacting surfaces are perfectly flat and indistinguishable, then the measured work of adhesion will be twice the surface energy of the individual surfaces [21]. However, as has been shown, the polysilicon surfaces used in micromachining are rough, and hence, the CBA method will yield only the apparent work of adhesion.

Several actuation methods have been employed. Mastrangelo and Hsu [30] used the large liquid capillary force during the microstructure drying to pull the beams in contact with the surface. After
drying, transition from stuck to unstuck beams determined the detachment length. The difficulty with this approach is the long exposure to water during the drying process which is known to change the chemistry of the surface and hence its mechanical properties. Houston et al. instead first released the microstructures, either by employing the supercritical CO$_2$ drying technique [31,32], or by coating the surfaces with hydrophobic self-assembled monolayers [33] so that no capillary force developed as the structures were pulled out of water. After successful release of the beams, either a sharp tungsten probe tip (typical radius of curvature 1 μm) was employed to bring the beams in contact with the surface, or the beams were brought in contact with the underlying substrate by applying a voltage between the beams and the actuation pad on the substrate (Fig. 5).

The rough nature of the micromachined polysilicon surfaces has been reported to cause a statistical variation in the effective contact area from beam to beam, which in turn leads to a statistical variation in the value of the detachment length [32]. For this reason, for each surface treatment, several sets of cantilever beam arrays need to be probed to obtain statistically significant behavior. Then, to each beam length can be associated a sticking probability, $S(l)$, defined as the ratio of the number of beams of length $l$ which remained adhered to the substrate after contact to the total number of beams of length $l$.
actuated. An “average” detachment is then determined using the following equation:

$$\bar{\ell}_d = \int_0^\infty (1 - S(l)) \, dl \approx \sum_{i=0}^{l_{\text{max}}} [1 - S(l_i)] \Delta l,$$

where $l_{\text{max}}$ corresponds to the beam length above which unity sticking probability was obtained and $\Delta l$ corresponds to the incremental increase in the beam length employed in the CBA design. Similarly, the average work of adhesion can be calculated using the equation:

$$\overline{W} = \frac{3}{2} Eh^2 r^3 \int_0^\infty \frac{S(l)}{l^5} \, dl \approx \frac{3}{2} Eh^2 r^3 \left[ \sum_{i=0}^{l_{\text{max}}} \frac{S(l_i)}{l_i^5} \Delta l + \frac{1}{4l_{\text{max}}^4} \right],$$

where the other constants are defined as in Eq. (3).

2.3. Hydrogen-terminating treatments

Hydrogen-terminated surfaces have been utilized for several years in the integrated circuit industry, where they have been used to obtain low-temperature epitaxial films, and low-defect gate oxides. These applications rely on hydrogen to passivate the silicon surface by saturating the dangling bonds and still allow access to the underlying crystalline substrate for the subsequent growth of films. There are several ways of achieving a hydrogen-terminated surface [34]. HF is known to etch silicon dioxide down to the Si/SiO₂ interface, at which point the etch rate becomes negligible. At the surface of the bulk silicon, this treatment results in a predominantly hydrogen-terminated surface, with a roughness determined largely by the quality of the initial interface between the Si and the SiO₂ film. Since the Si–H bond is less polar than a –OH termination, the hydrogen-terminated surfaces have been found to exhibit some degree of hydrophobicity, with water contact angles ranging from 60° to 75° [32,35].

More recently, it has been found that by etching in higher pH solutions such as saturated (40% in water) ammonium fluoride (pH of about 7.8), the oxygen and carbon contamination levels on the surface decrease significantly [34–38]. This treatment leads to a more complete hydrogen termination of the silicon surface, and hence, a more hydrophobic surface with water contact angles of about 85° on Si(1 0 0) [35]. In addition, the NH₄F solution continues to etch into silicon after the surface oxide is removed. The etch rate depends on the crystallographic directions. On Si(1 1 1), this treatment produces atomically flat domains thousands of ångströms in size. On Si(1 0 0), the etching yields atomically flat (1 0 0) terraces intermixed with (1 1 1) protrusions that are tens of nanometers high. Hence, a rougher topography results in comparison to the original surface. A similar roughening effect has been observed on polysilicon surfaces following etching in NH₄F [32].

2.3.1. Microstructure surface treatment

Surface treatment of microstructures using HF is a natural choice since the release process uses hydrofluoric acid to etch the sacrificial layer as one of the final steps in the micromachine fabrication process. Mastrangelo and Hsu [30] examined the effects of two surface treatments; one involved etching away the sacrificial layer in a concentrated (49% in water) HF bath to release the beams followed by thorough rinsing in water. Since HF is known to produce a hydrogen-terminated hydrophobic surface, this treatment was called hydrophobic. The sample was then pulled out of the rinse
solution and left to dry. On the second treatment, after etching the sacrificial layer in HF and rinsing in water, the wafer was immersed in H$_2$SO$_3$ : H$_2$O$_2$ for 20 min and rinsed thoroughly in water to render these surfaces hydrophilic, and then left to dry. For both treatments, a similar value of the work of adhesion of about 140 mJ/m$^2$ was obtained, which is nearly twice the surface tension of water (73 mJ/m$^2$), suggesting the presence of a layer of hydrophilic oxide on both samples. This is consistent with the fact that the hydrogen-terminated surfaces produced by HF quickly reoxidize in water [35], and hence, to study the effect of such treatments, contact with water should be minimized.

To minimize contact with water following the etching step, Houston et al. [31,32] have combined the HF and NH$_4$F hydrogen-terminating treatments with a methanol rinse followed by a supercritical carbon dioxide drying. In this way, a large reduction in the work of adhesion was observed. In particular, the four treatments listed in Table 2 were investigated. The most basic of these, Treatment I, simply uses the dilute HF etching solution to hydrogen-terminate the polysilicon microstructure surfaces. Treatment II utilizes NH$_4$F to both roughen and hydrogen-terminate the surface. Treatments III and IV are identical to I and II, respectively, except that a H$_2$O$_2$ oxidation step has been inserted in order to produce surfaces with an oxide passivation instead of a hydrogen termination. Treatment III was the conventional release process [39].

2.3.2. Surface characterization

Atomic force microscopy (AFM) was employed to image the surfaces following the four aforementioned treatments [32]. A representative AFM image of the HF-treated polysilicon surfaces (Treatment I) is shown in Fig. 6. This image is from the ground-plane polysilicon underneath the beam landing area. A similar roughness was obtained for the underside of the cantilever beams. Given the wet chemistry of the HF solution (little or no etching of bulk silicon), the image is expected to reflect the original surface topography of the polysilicon following the fabrication process. The AFM results show that the as-deposited polysilicon is quite rough, and the topographies of the two surfaces coming into contact are approximately equivalent, with rms values of 12 and 14 nm for the surfaces of ground-plane and structural layers, respectively.

<table>
<thead>
<tr>
<th>Step</th>
<th>Treatment I</th>
<th>Treatment II</th>
<th>Treatment III</th>
<th>Treatment IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dilute HF, 10 min</td>
<td>Dilute HF, 10 min</td>
<td>Dilute HF, 10 min</td>
<td>Dilute HF, 10 min</td>
</tr>
<tr>
<td>2</td>
<td>4 : 1 MeOH : H$_2$O rinse, 6 min</td>
<td>40% NH$_4$F etch, 6 min</td>
<td>H$_2$O rinse, soak, 10 min</td>
<td>40% NH$_4$F etch, 6 min</td>
</tr>
<tr>
<td>3</td>
<td>MeOH rinse, 6 min</td>
<td>4 : 1 MeOH : H$_2$O rinse, 6 min</td>
<td>H$_2$O$_2$ soak, 15 min</td>
<td>H$_2$O rinse, soak, 10 min</td>
</tr>
<tr>
<td>4</td>
<td>Supercritical CO$_2$ dry</td>
<td>MeOH rinse, 6 min</td>
<td>H$_2$O rinse, soak, 10 min</td>
<td>H$_2$O$_2$ soak, 15 min</td>
</tr>
<tr>
<td>5</td>
<td>Supercritical CO$_2$ dry</td>
<td>Supercritical CO$_2$ dry</td>
<td>MeOH rinse, 6 min</td>
<td>H$_2$O rinse, soak, 10 min</td>
</tr>
<tr>
<td>6</td>
<td>Supercritical CO$_2$ dry</td>
<td>Supercritical CO$_2$ dry</td>
<td>Supercritical CO$_2$ dry</td>
<td>MeOH rinse, 6 min</td>
</tr>
<tr>
<td>7</td>
<td>Supercritical CO$_2$ dry</td>
<td>Supercritical CO$_2$ dry</td>
<td>Supercritical CO$_2$ dry</td>
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</tr>
</tbody>
</table>

All treatments include the release of the polysilicon microstructures using a dilute HF etch of the sacrificial PSG layer as the first step. After producing the chemical passivation and surface topographies of interest, all structures were dried using the supercritical CO$_2$ drying technique in the last step.
The release process involving NH$_4$F (Treatment II) results in a hydrogen-terminated surface with a rougher topography than the original polysilicon since NH$_4$F roughens the surface due to its direction-dependent etch rate. Fig. 7 shows the substantial roughening caused by the NH$_4$F etching of the ground-plane layer. The AFM results show that the topographies of the two surfaces coming into contact are similar, with rms values of 38 and 40 nm for the surfaces of the ground-plane and the structural layers, respectively.

The release treatment involving the H$_2$O$_2$ oxidizing step following etching in HF (Treatment III) results in a hydrophilic oxidized surface with essentially the same topography as the original polysilicon, since only a thin chemical oxide (5–15 Å) is produced on the pristine surface [34,40] by this treatment. This was confirmed by AFM. The same observation holds for the fourth treatment where the hydrogen-terminated, roughened surface produced by NH$_4$F was then oxidized chemically with H$_2$O$_2$.

The authors have employed X-ray photoelectron spectroscopy (XPS) to determine the chemical composition of the surfaces thus obtained [32]. Broad scans showing the chemical species present in the near-surface region after each treatment are shown in Fig. 8. All surfaces exhibit the presence of oxygen (530 eV), carbon (286 eV), and silicon (99 eV). As expected, the oxidized surfaces have more oxygen in the near-surface region. The amount of carbon on the surfaces remains roughly constant for all treatments and is attributed to contamination. High resolution scans for the Si 2p regions of the spectra are shown in Fig. 9, where the emergence of a chemically shifted Si 2p peak at approximately
102 eV is apparent. This new peak can be attributed to silicon present in a silicon dioxide matrix, based on which the oxide layer thickness can be estimated for each of the surfaces. The data, shown in Table 3, indicate the presence of an oxide layer approximately 10–15 Å thick on the hydrophilic oxidized surfaces, and 2–4 Å thick on the hydrophobic samples. The presence of oxide after the HF or NH₄F etching treatments is attributed to the additional steps required for the integration of these treatments into the fabrication process (Table 2) as well as the fact that polysilicon, due to the presence of high energy binding sites such as defects, oxidizes more rapidly than the Si(100) surface [32].

To quantify the hydrophobicity of the HF-, NH₄F-, and H₂O₂-treated polysilicon surfaces, water contact angles were measured on each of the four surfaces (see Table 3). In general, all hydrophilic surfaces were found to be wetting with water (contact angle ≈ 0°), whereas the hydrophobic surfaces displayed finite contact angles (75–85°). These contact angles were typically lower than those reported on Si(1 0 0) subjected to the same treatments [32], possibly due to the difference in surface roughness and/or chemical composition.

2.3.3. Measurement of the work of adhesion

Cantilever beam arrays were employed to quantify the work of adhesion of the polysilicon surfaces following Treatments I–IV. The beams were 10 μm wide, 2.2 μm thick, 2 μm above the surface, and their lengths varied from 50 to 260 μm in 10 μm increments, and then from 260 to 1000 μm in 20 μm increments. The determination of the work of adhesion using the CBA technique described above
Fig. 8. X-ray photoelectron survey spectra of the polysilicon surfaces after the four surface treatments listed in Table 2.

depends critically on the beams being parallel to the substrate. This becomes a major challenge when dealing with a surface treatment that leads to a significant reduction in the work of adhesion. For example, for the hydrogen-terminating treatments, detachment lengths as large as 900 µm have been observed. Fabrication of a flat beam that is a few microns thick, a few microns off the surface, and a millimeter long is a difficult task, and relies on the proper sequence of steps to insure minimal stress and strain gradients [32]. Furthermore, since the morphology and grain size, and hence the roughness, of the polysilicon can impact the surface–surface interactions, and are determined by the details of the fabrication process, caution must be taken when comparing the effectiveness of different surface treatments to ensure that the initial samples possessed the same topography, and are only varied by the surface treatments under investigation.

Representative SEM images of the actuated cantilever beam arrays following the NH₄F hydrophobic (Treatment II) and H₂O₂ hydrophilic (Treatment III) release processes are displayed in Figs. 10(a) and (b), respectively, showing typical transitions from stuck to unstuck. The sticking probability data for the four different microstructure surfaces are shown in Fig. 11, where the sticking probability is plotted as a function of the beam length. The measurements were taken under 40–50% relative humidity. For the hydrophilic samples, data were also obtained under 100% relative humidity. In this case, an average detachment length of approximately 65 µm was reported, corresponding to a work of adhesion of 140 mJ/m², which is about twice the surface energy of water. This is in good agreement with the expected value based on the picture of capillary condensation described in Section 2.1.

The average detachment length and work of adhesion can be obtained from Fig. 11 for each surface treatment using Eqs. (4) and (5), respectively. The results are tabulated in Table 4. The work of adhesion following the NH₄F treatment was determined to be about 10 μJ/m², more than three orders
Fig. 9. X-ray photoelectron spectra of the Si 2p region for the polysilicon surfaces after the four surface treatments listed in Table 2. The bottom two spectra clearly show an additional peak chemically shifted by 3–4 eV, indicating the presence of oxide-bound silicon.

Table 3
Oxide thicknesses (calculated from XPS measurements) and water contact angles on both polysilicon and Si(1 0 0) samples for each of the four release treatments listed in Table 2

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Polysilicon</th>
<th>Si(1 0 0)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxide thickness (Å)</td>
<td>Water contact angle (°)</td>
</tr>
<tr>
<td>I</td>
<td>2.4</td>
<td>86</td>
</tr>
<tr>
<td>II</td>
<td>3.3</td>
<td>76</td>
</tr>
<tr>
<td>III</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>IV</td>
<td>13</td>
<td>0</td>
</tr>
</tbody>
</table>
Fig. 10. Cantilever beam arrays released with (a) the NH$_4$F (hydrophobic) process, and (b) the conventional H$_2$O$_2$ (hydrophilic) process. The square structures to the left of the beams ends in (a) are sighting aids used to verify the position of the beam and the numbers represent the beam lengths in microns. The sighting aids have been removed in (b) for clarity.

Fig. 11. Sticking probability data for the four surface treatments, listed in Table 2, plotted as a fraction of the beams stuck versus beam length tested. The curves (a), (b), (c) and (d) correspond to Treatments I, II, III and IV, respectively. Curve (e) shows the results for beams released with Treatment III, then tested under conditions of near 100% humidity.

of magnitude weaker than that for the conventional H$_2$O$_2$ treatment for which a value of 20 mJ/m$^2$ was obtained. In contrast, the work of adhesion on the HF-treated surface was about a factor of 3 larger than that on the NH$_4$F-treated surface. Hence, it was argued that the effect of NH$_4$F-induced surface
Table 4
Average detachment lengths and the corresponding work of adhesion values for each of the four release treatments listed in Table 2

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Detachment length (μm)</th>
<th>Work of adhesion (μJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>520</td>
<td>30</td>
</tr>
<tr>
<td>II</td>
<td>680</td>
<td>10</td>
</tr>
<tr>
<td>III</td>
<td>110</td>
<td>20,000</td>
</tr>
<tr>
<td>IV</td>
<td>110</td>
<td>20,000</td>
</tr>
</tbody>
</table>

Roughening was secondary in the observed reduction in the work of adhesion compared to the conventional hydrophilic surface.

Comparing the work of adhesion for HF-treated surfaces to that following H₂O₂ treatment, a factor of 600 reduction in the work of adhesion was observed. Since the topographies are believed to be essentially identical for these two surfaces, this factor reflects mostly the effect of change in chemistry. Assuming that following the HF treatment, the contacting surfaces interact with one another via van der Waals attraction, the work of adhesion was estimated to be about 29 mJ/m², about a factor of a thousand greater than the value of 30 μJ/m² measured on the HF-treated surface.

Given the surface topography (Figs. 6 and 7), the assumption of perfectly flat surfaces used to estimate the magnitude of the van der Waals attraction is not justified, even in the case of HF-treatment which produces no further roughening beyond that originally existing on the polysilicon surfaces. To estimate the magnitude of the van der Waals attraction, the authors qualitatively took the surface roughness into account by choosing the separation at contact to be the sum of the rms values of the two contacting surfaces. This value is approximately 26 nm for the HF-treated surfaces, and 78 nm for the NH₄F-treated surfaces, and the corresponding values of the works of adhesion are 11 and 1 μJ/m², respectively. These estimates compare well to the experimentally measured values of 30 and 10 μJ/m² obtained on these surfaces.

The four surfaces examined above show that neither hydrogen termination nor rough topography was the sole reason for the large reduction observed between the hydrophobic (HF- and NH₄F-treated) surfaces, and their hydrophilic counterparts, but rather it was the combined effect of H-termination and the surface topography which produced this observed reduction.

2.3.4. Long-term stability

The stability of the hydrophobic, hydrogen-terminated silicon surfaces is important in determining the usefulness of these treatments for adhesion reduction in microstructures. Previous work investigating the stability of single-crystal Si(100) surfaces etched in both HF and NH₄F showed a metastable behavior where the hydrogen-terminated silicon surfaces began to reoxidize after 4–7 days in air [31,32,41], as judged by an increase in the rate of oxygen uptake. This was in contrast to the observation that the water contact angle remains essentially the same over the first couple of weeks of storage in air [35]. More recently, it has been shown that on the NH₄F-treated Si(100) surfaces, the oxygen uptake initially takes place by oxygen insertion in the silicon back bonds, leaving the surface Si–H bond intact [42]. This result explains why the contact angle remains constant while the XPS spectra show a growing oxygen uptake.

Along the same lines, Houston et al. [32] have monitored the oxide film thickness, water contact angle, and sticking probability on NH₄F-treated polysilicon (Treatment II in Table 2) as a function of
storage time in air. After a week of storage in air, the water contact angle decreased from 84° to 71°, indicating that the hydrogen termination of the polysilicon surfaces was less stable than that of Si(1 0 0). During this period, the detachment length was found to decline to about 600 µm. After a storage time of about a month in air, these surfaces were found to possess an oxide thickness of approximately 14 Å and a water contact angle of 57°. During this time period, the degradation of the hydrogen-terminated surface was sufficient to lower the detachment length from 680 to about 110 µm, giving sticking behavior similar to that observed on hydrophilic surfaces.

2.4. Alkyltrichlorosilane self-assembled monolayer coatings

Another approach to surface passivation involves coating of the microstructural surfaces with self-assembled monolayers (SAMs). The most extensively studied SAM coating deposited on silicon are based on octadecyltrichlorosilane (OTS) precursor molecules having a chemical formula of C_{18}H_{37}SiCl_3 [43]. The precursor molecules are dissolved into a suitable solvent such as a 4:1 hexadecane:carbon tetrachloride (CCl_4) mixture and an oxidized silicon surface is immersed in the solution. Although the detailed mechanism of film formation has not yet been fully elucidated, it is believed that the water layer, inevitably present on the hydrophilic oxidized surface, plays a crucial role [44,45]. The trichlorosilyl head groups hydrolyze and adsorb onto the water layer, where they can diffuse and react both with each other, forming Si–O–Si cross-links between chains, and with surface OH groups, resulting in a stable graft to the surface. The process of cross-linking between chains is aided by a low-temperature (∼ 100°C) anneal after film formation. When prepared correctly, a SAM-coated Si(1 0 0) oxide surface (prepared using OTS) exhibits a water contact angle of 110° ± 2°, which corresponds to a surface energy of about 20 mJ/m² [45,46]. The film thickness is about 25 Å, and the film density is approximately 5 chains per nm². This packing corresponds to ∼ 90% of the density of crystalline polyethylene, indicative of a true monolayer coverage. One remarkable property of these films is their stability after formation. Specifically, film thickness and contact angle were unchanged following storage times of up to 18 months in air. Furthermore, SAM films appear to be impervious to hot organic solvents, acidic media, and boiling water [46]. The long-term stability of these films in various ambients, coupled with their low surface-energy, hydrophobic, densely packed structure, makes self-assembled monolayers an attractive option for anti-stiction coatings in microstructures.

2.4.1. Microstructure surface treatment

Hornbeck [47] used self-assembled monolayers of perfluorinated decanoic acid as lubricants for the digital micromirror devices as early as 1987. Alley et al. [39] considered the use of alkyltrichlorosilane self-assembled monolayers for alleviating adhesion in microstructures. In particular, they examined two precursors, the OTS and the fluorinated chain C_6F_{13}CH_2SiCl_3 which were incorporated into the microstructure release process as follows. Once structures were released in HF, the polysilicon surfaces had to be reoxidized for the SAM formation to occur. This was accomplished by forming a chemical oxide using a RCA-1 (5:1:1 mixture of H_2O:H_2O_2:NH_4OH at 70°C) solution. Before immersion in the OTS solution, the bulk water had to be removed from the samples. Hence, samples were rinsed with methanol, then carbon tetrachloride prior to entering the OTS mixture. After SAM formation, the excess precursor molecules were rinsed from the surface with CCl_4, and the CCl_4 was rinsed away with methanol. An IR lamp was then used to dry the structures. They used butterfly suspension test structures to examine the effect of the SAM coating. However, despite the fact that their work showed some
promise for the OTS coating, the test structures used did not allow the quantification of their effect. For example, the same lower bound was achieved following the same release process without the OTS step. In the case of the fluorinated monolayer, the authors reported that the surfaces coated with this monolayer did not perform as well when compared to OTS. More recently, excellent results have been obtained with the fluorinated monolayer as will be discussed in Section 2.5. The discrepancy may be attributed to the fact that the fluorinated SAMs require an inert ambient to prevent bulk polymerization caused by their highly water-sensitive headgroups.

Further work involving SAM films by Deng et al. [48] showed a marked improvement in the release and wear properties of polysilicon flange-bearing micromotors. In the case of alkylsiloxane monolayers, the authors examined the effect of chain length, and found that C_{18} monolayer (OTS) produced the most desirable results, in terms of stability of rotor speed, minimum operating voltage, and wear.

2.4.2. Measurement of release and in-use adhesion

Houston et al. [33] demonstrated that the SAM coating is effective at reducing adhesion during microstructure release. In particular, the release process developed by Alley et al. [39] was refined a step further (see Table 5). Following the last rinse iso-propanol (used instead of methanol), the microstructures were then rinsed in water. At this stage, the structures were pulled directly out of the water, where they emerged released and completely dry. The structures required no further drying because water dewetted the SAM-coated surfaces immediately as the structures came out of the water. This release technique was used to successfully release cantilever beam arrays containing beams up to 1 mm long, as pictured in Fig. 12. The success of the SAM treatment was argued to result from the extremely hydrophobic nature of the coated surfaces, with water contact angle of \(~ 114^\circ\) present on these polysilicon surfaces. As discussed in Section 2, as the microstructures are pulled out of water, the liquid meniscus creates a pressure, given by Eq. (2). On the hydrophilic surfaces (\(\theta < 90^\circ\)), the meniscus shape will be concave underneath a structure (Fig. 2(b)), creating an attractive capillary force.

<table>
<thead>
<tr>
<th>SAM Process Sequence</th>
<th>Concentrated HF</th>
<th>Approximate time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sacrificial layer etch</td>
<td></td>
<td>10 min</td>
</tr>
<tr>
<td>Surface oxidation (necessary for SAM formation)</td>
<td>H_{2}O rinse</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td>H_{2}O_{2} rinse</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td>H_{2}O rinse</td>
<td>5 min</td>
</tr>
<tr>
<td>SAM formation</td>
<td>2-Propanol rinse</td>
<td>5 min</td>
</tr>
<tr>
<td></td>
<td>Carbon tetrachloride rinse</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td>Carbon tetrachloride rinse</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td>OTS mixture</td>
<td>15 min</td>
</tr>
<tr>
<td></td>
<td>Carbon tetrachloride rinse</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td>Carbon tetrachloride rinse</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td>2-Propanol rinse</td>
<td>5 min</td>
</tr>
<tr>
<td>Rinse and dry</td>
<td>2-Propanol rinse</td>
<td>5 min</td>
</tr>
<tr>
<td></td>
<td>H_{2}O rinse</td>
<td>5 min</td>
</tr>
<tr>
<td></td>
<td>Pull structures from water</td>
<td></td>
</tr>
</tbody>
</table>

All rinses are gentle dilutions; the structures are not removed from the liquid phase until the last step.
Fig. 12. SEM of a SAM-coated cantilever beam array. Even the longest beam (1 mm) was successfully released without sublimation or supercritical drying techniques.

Fig. 13. Sticking probability data for FDTS and OTS SAM treatments as well as the conventional oxide coating for cantilever beam arrays made from (a) poly A, and (b) poly B. See Fig. 21.

which is sufficiently strong to pull the compliant structures into contact. Conversely, on a SAM-coated structure ($\theta > 90^\circ$), the water meniscus will maintain a convex curvature, giving rise to no capillary attraction between the two surfaces, and hence, no stiction during release.
After coating and releasing, the cantilever beam arrays were used to quantitate the in-use adhesion properties of SAM-coated devices. The sticking probability data are shown in Fig. 13. Following the same procedure as described in Section 2.2, the average detachment length on the OTS-coated structures was found to be about 950 μm, corresponding to a work of adhesion of 3 μJ/m², as compared to 20 000 μJ/m² for structures released with conventional H₂O₂ hydrophilic treatment. This corresponds to a reduction of nearly four orders of magnitude in the work of adhesion compared to the conventional treatment. As will be discussed in Section 2.7, in addition to surface chemical composition, surface topography also affects the magnitude of adhesion. The numbers listed here are obtained on a surface with topography similar to the AFM image shown in Fig. 6, and rms roughness of about 12 nm. The SAM treatment also compares well with the NH₄F release process for which a work of adhesion of 10 μJ/m² was obtained.

2.4.3. Thermal stability

The thermal stability of SAMs is a property of great technological interest, since most packaging processes involve steps at elevated temperatures. Fig. 14 shows the water contact angles on polysilicon OTS-coated surfaces as a function of anneal temperature. These samples were annealed in either a nitrogen, oxygen, room air, or vacuum environment. For the samples annealed in nitrogen, the contact angles remained constant to 400°C, above which the contact angle began to decrease. Annealing experiments in vacuum were carried out to mimic an actual vacuum packaging process, and SAM films remained intact up to at least 400°C (the highest attainable temperature in the apparatus used). Thus, it appears that the SAM thermal stability in vacuum or inert atmospheres is adequate for some packaging processes. Ultrahigh vacuum studies of the thermal desorption of OTS SAMs on silicon have been performed by Kluth et al. [49] and will be reviewed in depth in Section 3. Here, we note that the authors report that the hydrocarbon SAM is stable up to 470°C in vacuum, at which temperature C–C

![Water contact angle versus annealing temperature for SAM-coated polysilicon surface under different ambients.](image-url)
Table 6
Sacrificial layer etch, SAM formation, and quick-dry release process for FDTS-coated polysilicon microstructures

<table>
<thead>
<tr>
<th>SAM Process Sequence</th>
<th>Concentrated HF</th>
<th>Approximate time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sacrificial layer etch</td>
<td></td>
<td>10 min</td>
</tr>
<tr>
<td>Surface oxidation (necessary for SAM formation)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O rinse</td>
<td></td>
<td>10 min</td>
</tr>
<tr>
<td>H₂O₂ rinse</td>
<td></td>
<td>15 min</td>
</tr>
<tr>
<td>H₂O rinse</td>
<td></td>
<td>5 min</td>
</tr>
<tr>
<td>2-Propanol rinse</td>
<td></td>
<td>5 min</td>
</tr>
<tr>
<td>Iso-octane rinse</td>
<td></td>
<td>5 min</td>
</tr>
<tr>
<td>Iso-octane rinse</td>
<td></td>
<td>5 min</td>
</tr>
<tr>
<td>FDTS mixture</td>
<td></td>
<td>10 min in N₂ drybox</td>
</tr>
<tr>
<td>2-Propanol rinse</td>
<td></td>
<td>5 min</td>
</tr>
<tr>
<td>2-Propanol rinse</td>
<td></td>
<td>5 min</td>
</tr>
</tbody>
</table>

Rinse and dry

<table>
<thead>
<tr>
<th>Rinse and dry</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Propanol rinse</td>
<td></td>
<td>5 min</td>
</tr>
<tr>
<td>H₂O rinse</td>
<td></td>
<td>5 min</td>
</tr>
<tr>
<td>Pull structures from water</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All rinses are gentle dilutions; the structures are not removed from the liquid until the last step.

Table 7
Contact angle data for SAM coated polysilicon

<table>
<thead>
<tr>
<th>SAM coating</th>
<th>Water (°)</th>
<th>Hexadecane (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTS</td>
<td>112</td>
<td>38</td>
</tr>
<tr>
<td>FDTS</td>
<td>115</td>
<td>68</td>
</tr>
</tbody>
</table>

bond cleavage begins. The film stability is much lower when annealed in oxygen or air, as shown in Fig. 14, indicating a mechanism for chemical reaction at elevated temperatures in oxygen-containing environments. These results appear to be consistent with literature reports of film stability in inert atmospheres up to around 450°C [50] and film stability in air up to at least 140°C [51].

2.5. Fluorinated alkyltrichlorosilane self-assembled monolayer coatings

One drawback of the SAM coating process described above is that it uses chlorinated solvents, such as CCl₄ which is banned from industrial use under the Montreal protocol. An alternative process has been developed, which produces fluorinated SAM coatings and does not use chlorinated solvents [52,53].

2.5.1. Microstructure surface treatment

The fluorinated SAM solution consisted of 1 mM solution of 1H,1H,2H,2H-perfluorodecyltrichlorosilane (CF₃(CF₂)₇(CH₂)₂SiCl₃, FDTS) in iso-octane, and was mixed and used in a N₂-filled drybox to prevent bulk polymerization caused by its highly water-sensitive headgroup. The details may be found in Table 6.

The contact angle data for OTS and FDTS SAM-coated polysilicon given in Table 7 confirm that well-packed monolayers were formed in both cases [43]. When a polar solvent such as water is used as
the test liquid, the contact angle is primarily affected by the surface polarity. Here, both SAMs are almost equally non-polar so the water contact angles are similar. On the other hand, when the test liquid is non-polar, as with hexadecane, the contact angle reflects the van der Waals attractions to the surface. Since the C–F bond has a lower polarizability than C–H, a perfluorinated surface is less susceptible to induced dipole attractions than its hydrogenated counterpart [54]. Thus, the hexadecane contact angle on the FDTS SAM was found to be higher.

2.5.2. Measurement of release and in-use adhesion

Due to the highly hydrophobic nature of the FDTS SAMs, the coated microstructures emerge from the final water wash completely dry [52,53]. 98% of the beams up to 1 mm in length and approximately 90–95% of those between 1 and 2 mm long were released successfully. An optical micrograph of flat released beams 1–1.5 mm long is shown in Fig. 15; note that only two light colored beams in the array are stuck to the substrate.

Upon electrostatic actuation to contact the underlying substrate, all beams out to the maximum length of 1 mm remained unstuck, as shown in Fig. 13. Thus, the fluorinated SAM films reduce adhesion below the measurement capabilities of this set of test structures, with the apparent work of adhesion less than 2.4 μJ/m² (with \( h = 2.0 \) mm and \( t = 2.2 \) mm). This value is more than four orders of magnitude lower than that of the SiO₂ coating, a reduction mainly caused by the elimination of water capillary attractions. The adhesional energy between the SAM-coated surfaces is ideally due to van der Waals attractions, so the lower polarizability of perfluorinated surfaces versus hydrogenated ones may be responsible for the difference in the in-use stiction behavior of the two SAM coatings. Furthermore, in these measurements, the rms roughness was about 12 nm as depicted in the AFM image of Fig. 6. As will be discussed in Section 2.7, surface topography also affects the adhesion values.
2.5.3. Thermal stability

With regard to long-term stability, all FDTS-coated beams remained unstuck following actuation after four months of storage in room air. With regard to thermal stability, using contact angle measurements, it was found that the FDTS films survive heat treatment at 400°C in air (Fig. 16) while the OTS coatings degrade in air above 100°C [52,53]. Suction tests on FDTS-treated beam arrays confirmed this stability; tests on arrays heated to 400°C in air and 500°C in N₂ resulted in the same behavior after actuation as unheated FDTS-coated controls. When arrays were heated to 550°C in N₂ and tested immediately, beams longer than 800 μm adhered to the substrate. After a day of storage in room air, the transition length decreased to 400 μm, indicating further degradation.

Ultrahigh vacuum studies on FDTS SAMs reveal a similar desorption mechanism as OTS SAM, i.e., desorption through C–C bond breakage [55]. In air, the thermal stability of fluorinated SAMs is considerably better than that of the corresponding hydrocarbons. A common path for hydrocarbon decomposition in the presence of water is through water attack and dehydrogenation. While perfluorocarbons are also thermodynamically vulnerable to hydrolysis, they are essentially inert in air until heated to a temperature around 500°C. This can be explained kinetically by a high activation energy for hydrolysis and the difficult-to-polarize fluorines which shield the carbon skeleton. In contrast to hydrocarbons, fluorocarbons usually cleave at the C–C bond leaving the strong C–F bond intact [54]. The oxygen in air may also play a role in the observed thermal behavior. The fluorinated SAMs survive heat treatment in both air and N₂ at 400°C for 5 min and are thus compatible with several MEMS packaging processes.

2.6. Fluorocarbon films

In another approach recently introduced, Man et al. [56] have shown that fluorocarbon (FC) films formed by a plasma polymerization reaction are promising in reducing post-release adhesion. In a
plasma, the ionized species are accelerated towards the surface, resulting in a highly directional ion impingement which may result in etching or polymerization depending on the gas stoichiometry and composition. However, the highly directional ion impingement coupled with the short diffusion length of the plasma, results mostly in a line of sight growth. For an anti-adhesion coating to be effective, the active species must penetrate underneath the microstructure. The plasma, in addition to ionized species, also generates excited neutral and radical species. Unlike ions, the diffusion of the neutral species inside cracks is substantial, yielding a relatively conformal growth. The authors used the field-free zone of a plasma reactor to produce a relatively conformal polymerized fluorocarbon film growth. To determine the uniformity of the FC film on undercut, a set of 135 × 135 and 200 × 200 μm², 3.3 μm thick polysilicon plates with a 3 μm gap height were employed. After the film deposition, the plates were peeled off and contact angle analysis was employed to determine the degree of growth underneath the microstructure. These experiments confirmed the presence of FC film on the surface of 100 μm undercut with water contact angle of 110°. Cantilever beams were used to examine the effectiveness of the coating. Even after immersion of the structure in water, 230 μm long beams remained free. Using Eq. (3), this yields the work of adhesion value of about 7000 μJ/m².

The samples were also subjected to accelerated aging tests which consisted of heating of the coated sample and monitoring the water contact angle. The FC films were found to withstand temperatures up to 400°C. To determine the wear under periodic contact, a periodic potential was applied between the beam and the substrate to cause the beam to collapse. It was found that 20 nm thick films withstood 10⁸ collapse cycles without any noticeable degradation. These results indicate that the FC films are an excellent candidate for adhesion reduction in microdevices.

Utilizing the field-free zone of a plasma reactor to produce a conformal fluorocarbon film distinguishes this work from an earlier effort [57] whereby small holes were made through a membrane. A plasma polymerized fluorocarbon film was then deposited such that the ionized molecules would hit the surface at angles between 70° and 90°. Thus, below the holes of the membranes, small bumps were formed with diameters slightly larger than the holes. In this way, when the membrane was deflected towards the substrate, the contact would occur at the edges of the holes, thereby reducing adhesion.

2.7. Surface topographic modifications

The topography of the contacting surfaces is critical to adhesion and friction at the microscale [15,16,58]. Surface texture determines the real area of contact which, in lightly loaded MEMS, may be a very small fraction of the apparent area.

2.7.1. SiO₂ surfaces

Alley et al. [59] have used texture etch back techniques to obtain rough oxidized polysilicon surfaces. The authors have observed that the microstructures’ surfaces formed by deposition and etch processes that are random on the nanoscopic scale, are typically bifractal. That is, their roughness exhibits a power-law scale dependence in two distinct regimes, corresponding to the inter- and intra-grain roughness of the material. This behavior is shown in Fig. 17 by plotting the structure function, S(r), defined as

\[ S(r) = \langle [z(x+\tau, y) - z(x, y)]^2 \rangle, \]  

(6)
where the surface topography is in the form of a surface height array, \( z(x, y) \), and the bracket indicates an average over one data array, \( z(x, y) \). To study adhesion between rigid bodies, a method based on the moments of the surface height distribution, \( p(z) \), was employed. More specifically, to describe the surface topography, the authors used the variance, \( \sigma^2 \),

\[
\sigma^2 = \int_{-\infty}^{\infty} p(z) [z - \bar{z}]^2 \, dz,
\]

the reduced skewness, \( Sk \),

\[
Sk = \frac{1}{\sigma^3} \int_{-\infty}^{\infty} p(z) [z - \bar{z}]^3 \, dz,
\]

and the reduced kurtosis, \( K \),

\[
K = \frac{1}{\sigma^4} \int_{-\infty}^{\infty} p(z) [z - \bar{z}]^4 \, dz,
\]

where \( \bar{z} \) is the mean plane of the surface. The physical significance of the last two quantities is shown in Fig. 18. It was argued that a low-adhesion surface should be very rough (i.e., large \( \sigma^2 \)) with narrow asperities minimizing the real contact area (i.e., \( Sk > 0 \), and \( K > 3 \)).

Alley et al. [59] textured the polysilicon surfaces in the following manner. After depositing a 100 nm layer of thermal SiO\(_2\) on a Si(100) wafer, a 960 nm layer of undoped polysilicon was deposited at 630°C by LPCVD which produced films with large columnar grains and a relatively rough top surface.
Then the wafer underwent an 800°C thermal oxidation for 30, 60 and 120 min. These times correspond to 20, 35 and 65 nm thermal oxides on Si(1 0 0) and somewhat thicker layers on polysilicon surfaces. The SiO₂-covered polysilicon was then textured by plasma etching using CCl₄/He/O₂ chemistry. Two types of texturing effects were observed. Since the SiO₂ layer was removed nonuniformly, the polysilicon was exposed more quickly in some spots than others. The high polysilicon-to-oxide selectivity then exaggerated the existing nonuniformity. In some places where steep-angled sidewalls had formed, unsaturated Si–Cl species were deposited and reacted with oxygen in the etch to form passivation material more quickly than it could be removed, shielding larger pyramid-shaped asperities and preventing their etching.

The evolution of surface parameters versus polysilicon exposure time and the textured SiO₂ thickness was monitored by AFM; the results are shown in Fig. 19. The untextured polysilicon surface is much smoother, and exhibits a small skewness and a kurtosis of 3. The variance of the textured surface is determined in the initial stages of the etch by microscale nonuniformity in removing the textured SiO₂ layer, since it changes little during the latter part of the etch. The skewness and kurtosis are more affected by the isolated, slow etching asperities which emerge further from the background polysilicon as the etch progresses. To examine the effect of texturing on adhesion characteristics of microdevices, cantilever beam array test structures were fabricated, incorporating as the ground plane, a smooth Si(1 0 0), an untextured polysilicon, and three degrees of texturing with 35 nm texture SiO₂ layer. The beams were 1.7 μm thick, and 2.1 μm off the surface. The structures were released using concentrated HF etch, followed by rinsing in water. A layer of chemical oxide was then formed on the surface using an RCA SC-1 (6:1:1 H₂O:NH₄OH:H₂O₂ at 80°C) treatment. This step was followed by rinsing in water, and the surface tension of water was used to pull the beams down in contact with the substrate. After drying with an IR lamp, the detachment lengths were measured. The results of the comparison are shown in Fig. 20, plotted as the critical cantilever stiffness below
which the cantilever is stuck to the substrate. Indeed, texturing has led to a reduction in microstructure adhesion. Over a factor of 10 reduction is observed between Si(100) and the untextured polysilicon surfaces, and about a factor of 5 reduction between the untextured and the roughest polysilicon surface examined.

Yee et al. [60] used a different approach for surface roughening. When polysilicon is heavily doped with phosphorus, phosphorus segregates preferentially to grain boundaries at elevated temperatures. Oxidizing a heavily doped ($\sim 10^{20}$ cm$^{-3}$) polysilicon results in a thicker oxide formation at grain boundaries due to phosphorus-enhanced oxidation of polysilicon. The thicker oxide at grain boundaries was then used as a mask for etching the polysilicon. While the thicker oxide at the vicinity of the grain boundaries remains (preventing etching of the polysilicon underneath), the oxide over the grains is etched away, allowing the polysilicon layer beneath it to etch. The net result is an enhanced roughening of polysilicon. The authors used the CBA technique to quantify the effect of this treatment on adhesion characteristics of microdevices. For samples with deepest grain holes which were estimated using SEM to be about 300 nm, the detachment length was twice as large as that obtained without any
roughening treatments. This corresponded to nearly a factor of 20 reduction in the work of adhesion based on Eq. (3).

2.7.2. Self-assembled monolayer coated surfaces

Srinivasan et al. [52,53] have studied the effect of roughness on the work of adhesion. The CBA technique was employed to characterize in-use stiction of OTS and FDTS-coated microstructures. AFM images from 5 × 5 μm² areas of two sets of polysilicon microstructures are shown in Fig. 21. The rms roughnesses of the surfaces are 12 and 3.2 nm for poly A and B, respectively.

Sticking probability data for FDTS and OTS SAM-coated poly A beams are shown in Fig. 13. Upon electrostatic actuation to contact the underlying substrate, the 1000 μm long beams of the FDTS-coated poly A structures did not remain stuck whereas an average detachment length of 950 μm was obtained for the OTS coating. The corresponding data for SAM-coated structures made with poly B are shown in Fig. 22. The average detachment length for the FDTS-coated beams is approximately 780 μm, in comparison to 550 μm for the OTS treatment. Work of adhesion values were calculated (h = 2.1 μm and t = 1.9 μm) as 5.2 and 23 μJ/m² for FDTS and OTS SAMs, respectively. The authors argue that the differences in W between SAM-coated poly A and poly B can be attributed to their different topographies.

2.8. Implications for surface science

The aforementioned treatments for micromachining applications have brought to the forefront several intriguing questions regarding their chemical stability in various environments. These include the stability of hydrogen-terminated treatment under ambient condition, the reactivity of self-assembled monolayers in various gaseous environments, and their thermal stability. These are
a) Poly A

b) Poly B

Fig. 21. 5 × 5 μm² AFM images of ground plane polysilicon surfaces from microstructures made with (a) poly A and (b) poly B. The plots have the same z scale, with maximum heights of 52 and 13 nm in (a) and (b), respectively.
Fig. 22. Sticking probability data for FDTS and OTS SAM treatments as well as the conventional oxide coating for cantilever beam arrays made from poly B. See Fig. 21.

interesting issues from the scientific point of view, and are crucial for the development of the next generation of coatings. In the next section, I shall present a review of our current knowledge on these surface science issues.

3. Reactivity of chemically modified silicon surfaces

3.1. Oxidation of hydrogen-terminated Si(100) surface

The production of sub-micron sized features in electronic devices requires the ability to prepare silicon surfaces that are free of contamination and passivated against chemical attack. One way of achieving such surfaces is by wet chemical etching using solutions such as hydrofluoric acid. It is well established that etching of silicon in HF results in a hydrogen-terminated surface nearly free of contaminants such as carbon and oxygen [34–38,41]. HF readily etches the oxide, while leaving the underlying silicon essentially intact. Thus, the Si–SiO₂ interface before etching determines to a large extent the quality of the resulting hydrogen-terminated surface. The (100) and (111) surfaces prepared in this manner are observed to be atomically rough. Increasing the pH of the etching solution, however, improves the morphology of Si(111) surfaces. By using ammonium fluoride with pH= 7.8, Si(111) surfaces were prepared which were atomically flat over thousands of ångströms, completely monohydride terminated, and free of contamination. This is partly due to the fact that NH₄F etches silicon more readily than does HF, thus removing the dependence on the initial Si–SiO₂ interface. The morphology of the Si(100) surface is also sensitive to pH, but remains rough for all values of pH. Because (100) surfaces are etched preferentially, the resulting surface consists of (100) terraces and pyramids with (111) facets, thus accounting for the roughness [61].

The chemical stability of hydrogen-terminated surfaces has been studied by a number of researchers. XPS and high resolution electron energy loss spectroscopy have been used to examine HF-treated surfaces exposed to both water [62] and air [41]. In each case two stages of oxidation were observed, an
initial, slow oxidation (termed an induction period) followed by a period of more rapid oxidation. It was suggested that hydroxyl groups left on the surface following a water rinse are primarily responsible for the initial oxidation. The presence of hydroxyl groups is traced to the observation that the HF etch leaves Si–F groups on the surface. These Si–F groups are replaced by Si–OH in a rapid exchange reaction during water rinsing. It was suggested that additional hydroxyl groups are added to the surface through the attack of Si–H bonds. These reactions constitute the initial, slow oxidation period. As the hydroxyl coverage increases, it is thought that a condensation reaction between adjacent Si–OH groups leads to the formation of Si–O–Si groups. These oxide groups result in strain in the lattice, which is argued to be responsible for the onset of the second, more rapid stage of oxidation. The oxidation rate in this second region was observed to be logarithmic. The effect of air exposure on HF-treated surfaces was also studied using infrared (IR) spectroscopy [63]. There, it was suggested that water in air reacts with the Si–H bond to give Si–OH species, which then react with additional Si–H groups to yield bridge-bonded oxygen groups. By comparing samples exposed to an oxygen ambient and samples exposed to low relative humidity, oxygen was also shown to play a role in the oxidation of the top layer. NH₄F-treated surfaces exposed to air and water have also been examined using XPS and contact angle analyses [35]. NH₄F etching leaves relatively few Si–F groups compared to HF etching, and thus, Si–OH groups are not present following the final rinse. The XPS analysis showed the same two-stage behavior, however, with induction periods approximately equal to those obtained on HF-treated surfaces exposed to both air and water. Despite the increase in oxygen uptake, the water contact angle was found to remain essentially constant for several weeks in air.

3.1.1. High resolution electron energy loss spectroscopy studies

Using HREELS, it has been shown recently that oxidation occurs through oxygen insertion in the silicon backbonds, while the hydrogen termination remains intact [42]. It was argued that this

![HREEL spectrum of an NH₄F-treated Si(100) surface exposed to air for 2h.](image-url)
Table 8
Peaks assignments for NH$_4$F-treated Si(100) exposed to air for various times

<table>
<thead>
<tr>
<th>Peak position (cm$^{-1}$)</th>
<th>Assignment</th>
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</thead>
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<tr>
<td>2920</td>
<td>C-H stretch</td>
</tr>
<tr>
<td>2250</td>
<td>Si-H stretch (oxygen backbonds)</td>
</tr>
<tr>
<td>2100</td>
<td>Si-H stretch (silicon backbonds)</td>
</tr>
<tr>
<td>1450</td>
<td>C-H bend</td>
</tr>
<tr>
<td>1360</td>
<td>C-H bend</td>
</tr>
<tr>
<td>1260</td>
<td>C-H bend</td>
</tr>
<tr>
<td>1180</td>
<td>Si-O-Si asymmetric stretch (bulk)</td>
</tr>
<tr>
<td>1060</td>
<td>Si-O-Si stretch (surface)</td>
</tr>
<tr>
<td>910</td>
<td>SiH$_2$ scissor</td>
</tr>
<tr>
<td>750</td>
<td>Si-O-Si symmetric stretch</td>
</tr>
<tr>
<td>650</td>
<td>Si-H bend</td>
</tr>
<tr>
<td>500</td>
<td>Hydrogen-induced phonon</td>
</tr>
<tr>
<td>420</td>
<td>Si-O-Si bend</td>
</tr>
</tbody>
</table>

observation explains the water contact angle results [35] discussed in Section 2.3.4. Comparison with HREELS results from molecular oxygen adsorption on silicon [64] has revealed that initial oxidation occurs simultaneously in both surface and bulk sites, not in a layer-by-layer manner. Furthermore, water is found to make a significant contribution to the observed oxidation.

Fig. 23 shows a typical HREEL spectrum for an NH$_4$F-treated surface that has been exposed to air for 2 h. The peak assignments are summarized in Table 8. The peak position of the Si–H stretch indicates that the surface is primarily dihydride terminated. The presence of the SiH$_2$ scissor mode is a further evidence of this fact. The small peak at 1060 cm$^{-1}$ is assigned to the asymmetric stretch of bridge-bonded oxygen. Fig. 24 shows the HREEL spectra as a function of exposure time to air. Several changes are readily observed. The bridge-bonded oxygen peak at 1060 cm$^{-1}$ increases in intensity, and a second, higher energy peak appears and increases in intensity. This peak shifts to slightly higher energy as air exposure time increases, ending up at 1180 cm$^{-1}$ after 100 days. As air exposure time increases, two other bridge-bonded oxygen modes appear, the symmetric stretch at 750 cm$^{-1}$ and the bend at 420 cm$^{-1}$.

Fig. 25 shows the close-up HREEL spectra of the bridge-bonded oxygen asymmetric stretch region. The presence of the bridge-bonded peak indicates that oxidation has begun even in the span of 2 h of air exposure, although the amount of oxygen was below the detection limit of AES. Previous HREELS studies on HF-treated surfaces observed one peak which shifted to higher energy as oxidation proceeded [41,62]. With improved energy resolution, Kluth and Maboudian observed two peaks, one centered at about 1060 cm$^{-1}$ and the second centered between 1130 and 1180 cm$^{-1}$ (this peak shifts to higher energy as oxidation proceeds). The two peaks are seen most explicitly in the spectrum for the two-day old sample in Fig. 25, but are also evident in the asymmetric peak shape at high air exposure times. A study of molecular oxygen adsorption at elevated temperatures on clean Si(111) and (100) surfaces also reported the presence of two peaks in the bridge-bonded oxygen asymmetric stretch region [64]. The lower energy peak, centered at 1060 cm$^{-1}$, was attributed to oxygen bridge-bonded between the first and second layer silicon atoms (surface sites). The higher energy peak, centered between 1150 and 1180 cm$^{-1}$, was attributed to oxygen bridge-bonded below the second layer silicon.
Fig. 24. HREEL spectra of NH₄F-treated Si(100) surfaces as a function of air exposure time. The spectra for 48, 74 and 100 days of exposure are multiplied by a factor of 2 because of the lower count rate from these highly oxidized surfaces.

Fig. 25. Close-up HREEL spectra of the asymmetric bridge-bonded oxygen stretch as a function of air exposure time. For these and all other close-up spectra, the background has been subtracted assuming a linear background.
Fig. 26. HREEL spectra of the asymmetric bridge-bonded oxygen stretch as a function of time. The data (●) are fitted with a surface oxide peak (the lower energy peak at ~1060 cm\(^{-1}\)) and a bulk oxide peak, both shown using dashed lines. The solid line is the sum of these two fitted curves.

Fig. 27. HREELS peak areas for the surface oxide (●), bulk (▲) oxide, and oxygen backbonded Si–H stretch (×). The surface oxide peak saturates, while the bulk oxide peak continues to increase. The behavior of the oxygen backbonded Si–H stretch mirrors that of the surface oxide.

atoms (bulk sites). Fitting the bridge-bonded oxygen region with a surface oxide peak and a bulk oxide peak, as shown in Fig. 26, provided a good fit to the experimental data. Therefore, the peak at 1060 cm\(^{-1}\) was assigned to surface oxide and the higher energy peak to bulk oxide. The surface oxide
peak appears to reach a saturation point, while the bulk oxide peak increases without saturation. This behavior is summarized in Fig. 27 which plots the fitted HREELS peak areas as a function of air exposure time. The bulk oxide peak displays the same two-stage oxidation behavior reported previously for both HF- and NH₄F-treated surfaces [41,35]. The saturation of the surface oxide peak was attributed to oxygen insertion in all the backbonds on the surface, i.e., the backbonds between the first and second layer silicon atoms. The fitted peaks in Fig. 26, showing that both surface and bulk oxide species are present on the NH₄F-treated Si(1 0 0) surfaces even for the shortest air exposure times, suggest that initial oxidation of these surfaces does not occur in a layer-by-layer fashion.

Fig. 28 shows the close-up HREEL spectra of the Si–H stretch region. This peak is centered at 2100 cm⁻¹ for the two-hour old sample, indicating that mainly Si–H species with silicon backbonds are present. As oxidation proceeds, higher energy peaks appear. Since the position of the Si–H stretch is known to shift to higher energy as the number of oxygen backbonds increases [65], it was argued that as oxidation proceeds, the silicon backbonds of the Si–H species are replaced by oxygen backbonds. This progression of the Si–H stretch from silicon backbonds to oxygen backbonds is completed after about 12 days of air exposure, as shown in Fig. 27. The area for the fully oxidized Si–H stretch (the peak at 2250 cm⁻¹) closely follows the growth of the surface oxide peak. Further air exposure results in a decrease in intensity of the Si–H stretch, but this mode is still observed after 100 days of air exposure.

3.1.2. Implications

The results described above suggest the following picture for oxidation of NH₄F-treated hydrogen-terminated Si(1 0 0) surfaces exposed to air: oxidation begins with oxygen insertion in the Si–Si
backbond, while the surface remains hydrogen-terminated. It is important to note that the surface remains hydrogen-terminated after this initial oxidation period, and that there is evidence of Si–H groups even after 100 days of air exposure. This observation explains why the contact angle measurements reported in Ref. [35] (see Section 2.3.4) found that the water contact angle (a measure of surface hydrophobicity) remained essentially constant for the first several weeks of air exposure, despite the fact that the oxygen uptake increased.

On the NH$_2$F-treated surfaces studied in Ref. [42], both surface and bulk oxide peaks were observed for all air exposure times (Fig. 26), indicating that initial oxygen uptake does not occur in a layer-by-layer manner. The lower energy oxide peak appears to saturate (Fig. 27), further supporting its assignment as the surface oxide. Subsequent oxide growth results from oxidation in bulk sites. The growth of the fully oxidized Si–H stretch mirrors the growth of the surface oxide peak, and also reaches a saturation point. The saturation of these two peaks is likely due to oxidation of all the surface silicon backbonds, indicating the completion of the first layer of oxide.

3.2. Self-assembled monolayers on silicon surfaces

Self-assembled monolayers have been the subject of intense study because of their potential applications in such areas as wetting, adhesion, lubrication, high resolution lithography, and pattern transfer. Several different varieties of SAMs have been investigated, including alkanethiols (CH$_3$(CH$_2$)$_{n-1}$SH) on Au, Ag, and Cu, and alkyltrichlorosilanes (CH$_3$(CH$_2$)$_{n-1}$SiCl$_3$) on SiO$_2$, Al$_2$O$_3$, and mica. Several reviews have been published recently on this topic [43,66,67]. Briefly, SAMs have the following characteristics. Each of these monolayer systems consists of three main parts. The first is the head group, which chemisorbs to the surface. Because of the strong interaction between the head group and the substrate, the molecules attempt to adsorb at all surface sites, resulting in a close-packed monolayer. The second part of the monolayer is the alkyl chain. In the simplest case this is a long chain normal alkane. The van der Waals interactions between chains further contribute to the ordering of the monolayer. Alkanethiols on Au(1 1 1), e.g., are tilted approximately 30° with respect to the surface normal in order to maximize the van der Waals interactions. The third part is the terminal group. The simplest terminal functionality is a methyl group; however, the chain may be terminated with a number of different groups (e.g., NH$_2$, OH, or COOH), allowing SAMs to be tailored to a particular application. Functionalization of the end group also allows multiple layers to be adsorbed on top of the monolayers [43].

The majority of work on SAMs has focused on the formation of the monolayers and their structure. In the case of alkanethiols on Au(1 1 1), the S–H bond is broken, and the molecule adsorbs as a thiolate [68]. FTIR data suggest that short alkanethiols ($n \leq 9$) are liquid-like, while longer chains ($n > 9$) are similar to solid alkanes [69]. Shorter chains are also more sensitive to thermal disorder [70]. Helium diffraction studies show that the monolayers form a ($\sqrt{3} \times \sqrt{3}$)R30° overlayer with four molecules per unit cell [71]. These molecules were originally thought to occupy the threefold hollow site on the Au(1 1 1) surface. More recent X-ray diffraction studies have found that molecules occupy different sites, and suggested that the sulfur head groups form dimers [72]. This picture is supported by X-ray photoelectron spectroscopy [73] and temperature programmed desorption data [74], although the dimers have not been observed directly.

In the case of alkyltrichlorosilanes on SiO$_2$, adsorption takes place through the hydrolysis of the Si–Cl bonds to form Si–OH groups. All Si–Cl bonds become hydrolyzed, as no chlorine is detected following monolayer formation [46]. The OH groups interact with OH groups on the oxidized surface,
forming Si–O–Si bonds to the substrate through condensation reactions. It is believed that Si–O–Si bonds are also formed between adjacent head groups, creating a cross-linked network at the surface. Water is found to play a key role in the formation step [44–46]. The presence of too much water causes polymerization of the precursor molecules and leads to poor monolayer formation. But a small amount of water is required for the formation of high quality films. It has been proposed that a thin water layer exists on the hydrophilic SiO₂ surface, and that the chains physisorb on this water film [44,45]. In this stage, the chains are laterally mobile and hence, can pack more closely before the condensation reaction takes place, at which point they become pinned to the surface.

Deposition temperature is found to have a significant effect on the resulting monolayers [44,45]. There is some evidence that a “critical” temperature exists, which is dependent on the chain length. Below this temperature, monolayers are densely packed in an all-trans configuration. Above the “critical” temperature, the surface tension of the resulting monolayer increases, indicating that the monolayers become increasingly disordered. This behavior has been explained through analogy with Langmuir monolayers. The observed critical temperature for the self-assembled monolayers corresponds well with the triple-point temperature for the Langmuir monolayers, where liquid condensed, liquid expanded, and two-dimensional gas states coexist.

Chain length is observed to affect the quality of the monolayers, as indicated by contact angle analysis. For \( n \geq 6 \) the water contact angle is approximately 110°; for shorter chain lengths, the contact angle decreases to about 90° [46], indicating that the shorter chains are not as well-packed. Similar behavior has been observed by high-resolution electron energy loss spectroscopy.

3.2.1. **HREELS studies of alkyltrichlorosilane monolayers on SiO₂**

A typical HREEL spectrum for the oxidized, then OTS-coated Si(100) surface is shown in Fig. 29 [49]. The peak assignments are summarized in Table 9. The presence of the monolayers is indicated by the broad C–H stretch at about 2920 cm⁻¹ and the C–H bends between 1280 and 1450 cm⁻¹. The positions of these modes are consistent with those for normal alkanes such as butane and hexane [75,76]. Small peaks are also present at 730 and 880 cm⁻¹, which are assigned to C–H bending modes. The region from 1000 to 1200 cm⁻¹ contains peaks due to the asymmetric stretch of bridge-bonded oxygen. Evidence of the underlying oxide is also seen in the bending mode at 470 cm⁻¹.

Figs. 30(a)–(c) show the HREEL spectra of alkylsiloxane-coated oxidized Si(100) surfaces as a function of chain length. For comparison, a HREEL spectrum of a sample that has been oxidized but not placed in a monolayer solution is also shown in Fig. 30(d). For trichlorosilane-derived monolayers, as the chain length decreases from 18 to 4 carbon atoms, the Si–O modes from the underlying SiO₂ substrate become more intense relative to the C–H modes. For \( n = 4 \), the C–H bending modes at 730 and 880 cm⁻¹ become harder to resolve, possibly because of the appearance of the Si–O–Si symmetric stretch at 800 cm⁻¹. The small peak at about 2250 cm⁻¹ may be due to an overtone of the Si–O–Si asymmetric stretch. This peak is observed only for the butylsiloxane sample because the Si–O–Si asymmetric stretch is more intense for that sample than for the longer chain monolayers. The position of the C–H stretch is shifted to higher energy on the oxidized sample, however, indicating that the hydrocarbon is different from the self-assembled monolayers, and it is likely due to contamination.

Fig. 31 shows close-up scans of the bridge-bonded oxygen region for (a) OTS-coated Si(100) and (b) butyltrichlorosilane-coated Si(100). Also shown is the same region for an oxidized sample with no monolayer adsorbed (c). The large peak at about 1180 cm⁻¹ for the oxidized sample cannot be fit using a single Gaussian peak; peaks at 1135 and 1200 cm⁻¹ are used to fit this region. These peaks are present
for all samples; therefore, they are assigned to the bridge-bonded oxygen stretch of the bulk, chemically prepared oxide that serves as the substrate for monolayer adsorption. For all samples on which the monolayers have been adsorbed, an additional peak is observed at 1060 cm\(^{-1}\); this peak is not present for the oxidized sample. Based on an IR study of methylsilanols on silica surfaces, this peak at 1060 cm\(^{-1}\) is assigned to the Si–O–Si bond between the alkylsiloxane head group and the oxidized surface [77].

### Table 9

<table>
<thead>
<tr>
<th>Peak position (cm(^{-1}))</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>2920</td>
<td>C–H stretch</td>
</tr>
<tr>
<td>1450</td>
<td>CH(_2) scissor</td>
</tr>
<tr>
<td>1360</td>
<td>CH(_3) symmetric bend</td>
</tr>
<tr>
<td>1280</td>
<td>CH(_2) twist-rock</td>
</tr>
<tr>
<td>1180</td>
<td>Si–O–Si asymmetric stretch (bulk oxide)</td>
</tr>
<tr>
<td>1060</td>
<td>Si–O–Si stretch (between the surface and the head group)</td>
</tr>
<tr>
<td>880</td>
<td>CH(_3) rock</td>
</tr>
<tr>
<td>800</td>
<td>Si–O–Si symmetric stretch</td>
</tr>
<tr>
<td>730</td>
<td>CH(_3) rock-twist</td>
</tr>
<tr>
<td>470</td>
<td>Si–O–Si bend</td>
</tr>
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</table>

#### 3.2.2. Effect of substrate: alkyltrichlorosilane monolayers on Si\(_3\)N\(_4\)

Much attention has been focused on the formation mechanism of alkyltrichlorosilane-based SAMs on hydrophilic oxidized surfaces. As I have already discussed, the presence of a water layer on oxidized
Fig. 30. HREEL spectra of alkylsiloxane-coated oxidized Si(1 0 0) surfaces as a function of chain length for (a) \( n = 18 \), (b) \( n = 8 \), and (c) \( n = 4 \). The oxidized sample (d) was prepared in exactly the same manner as the others, with the exception that no precursor was present in the hexadecane:chloroform solution. All samples were annealed to 520 K for 30 min. Each spectrum has been normalized by the elastic peak intensity.

Fig. 31. Bridge-bonded oxygen stretch region of the HREEL spectra for (a) OTS- (b) butyltrichlorosilane-, and (c) oxidized sample with no monolayer adsorbed. Experimental data (·) are fit using Gaussian peaks (dashed lines).
surfaces is found to play a critical role in monolayer formation, as indicated by the dependence of formation rate on humidity [46,78]. The water layer gives the chain mobility and serves to decouple the monolayer from the substrate. This decoupling has been suggested by the formation of equivalent quality monolayers on silicon dioxide and on a UV–ozone-treated gold surface [79]. For an untreated gold surface, one which would not have a significant layer of water, monolayer formation was poor. By oxidizing the gold surface through a UV–ozone treatment, followed by a water rinse, it was possible to produce high quality monolayers, despite the fact that the surface did not have any active sites such as hydroxyl groups. From these observations, it was concluded that there must be insignificant bonding between the chains and the substrate [79].

Given the role the water layer plays in decoupling the monolayer from the substrate, one would expect monolayers to form on any polar surface. In this section, I review a study of the formation of alkyltrichlorosilane-based monolayers on silicon nitride surfaces [80]. Silicon nitride has a higher dielectric constant than SiO₂; it is also a tough, corrosion-resistant material, and as such, is often used in micromachining technology [1–3]. It was shown that monolayers can be formed directly on the silicon nitride surface, without requiring an intervening oxide layer. This behavior was attributed to the polar nature of the silicon nitride surface, on which a water layer forms under ambient conditions. HF-treated silicon nitride films containing less than 0.2 monolayers of oxygen were used as substrates for monolayer formation. The resulting monolayers were found to be of similar quality to those formed on silicon oxide, despite the significantly smaller number of silanol bonding sites. Furthermore, monolayers formed from a dimethylchlorosilane precursor molecule, which is not able to cross-link, were found to be of much lower quality than trichlorosilane-derived monolayers. Both of these observations highlight the importance of cross-linking in alkyltrichlorosilane-based monolayers.

The quality of the full monolayer was checked by water contact angle, which was 110° for OTS-coated Si₃N₄ and 100° for BTS-coated Si₃N₄, in good agreement with values on oxidized silicon surfaces [46]. To study their formation kinetics, partial monolayers were formed on the nitride and oxide surfaces by reducing the time the substrate was immersed in the monolayer solution. It was found

![Fig. 32. Water contact angle as a function of immersion time in OTS solution for Si₃N₄ (□) and SiO₂ (▲).](image-url)
that, initially, the contact angle of the monolayer on Si$_3$N$_4$ increases faster than that on the oxide surface, as shown in Fig. 32. AFM images of partial monolayers also show differences between silicon nitride and oxide in the nucleation step. Images obtained after 1 s, 10 s, 1 min, and 20 min of immersion time are displayed in Fig. 33 for Si$_3$N$_4$ and in Fig. 34 for SiO$_2$. Initially, a larger density of smaller islands is formed on Si$_3$N$_4$ compared to SiO$_2$. This behavior is most clearly observed in Figs. 33(b) and 34(b). Monolayer growth on the surface in the initial stage is dominated by nucleation, i.e., reaction of chains with the surface silanol groups. Thus, the data indicate that nucleation occurs more rapidly on Si$_3$N$_4$, despite the XPS data indicating that fewer hydroxyl sites exist on nitride. The faster nucleation on the nitride suggests that the active sites are more reactive than those on the oxide. After the nucleation step, however, the contact angles on the two surfaces coincide with each other, and the AFM
Fig. 34. AFM images of SiO$_2$ as a function of immersion time (1 s, 10 s, 1 min, and 20 min) in OTS solution. The z-axis range is 5 nm.

images appear essentially the same. These observations suggest that monolayer formation at longer immersion times is dominated by cross-linking between adjacent chains, which should take place independently of the underlying substrate.

3.2.3. Alkyl monolayers on silicon surfaces

Recently it has been demonstrated that monolayers can be formed which are directly bonded to silicon surfaces [81,82]. These monolayers are formed by reacting an alkene (such as octadecene) with a hydrogen-terminated surface. The resulting monolayer bonds to the surface through a Si–C bond and shows packing and wetting properties similar to those employing alkanethiol and alkyltrichlorosilane precursor molecules. Thus, these monolayers can provide an alternative to OTS-based monolayers as a passivating organic film in situations when an oxide film is not desirable [16].
Fig. 35. HREEL spectrum of a self-assembled monolayer formed from the reaction of octadecene with NH₄F-treated Si(100).

Table 10
Peak assignments for alkyl monolayers prepared from the reaction of octadecene with NH₄F-treated Si(100)

<table>
<thead>
<tr>
<th>Peak position (cm⁻¹)</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>2920</td>
<td>C–H stretch</td>
</tr>
<tr>
<td>2280</td>
<td>Si–O–Si overtone</td>
</tr>
<tr>
<td>2100</td>
<td>Si–H stretch</td>
</tr>
<tr>
<td>1450</td>
<td>CH₂ scissor</td>
</tr>
<tr>
<td>1360</td>
<td>CH₃ symmetric bend</td>
</tr>
<tr>
<td>1280</td>
<td>CH₃ twist-rock</td>
</tr>
<tr>
<td>1060</td>
<td>Si–O–Si stretch</td>
</tr>
<tr>
<td>880</td>
<td>CH₃ rock</td>
</tr>
<tr>
<td>780</td>
<td>SiC</td>
</tr>
<tr>
<td>730</td>
<td>CH₂ rock-twist</td>
</tr>
<tr>
<td>620</td>
<td>Si–H bend</td>
</tr>
</tbody>
</table>

Fig. 35 shows a typical HREEL spectrum for octadecene reacted with a hydrogen-terminated Si(1 0 0) surface [83]. The peak assignments are summarized in Table 10. The spectrum is dominated by the C–H stretch at 2920 cm⁻¹ and the C–H bends between 1280 and 1450 cm⁻¹. The C–H modes are also present at 730 and 880 cm⁻¹. The peak at 1060 cm⁻¹ is assigned to the Si–O–Si asymmetric stretch [76]. There may also be a contribution to this peak from the C–C stretch at 1050 cm⁻¹, as has been observed for ethyl groups adsorbed on Si(1 0 0) [84]. The presence of oxygen is confirmed by AES. The oxide is likely due to oxidation of the NH₄F-treated surface; its concentration is much lower than on SiO₂. The positions of the C–H modes are consistent with those of normal alkanes such as butane and hexane [85,86], and the spectrum is similar to that of alkylsiloxane monolayers on oxidized Si(1 0 0).
[49], except for the significantly smaller intensity of the Si–O–Si stretch. Similar quality monolayers were also formed on Si(111) as judged by the HREEL spectrum.

3.3. Thermal stability of self-assembled monolayers on silicon surfaces

An important consideration in the application of SAMs to MEMS technology is their thermal stability. To successfully incorporate these films into the production of low surface energy structures, it is necessary for the films to withstand the temperatures used in subsequent processing and packaging steps. A temperature-programmed desorption study of octadecanethiol (n = 18) adsorbed on Au(111) observed desorption of entire chains at about 450 K [74], indicating that desorption takes place through cleavage of the Au–S bond. Camillone et al. have used scanning tunneling microscopy and low-energy He atom diffraction to study the structures of n-alkane thiols self-assembled monolayers on Au(111). As the sample was annealed to successively higher temperatures (see Fig. 36), the SAM converts from a c(4 × 2) superlattice of (\(\sqrt{3} \times \sqrt{3}\))R30° through a two-phase regime to a pure (p × \(\sqrt{3}\)) phase [87]. The conversion was suggested to be driven by a loss of thiolate density due to desorption. Above 423 K, the SAM completely desorbs and (22 × \(\sqrt{3}\)) herringbone reconstruction of bare gold appears.

3.3.1. Alkytrichlorosilane monolayers on SiO₂

For alkytrichlorosilane-derived monolayers, the contact angle studies reviewed in Section 2.4.3 have shown that water contact angles on octadecytrichlorosilane (OTS) coated surfaces remain the same upon annealing for 5 min to temperatures as high as 675 K in a nitrogen ambient [33]. Above this temperature the contact angle was observed to decrease, indicating degradation of the films (Fig. 14). The contact angle analysis does not reveal information about the mechanism by which these films degrade, however.

More recently, HREELS has been employed to study the thermal behavior of alkylsiloxane monolayer on oxidized Si(100) surface under ultrahigh vacuum conditions [49]. HREEL spectra for a butylsiloxane monolayer as a function of annealing temperature are shown in Fig. 37. The spectrum of the sample annealed to 520 K shows a broad C–H stretch which can be well fit using the reported positions of the symmetric and asymmetric stretches of CH₂ and CH₃ groups in normal alkanes [75]. The monolayers remain intact up to temperatures of about 740 K. After annealing to 815 K the intensity of the C–H stretch decreases and its shape changes, as will be discussed below. The intensities of the Si–O–Si modes increase, with the symmetric Si–O–Si stretch at 800 cm⁻¹ becoming more apparent. After annealing to 960 K the monolayers have almost completely desorbed as indicated by the virtual disappearance of the C–H modes, and the spectrum is dominated by Si–O–Si modes, including the oxide overtone at 2250 cm⁻¹. The oxide desorbs upon annealing to 1100 K, as indicated by the disappearance of the oxide modes at 470, 800 and 1180 cm⁻¹. The C–H stretch at 2960 cm⁻¹ and the Si–H stretch at 2090 cm⁻¹ indicate the presence of a small amount of carbon and hydrogen contamination.

The C–H stretch region of the HREEL spectra for a butylsiloxane monolayer is shown in Fig. 38 as a function of annealing temperature. The spectra show that upon annealing to 815 K, the C–H stretch decreases in intensity, and individual peaks are resolved at 2920 and 2980 cm⁻¹. In addition, a peak appears at 1400 cm⁻¹ in the C–H bending region. Based on IR studies [88–91], the peaks at 2920 and 2980 cm⁻¹ are assigned to the C–H stretch of SiCH₃ species, while the peak at 1400 cm⁻¹ is assigned to the bending mode. With these assignments, the HREEL spectra show that following annealing to 815 K,
Fig. 36. (a) STM image of decanethiol SAM as deposited from 5 μM ethanolic solution. Dark features are single-atom deep pits in the Au surface. (b) Following annealing to 323 K, (c) 348 K, (d) 373 K, (e) 423 K, and (f) 573 K. (From Ref. [87], © 1994 AIP, with permission.)
Fig. 37. HREEL spectra as a function of annealing temperature for the butylsiloxane-coated oxidized Si(100) surface.

Fig. 38. C–H stretch region of the HREEL spectra as a function of annealing temperature for the butylsiloxane-coated oxidized Si(100) surface.
CH$_3$ groups remain on the surface. Furthermore, the spectra indicate that the methyl groups are attached to silicon and not oxygen atoms. Attachment to oxygen atoms would result in surface methoxy species. Such species would give rise to a peak at about 2820 cm$^{-1}$ due to the symmetric C–H stretch of the methoxy group [92,93]. Also, the C–H bending mode of methoxy species occurs at about 1450 cm$^{-1}$, instead of 1400 cm$^{-1}$. The absence of these modes indicates that methoxy groups are not present following high temperature annealing, and thus, the carbon present following the initial desorption step must be attached directly to silicon atoms. Upon further heating to 890 K, the intensities of the Si–CH$_3$ peaks decrease, indicating reaction of the CH$_3$ groups. Similar behavior as a function of annealing temperature was observed for $n = 18$ and for the intermediate case of $n = 8$.

In analyzing the initial decomposition mechanism of the monolayers, the authors considered three possibilities: cleavage of the Si–O head group bond, cleavage of the Si–C bond, and cleavage of C–C bonds [49]. Si–O–Si modes are observed in HREEL spectra up to temperatures of about 1100 K, in agreement with TPD studies of the decomposition of thin (∼2 ML) oxide layers on Si(1 0 0) [94]. The Si–O bonds of the head groups are slightly different from those of the substrate, as evidenced by their position in HREEL spectra. This difference is unlikely to result in a large decrease in desorption temperature, however. Furthermore, octadecyldimethyltrichlorosilane (ODMS) based monolayers, for which no cross-linking is expected, showed similar desorption behavior to the OTS monolayers. This suggests that the thermal behavior of the monolayers does not depend on the Si–O cross-linking of adjacent chains, and thus, that the silicon head groups remain on the surface even after the monolayer has decomposed until about 1100 K. Thus, desorption of the monolayer must be the result of Si–C or C–C bond cleavage. As the monolayers begin to desorb, the intensity of the C–H stretch decreases and two peaks are clearly resolved in the HREEL spectra. These peaks indicate the presence of methyl groups on the surface following the initial decomposition of the monolayers. Their positions are consistent with methyl groups directly attached to silicon atoms. These observations suggest that the Si–C bonds remain intact and that decomposition initially occurs primarily through C–C bond cleavage.

The authors used contact angle data as a function of annealing temperature to support this picture. The contact angle for OTS-coated Si(1 0 0) remains constant at 112° up to 780 K, shown in Fig. 39(a). Upon annealing to 795 K, the contact angle decreases to 106°. At this point, the HREEL spectra show a decrease in the C–H stretch intensity and an increase in the Si–O–Si intensity. The ratio of these two modes, also shown in Fig. 39(a), suggests that the chain length has significantly decreased, yet the contact angle data show that the monolayer is still reasonably well-ordered. If Si–C bond cleavage were occurring to a significant extent, leading to the desorption of entire chains, one would expect the remaining monolayer to become disordered, perhaps with some of the underlying oxide becoming exposed, resulting in a contact angle much lower than the observed 106°. Thus, the contact angle data are consistent with decomposition through C–C bond cleavage. This picture is further verified by more recent thermal desorption studies performed on deuterated alkyltrichlorosilane monolayer [95].

The thermal behavior of polyethylene also supports the picture of decomposition through C–C bond cleavage. It has been observed that upon heating polyethylene in the absence of oxygen, gaseous products are not formed until 640 K [96]. Decomposition occurs through the cleavage of C–C bonds. It is postulated that decomposition begins at weak links in the polymer, such as branching points [97]. The alkylsiloxane monolayers on oxidized silicon examined here are primarily straight chains, with few defects and branching points. The smaller number of defects compared to polyethylene may explain the slightly higher decomposition temperature observed for the monolayers.
Decomposition of the alkylsiloxane monolayers on the oxidized Si(100) surface presents an interesting contrast to the thermal behavior of alkanethiols. As discussed in Section 3.3, octadecanethiol desorbs from the Au(111) surface at about 450 K [74]. Desorption occurs through Au–S bond cleavage, with the chains remaining intact. The difference in behavior results primarily from the weaker bonding of the alkanethiol head group to the surface (the Au–S bond strength is estimated at about 44 kcal/mol) compared with the alkylsiloxane monolayers.

3.3.2. Alkyl monolayers on silicon surfaces

The thermal behavior of the alkyl monolayers formed on silicon surfaces has been studied by HREELS [83]. It is found that the monolayers are stable up to 615 K. Hydrogen is observed on the surface following desorption, likely the result of β-hydride elimination reactions. The desorption temperature is about 100 K lower than that found for alkylsiloxane monolayers on oxidized silicon, suggesting that desorption occurs through a hydrogen elimination pathway. At higher temperatures, a SiC vibrational mode becomes evident, indicating that the chains have decomposed.

Fig. 40 shows HREEL spectra for octadecene reacted with Si(100) as a function of annealing temperature. The sample was annealed to the indicated temperature for 1 min, then cooled to and held at 580 K until the pressure was \( <1 \times 10^{-9} \) Torr in order to minimize readsoption. The spectrum remains unchanged up to 615 K. Upon annealing to 650 K, however, several changes take place. The C–H stretching and bending modes decrease in intensity, indicating that the monolayers have begun to desorb. At the same time, the Si–H stretch at 2100 cm\(^{-1}\) and the Si–H bend at 620 cm\(^{-1}\) appear. Upon annealing to 720 K, the C–H bending modes have completely disappeared and the C–H stretch has further decreased in intensity. It has also broadened, with a shoulder becoming evident at 3050 cm\(^{-1}\). This shoulder was attributed to the C–H stretch of sp\(^2\) bonded carbon [14]. This shoulder was not observed for alkylsiloxane desorption; thus, it was judged to be unique to the desorption of the alkyl monolayers.
Further annealing to 785 K results in the disappearance of the Si–H stretch, corresponding to the desorption of hydrogen. Upon annealing to 785 K, the spectrum is dominated by a peak at 780 cm⁻¹, attributed to SiC vibrational mode [84], and the Si–O–Si stretch at 1080 cm⁻¹. The presence of carbon and oxygen is confirmed by AES. The carbon coverage is estimated from AES results to be 0.6 monolayer; the oxygen coverage is estimated to be 0.3 monolayer. Analogous experiments for monolayers formed on Si(1 1 1) gave similar results. Similar results were also obtained for octene monolayers on Si(1 0 0). Desorption in both cases was characterized by the appearance of Si–H modes and a final surface that consisted of SiC and Si–O–Si modes.

The desorption behavior of the alkyl monolayers is summarized in Fig. 41. The solid line plots the peak area of the C–H stretch as a function of annealing temperature for octadecene monolayers on Si(1 0 0). The peak areas have been normalized by the peak area prior to annealing. The dashed line plots the water contact angle as a function of annealing temperature. The contact angle decreases rapidly upon annealing to 650 K, which corresponds to the largest decrease in the C–H stretch intensity.

In Fig. 42, the desorption results for various monolayers are summarized by plotting the peak area of the C–H stretch as a function of annealing temperature. The solid line represents data for octadecene on Si(1 0 0). For comparison, Fig. 42 also shows the desorption behavior of octadecylsiloxane monolayers formed on oxidized Si(1 0 0) (short dashes). It is observed that the alkyl monolayers begin to desorb at about 615 K and have completely desorbed by 800 K. The octadecylsiloxane monolayer, on the other hand, did not desorb until 740 K. Furthermore, desorption of the octadecylsiloxane monolayer was not accompanied by the appearance of Si–H modes. More specifically, the octadecylsiloxane monolayers are found to desorb through cleavage of C–C bonds, resulting in the desorption of hydrocarbon fragments and a reduction in chain length up to 890 K, at which point only the underlying oxide was
Fig. 41. Peak area of the C–H stretch as a function of annealing temperature for octadecene reacted with NH₄F-treated Si(100) (solid line), and the corresponding water contact angle (dashed line). The C–H peak areas are normalized by the peak area observed prior to annealing.

Fig. 42. Peak area of the C–H stretch as a function of annealing temperature for octadecene reacted with NH₄F-treated Si(100) (solid line), and octadecyloxiloxane on oxidized Si(100) (short dash). The points are normalized by the peak areas observed prior to annealing.

observed. For the case of the alkyl monolayers, a different mechanism exists which leads to desorption before the cleavage of C–C bonds becomes significant.

The authors used comparisons with the desorption of other hydrocarbon adsorbates to interpret the observed alkyl monolayer desorption behavior. Exposure of clean silicon to molecules such as ethylsilane [98–100] and ethylzinc [101] results in adsorbed ethyl groups. Upon heating, the ethyl
groups undergo a $\beta$-hydrogen elimination reaction to form ethylene, which desorbs from the surface, and adsorbed hydrogen. The reaction has been observed to occur as low as 550 K [101] and as high as 700 K [100]. $\beta$-hydrogen elimination has also been observed for longer alkyl groups (such as butyl and hexyl groups) adsorbed on aluminum [102]. The presence of Si–H groups following annealing to 650 K suggests that desorption of the alkyl monolayers occurs through $\beta$-hydrogen elimination.

It has been proposed in a study of diethylsilane adsorption on silicon that the ethylene evolved upon heating remains on the surface [103]. Upon further heating the ethylene decomposes, resulting in the desorption of hydrogen and the formation of a preliminary stage of SiC. Similarly, it has been reported that ethyl groups are formed upon exposing ethylene adsorbed on Si(100) to atomic hydrogen [84]. These ethyl groups decompose at 700 K to produce hydrogen and SiC. For the alkyl monolayers, the appearance of a shoulder in the C–H stretch at 3050 cm$^{-1}$ upon annealing to 795 K is consistent with the occurrence of a hydrogen elimination reaction in which the evolved alkene remains on the surface. In analogy with ethylene in the presence of coadsorbed hydrogen, the adsorbed alkene decomposes upon further heating, resulting in the formation of SiC, as evidenced by the HREELS peak at 780 cm$^{-1}$.

Adsorption and thermal behavior of molecules such as propylene [104] and 2-butene [105] has also been studied on Si(100). Upon heating it has been observed that a fraction of the adsorbed molecules desorb intact, while the rest decompose. Such decomposition may also occur in the present case of the alkyl monolayers without the chains going through the hydrogen elimination reaction.

The desorption picture which the authors proposed for alkyl monolayers on silicon is the following: upon heating to 650 K, the monolayers undergo $\beta$-hydrogen elimination, resulting in the formation of hydrogen and an alkene. The hydrogen is adsorbed on the surface, whereas the alkene either desorbs or remains on the surface. Further heating results in decomposition of alkene that remained on the surface, leading to the formation of SiC type material. AES data indicate that the carbon coverage is less than one monolayer, suggesting that the number of chains that remain on the surface and subsequently decompose is small compared to the number that desorb. It is possible that some of the chains decompose without going through a hydrogen elimination reaction, in analogy with desorption of propylene and 2-butene. The water contact angle decreases rapidly above 650 K, consistent with the desorption of the majority of the chains. This behavior is in contrast to alkylsiloxane monolayers on oxidized silicon [49]. There, the contact angle remains high even after significant desorption has occurred, consistent with the picture that the chains desorb through breakage of C–C bonds and a reduction in chain length.

4. Future directions

4.1. Friction and wear

Many MEMS devices involve surfaces impacting or rubbing against one another [18,106–109]. An example is a microengine, shown in Fig. 43, approximately 60 $\mu$m in diameter coupled to a 1600 $\mu$m diameter optical shutter [109]. The operation of these micromachined devices which incorporate joints and bearings is significantly affected by friction and wear of the contact surfaces involved. For applications to MEMS design and fabrication, a friction-test microstructure is desirable for in situ measurements of friction locally on films that have undergone a specified sequence of fabrication steps. Such a test structure would make it possible to measure basic properties which would then be used to
model friction in microbearings fabricated on the same substrate. One such design is shown schematically in Fig. 44. A shuttle is suspended over an underlying electrode by a folded beam suspension [110]. Four dimples are fabricated into the shuttle to prevent the shuttle from contacting the underlying electrode. The shuttle is then displaced a specified distance, $\Delta x$, by applying a voltage to the electrostatic comb drives, $V_{\text{DC}}$. A clamp-down voltage, $V_{\text{c}}$, applied to the underlying electrode provides the normal force to pull down the shuttle so that the dimples contact the substrate. The tangential force on the contacting areas is $F = k\Delta x$ where $k$ is the spring constant of the suspension, obtained by resonating the structure. By ramping down $V_{\text{c}}$, the threshold voltage $V_t$ is measured at which the contacting surfaces slip and the structure returns to its original position. For this voltage, the normal force $N$ which corresponds to the tangential force $F$ is determined and then the coefficient of static friction $\mu_s$ is calculated as $F/N$. Using this test structure, the authors report static friction coefficients of $4.9 \pm 1.0$ between polysilicon–polysilicon interfaces, and $2.5 \pm 0.5$ between silicon nitride and polysilicon interfaces [110]. The effect of various coatings described in Section 2 on frictional and wear characteristics of microdevices is underway in the author’s laboratory using the above friction tester. Preliminary results indicate significant reduction in $\mu_s$ upon coating with self-assembled monolayers.
Fig. 44. Layout of a friction test microstructure. The shuttle is suspended above the underlying electrode by a folded beam spring structure. The shuttle is laterally displaced by $V_{\text{DC}}$ and is normally displaced and clamped by $V_c$. (From Ref. [110], © 1996 IEEE, with permission.)

Smith et al. [11] have also coated polysilicon microengines (shown in Fig. 43) with fluorocarbon films (Section 2.6) and by extensive modeling of the gear behavior, they have found a coefficient of friction of 0.07, similar to the value they obtained on OTS coating and significantly lower than the value of unity for an uncoated polysilicon. Although the FC films are expected to be more wear resistant than the SAMs, they require already released structures, i.e., they do not address the problem of release stiction. Furthermore, significant deposition is needed on the line-of-sight surfaces in order to get enough material underneath structures, and hence, this coating may affect to a greater extent the electrical and mechanical performance of the microdevice, e.g., in the case of microresonators.

4.2. New materials

A number of other materials either as coating or as structural layers are under investigation. These include diamond [112,113], diamond-like carbon [114,115] and silicon carbide [116–119]. In this review, we limit the discussion to the latter two since they are technologically more mature technologies for MEMS applications. Interested readers are referred to the references on diamond coating.

4.2.1. Diamond-like carbon coatings

A promising anti-stiction treatment for micromechanical devices is diamond-like carbon (DLC) coating. These films are hard, hydrophobic, exhibit relatively low surface energies, and can also be
doped to enhance their electrical conductivity. Other properties such as thermal stability, chemical inertness, and the ability to be deposited at or near room temperature make DLC an ideal candidate for integration into the micromachine fabrication process. Endurance of the carbon coatings is also important, especially in applications where wear due to repetitive contacts with the film may occur.

Houston et al. [114] have explored the potential of DLC coating for adhesion reduction. The films were deposited by a vacuum arc technique comprising plasma immersion ion implantation and deposition [120]. The apparatus generates a carbon plasma by a vacuum arc discharge to a graphite cathode, and then magnetically filters the plasma in order to remove the macroparticles. The carbon film is grown by a combination of plasma condensation on the surface when the substrate is unbiased, followed by both direct and recoil implantation of carbon ions when the substrate is biased. The
implantation of carbon ions is the necessary condition leading to films possessing diamond-like properties. During deposition the substrate temperature is below 50°C. This is an extremely attractive feature of this deposition technique, in comparison to other methods which require high substrate temperatures [16].

The surface properties of the DLC-coated surfaces were found to compare favorably to those of NH₄F-treated surfaces. For a carbon film approximately 100nm thick deposited onto a Si(1 0 0) substrate, a water contact angle of 87° was obtained, in comparison to the value of 84° on the ammonium fluoride-treated silicon surfaces. Atomic force microscopy was also employed to measure force curves on these surfaces. The results are shown in Fig. 45, along with the value for the actual pull-off force on each surface. The same silicon nitride tip was used for all of the curves shown, and the plots are shown on the same scale for comparison purposes. As a reference, a force curve obtained on the hydrophilic surface (Treatment III in Table 2) is also displayed. Once again, DLC compares well with NH₄F-treated surface, and hence, several orders of magnitude reduction in the work of adhesion may be expected following DLC coating.

In an effort to further improve the surface properties of the DLC coatings, a DLC film was subjected to a SF₆ fluorine plasma [114]. This work was based on earlier studies in which a graphite surface was fluorinated by exposure to a fluorine plasma, and this process was found to significantly raise the water contact angle on these surfaces [121]. Similarly, the water contact angle on the DLC-coated surfaces increased from 87° before treatment to 99° after the fluorine plasma exposure, and a smaller pull-off force was measured (Fig. 45(d)). Thus, the fluorination process appears useful for improving the surface properties of DLC films, and at the very least, these fluorinated films serve to further illuminate the role that surface properties play in determining adhesion forces.

Deng and Ko [115] have examined the frictional characteristics of DLC coating deposited by plasma-enhanced chemical vapor deposition. Their results are summarized in Table 11. As shown, both the surface material and the gas environment affect the friction significantly. The static coefficient of friction is 0.04 for DLC/DLC contact, in contrast to 0.4 between SiO₂/SiO₂ and 0.55–0.85 between SiNₓ–SiNₓ contacts measured in ultrahigh vacuum. Oxygen exposure is found to increase the coefficient of friction by 50% between DLC/DLC contacts, but this value is still an order of magnitude smaller than that between silicon-based materials. Hence the authors argue that the DLC is a promising friction-reducing coating for MEMS.

The challenge with DLC utilization in micromachining is the actual integration of this coating into a microstructure. The vacuum arc deposition comprising plasma immersion ion implantation is a line-of-sight process, and hence, it is not possible to perform a blanket deposition of DLC over an entire released or partially released microstructure. Rather, the DLC film deposition must be integrated

<table>
<thead>
<tr>
<th></th>
<th>DLC/DLC</th>
<th>SiNₓ/SiNₓ</th>
<th>SiO₂/SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before baking samples</td>
<td>0.060 ± 0.005</td>
<td>0.55–0.85</td>
<td>0.43 ± 0.05</td>
</tr>
<tr>
<td>UHV (∼8 × 10⁻¹⁰ Torr)</td>
<td>0.040 ± 0.005</td>
<td>0.40–0.70</td>
<td>0.20 ± 0.02</td>
</tr>
<tr>
<td>Ar (∼10⁻⁶ Torr)</td>
<td>0.040 ± 0.005</td>
<td>0.40–0.70</td>
<td>0.20 ± 0.02</td>
</tr>
<tr>
<td>O₂ (∼10⁻⁷ Torr)</td>
<td>0.055 ± 0.006</td>
<td>Increase from 0.44 to 0.68</td>
<td>0.75 ± 0.05</td>
</tr>
</tbody>
</table>

SiNₓ is PECVD silicon nitride. (From Ref. [115], © 1992 Elsevier.)
into the microfabrication sequence. For example, it may be possible to build small DLC bumpers on the device in certain areas which would serve as contact points where the two surfaces come together. Because the DLC deposition is performed near room temperature, a photoresist lift-off technique could be used to pattern the DLC. Another problem to bear in mind is associated with the stress in these films which limit the film thicknesses that can be used, and the way these films can be employed. Furthermore, following the deposition, microstructures most often are exposed to elevated temperatures, and hence, the chemical stability of DLC coatings at these temperatures needs to be determined. If these issues are resolved, DLC coatings should perform well for adhesion and friction reduction in microstructures.

4.2.2. Silicon carbide coatings

Silicon carbide is an attractive material for MEMS. Due to its high energy band gap of 2.2–2.9 eV, it can be used for high temperature electronics (up to 800°C). Applications include sensors for smart engines and on-chip signal conditioning for high temperature sensors and actuators. Silicon carbide also possesses low wear and friction characteristics leading to enhanced durability and operation of micromechanical structures either by coating mechanical contacts with SiC or by fabricating SiC bearings. Furthermore, SiC is extremely inert and hence can be used in harsh environments, e.g., valves and pumps for corrosives and flow sensors for acids. This combination of properties makes SiC an exceptional choice for complementing silicon as a material for MEMS.

Polycrystalline SiC surface-micromachined devices have been fabricated by using polysilicon as a sacrificial layer [122]. Cubic crystalline silicon carbide films epitaxially grown on silicon wafers provide a system which combines SiC with micromachining possibilities of silicon [123]. However, the epitaxial SiC films contain a large density of defects due to 20% lattice mismatch between Si and 3C-SiC, and at temperatures higher than 500 K, the SiC/Si heterojunction suffers from large leakage currents. One approach to circumvent this problem is the deposition of 3C-SiC on silicon-on-insulator (SOI) substrate. It has recently been shown that by this method, the leakage current through the substrate is prevented at temperatures as high as 723 K [118]. In another approach, Vinod et al. [117] have fabricated a single crystal 3C-SiC on SiO2 structure using a wafer bonding technique. The process uses the bonding of two polished polysilicon surfaces to transfer a 3C-SiC film grown on a Si wafer to a SiO2 film grown on a Si wafer. 3C-SiC films grown on SOI structure have shown to possess a much lower defect density than conventional 3C-SiC on Si films. Once these and other fabrication challenges are resolved, silicon carbide promises to be an exciting new material for MEMS.

4.3. Conclusions

Many novel microsensors and microactuators have been realized recently by advances in fabrication techniques. In parallel, several surface treatments with various degrees of success have been identified for alleviating the problem of stiction in MEMS technology. In order to be effective, the anti-stiction process must be incorporated into the highly constrained release, dicing, assembly, and packaging processes, with the latter step requiring elevated temperatures. Furthermore, the surface treatment must not degrade the electrical and mechanical performance of the microdevice. It seems unlikely that a single treatment will satisfy all these applications. Rather, a variety of coating technologies will be developed, each fine-tuned for a particular application. In addition, friction and wear are currently limiting the operation and lifetime of micromachines. It remains to be discovered how the
various anti-stiction surface treatments will affect friction coefficients and wear characteristics of micromachines. What is certain is that this technology will continue to provide us with intriguing surface science issues.

Acknowledgements

The author wishes to acknowledge the contributions made by her students, Dr. Michael Houston, Dr. Jonathan Kluth, Uthara Srinivasan, and Oranna Yaúw, and to acknowledge many valuable discussions with Prof. Roger T. Howe, Dr. Carlo Carraro, and Dr. Myung M. Sung. Correspondence with Prof. Mehran Mehregany and Dr. Christian Zorman on the applications of SiC is gratefully acknowledged. This work has been supported by the Sandia National Laboratories, the National Science Foundation (NYI award), and the Arnold and Mabel Beckman Foundation (BYI award).

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