Formation of alkylsiloxane self-assembled monolayers on Si₃N₄

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The structure of alkylsiloxane self-assembled monolayers formed on HF-treated Si₃N₄ has been studied using x-ray photoelectron spectroscopy, high-resolution electron energy-loss spectroscopy, and contact angle analysis. It is shown that the monolayers are similar in quality to those formed on oxidized silicon, despite the fact that upon etching in HF, the Si₃N₄ surface contains only 0.2 ML of oxygen. In contrast, on NH₄F-treated Si(100) surfaces with similar quantities of oxygen, high-quality monolayers cannot be formed. We argue that these results point to the importance of a water layer in monolayer formation. © 1999 American Vacuum Society.

I. INTRODUCTION

Self-assembled monolayers (SAMs) have been shown to be useful as passivating layers and also for the controlled modification of surface properties. Potential applications include wetting, adhesion, friction, chemical sensing, and ultra-fine-scale lithography. Several different varieties of SAMs have been investigated, including alkanethiols [CH₃(CH₂)ₙ₋₁SH] on Au, Ag, and Cu, and alkyltrichlorosilanes [CH₃(CH₂)ₙ₋₁SiCl₃] on SiO₂, Al₂O₃, and mica.

Since SiO₂ is widely used as an insulating or passivating layer in microelectronics and micromachining applications, the adsorption of alkyltrichlorosilanes on SiO₂ is of particular technological interest. The most commonly studied precursor molecule is octadecyltrichlorosilane (OTS) (n = 18). Monolayer formation occurs in a process referred to as silanization. In the first step of monolayer formation, it is believed that the Si–Cl bonds of the precursor molecule are hydrolyzed by reacting either with water in solution or a water layer on the surface, resulting in the formation of Si–OH groups. All Si–Cl bonds are hydrolyzed, as indicated by the absence of chlorine in x-ray photoelectron spectra of monolayers. The polar Si–OH groups physisorb on the water layer. Following this physisorption step, the chains are free to diffuse along the surface. Condensation reactions then result in the formation of covalent siloxane bonds between the chains and the surface and between adjacent head groups.

Silicon nitride is another material commonly used as an insulating or passivating layer and has several advantages over SiO₂. For example, the thermal stability, refractive index, and dielectric constant of silicon nitride are all superior to SiO₂. Because it is a tough and corrosion-resistant material, it is also suitable for micromachining applications, including the fabrication of thin membranes and bridges. In this article we show that alkyltrichlorosilane-based monolayers can be formed directly on the silicon nitride surface, without requiring an intervening oxide layer. The resulting monolayers are similar to those formed on oxidized silicon.

We argue that these results can be explained by the presence of a thin water layer on the surface.

II. EXPERIMENT

Boron-doped Si(100) wafers with resistivity in the range 1–50 Ω cm were used as substrates. The Si₃N₄ films were grown by low-pressure thermal chemical vapor deposition using an ammonia and silane gas mixture (flow rate ratio NH₃/SiH₄ = 100). The substrate temperature was 800 °C; the total pressure was 150 mTorr; the deposition time was 100 s; and the thickness of the Si₃N₄ film (refractive index = 2) was about 2000 Å as measured by ellipsometry.

Samples cut from the Si₃N₄-coated Si(100) wafers were degreased ultrasonically in chloroform. The natural oxide layer on the Si₃N₄ film was removed by etching with concentrated hydrofluoric acid for 1 min. The sample was rinsed several times in deionized water (resistivity = 18 MΩ), then dried using nitrogen. Monolayers were formed by placing the Si₃N₄ samples in a 2.5 mmol solution of the alkyltrichlorosilane precursor dissolved in 4:1 hexadecane:chloroform for 1 h at room temperature. The samples were then ultrasonically washed in chloroform to remove excess reactants and dried with nitrogen.

For comparison, monolayer formation was studied on two other substrates. One was oxidized silicon treated with HF to remove contaminants. The monolayer preparation method on oxidized silicon has been described previously. The second substrate was hydrogen-terminated Si(100) prepared through ammonium fluoride etching following the procedure described in Ref. 9. Finally, monolayers were produced using octadecyl(dimethyl)chlorosilane (ODMS) as a precursor on both Si₃N₄ and SiO₂. Because this molecule has only one chlorine atom attached to the silicon head group, it was expected to form few or no cross linking bonds. Silanization was performed at 10 °C for 6 h at a concentration of 5 mmol.

Samples were examined in two different ultra-high-vacuum chambers, both of which have been described previously. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Kratos XASAM-800 spectrometer using a Mg Ka source run at 15 kV and 10 mA. The binding energy scale was calibrated to 284.6 eV for the

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main C(1s) peak. Each sample was analyzed at a 90° angle relative to the electron analyzer. Peak areas were calculated using Shirley background subtraction and were corrected by the elemental sensitivity factors. All high-resolution electron energy-loss spectroscopy (HREEL) spectra were obtained using the LK Technologies LK3000 spectrometer in the specular mode with an incident electron energy of 6 eV; sample temperature was held at 120 K. The resolution of the elastic peak was typically between 40 and 50 cm\(^{-1}\) at about 10\(^4\) cps. The spectra were unchanged even after several hours of exposure to the incident electron beam. Contact angle analysis was performed using a model A-100 Ramé-Hart NRL goniometer to measure water contact angles in room air using the Sessile drop method.

### III. RESULTS

#### A. Structure of alkylsiloxane monolayers on Si\(_3\)N\(_4\)

An XPS spectrum for Si\(_3\)N\(_4\) following HF treatment is shown in Fig. 1(a). The water contact angle of this surface was about 30°. The Si(2p) peak is observed at 101.5 eV, indicative of silicon in a Si\(_3\)N\(_4\) matrix. The spectrum indicates the presence of silicon and nitrogen in stoichiometric 3:4 ratio, along with submonolayer coverages of carbon, oxygen, and fluorine. The peak area ratios for these elements, corrected by the elemental sensitivity factors, are summarized in Table I.

Figures 1(b)–1(d) show the XPS spectra of alkylsiloxane-coated Si\(_3\)N\(_4\) surfaces as a function of chain length. The presence of the monolayers is indicated by a large increase in the carbon and oxygen peak intensities, and a decrease in the silicon and nitrogen peak intensities. The carbon peak intensity increases as the chain length increases, and is due to the alkyl chains of the monolayers. The increase in oxygen intensity is due to the Si–O–Si bonds, which are formed between the head groups and the substrate, and the cross-linking bonds between head groups. The oxygen peak is most intense for the shortest monolayer, and decreases in intensity as the chain length increases. Approximately the same amount of oxygen should be present for all chain lengths; a smaller intensity is observed for the longer chain lengths because of photoelectron attenuation effects (i.e., the thicker the carbon film, the weaker the photoelectron intensity originating from the underlying oxygen atoms). The water contact angles for these samples were 110° for \(n=18\), 106° for \(n=8\), and 100° for \(n=4\), in good agreement with the values reported on SiO\(_2\).

#### B. Comparison to monolayers on SiO\(_2\) and hydrogen-terminated Si(100)

For comparison, OTS monolayers were also formed on oxidized silicon using the preparation method described previously. The surface was etched for 1–2 s in dilute HF prior to the SAM deposition process. The water contact angle changed from less than 30° before SAM deposition to 110° after deposition. The C(1s)/Si(2p) peak area ratio (Table I) is similar for both OTS-coated SiO\(_2\) and Si\(_3\)N\(_4\), consistent with the contact angle data suggesting that the monolayers are similar in quality on both surfaces.

To examine the effect of the submonolayer of oxygen remaining on the HF-treated Si\(_3\)N\(_4\), attempts were made to prepare monolayers on Si(100) (not a silicon nitride film) containing various amounts of oxygen. The Si(100) surface was first treated with NH\(_4\)F, which is known to etch away the surface oxide and terminate the surface with hydrogen. It has been shown that this surface oxidizes slowly, with the equivalent of a monolayer of oxygen building up after about seven days exposure to room air with 50% relative humidity. After treatment with NH\(_4\)F, samples were allowed to oxidize in air for a given amount of time. The amount of oxygen was checked by XPS. The samples were then placed in an OTS solution identical to that used to prepare monolayers on Si\(_3\)N\(_4\). For freshly prepared samples, which contained approximately 0.1 monolayer of oxygen, the water contact angle was 84°. Following immersion in the OTS solution, the contact angle remained 84°, indicating that monolayers did not form on this surface. The same procedure was carried out on a sample exposed to air, with approximately 1 ML of oxygen present and a water contact angle of 75°. Following the OTS deposition procedure, the

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**Figure 1.** X-ray photoelectron spectra of (a) Si\(_3\)N\(_4\) with no monolayers, (b) BTS-coated Si\(_3\)N\(_4\), (c) octyltrichlorosilane-coated Si\(_3\)N\(_4\), and (d) OTS-coated Si\(_3\)N\(_4\). In each case, the Si\(_3\)N\(_4\) was etched with HF before being placed in the monolayer solution.

**Table I.** Peak area ratios (estimated coverages) of elements as calculated from XPS results. The peak areas have been corrected by elemental sensitivity factors (Ref. 11).

<table>
<thead>
<tr>
<th>Sample</th>
<th>C(1s)/Si(2p)</th>
<th>O(1s)/Si(2p)</th>
<th>F(1s)/Si(2p)</th>
<th>Si(2p)/N(1s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF-etched Si(_3)N(_4)</td>
<td>0.23 (0.7 ML)</td>
<td>0.08 (0.2 ML)</td>
<td>0.13</td>
<td>0.76</td>
</tr>
<tr>
<td>C(_8) on Si(_3)N(_4)</td>
<td>1.1</td>
<td>0.72</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>C(_8) on Si(_3)N(_4)</td>
<td>1.3</td>
<td>0.43</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>ODMS on Si(_3)N(_4)</td>
<td>1.7</td>
<td>0.34</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>ODMS on SiO(_2)</td>
<td>0.35</td>
<td>0.14</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>HF-etched SiO(_2)</td>
<td>0.24</td>
<td>0.55</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>C(_8) on SiO(_2)</td>
<td>1.6</td>
<td>0.59</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>ODMS on SiO(_2)</td>
<td>0.43</td>
<td>0.63</td>
<td>0.02</td>
<td></td>
</tr>
</tbody>
</table>
C. Thermal stability

Thermal studies of different monolayer systems show that the thermal stability of the monolayers is sensitive to the head group–substrate bonding. For example, alkyl monolayers directly bonded to silicon through a Si–C bond desorb at about 620 K, about 100 K lower than alkylsiloxane monolayers, through a hydrogen elimination reaction. Alkanethiols on Au desorb as entire chains between about 450 and 500 K through breakage of the relatively weak Au–S bond. Hence, we have used HREELS to study the thermal behavior of alkylsiloxane monolayers on Si$_3$N$_4$ as another means of comparing these monolayers to those formed on SiO$_2$.

A typical HREEL spectrum for butyltrichlorosilane (BTS)-coated Si$_3$N$_4$ is shown in Fig. 2(a). The presence of the monolayers is indicated by the C–H stretch at 2920 cm$^{-1}$ and the C–H bend at 1450 cm$^{-1}$. Qualitatively, the features are very similar to those of BTS-coated oxidized silicon reported previously. The Si–N stretch appears at 1050 cm$^{-1}$ (Ref. 19) and may have a contribution from Si–O–Si bonds of the head groups, which result in a peak at 1060 cm$^{-1}$. HREEL spectra for BTS-coated Si$_3$N$_4$ as a function of annealing temperature are shown in Figs. 2(b)–2(d). Qualitatively, the features are very similar to those of BTS-coated oxidized silicon reported previously. The reader is referred to Ref. 8 for a detailed discussion of the spectra. Briefly, the monolayers are stable up to about 720 K. After annealing to 750 K, the intensity of the C–H stretch decreases and its shape changes. On oxidized silicon, two peaks were resolved at about 2920 and 2980 cm$^{-1}$. In the present case these peaks cannot be resolved, but the shifted position of the C–H stretch is consistent with the positions observed in the previous report. The same C–H bend at 1400 cm$^{-1}$ that was observed on the oxidized silicon surface is observed here upon annealing to 785 K. These peaks were assigned to the appearance of Si–CH$_3$ species on the surface following the initial desorption step and indicated that the chains decomposed through breakage of C–C bonds. The observation of the Si–CH$_3$ umbrella mode at 1260 cm$^{-1}$ is further confirmation of the presence of Si–CH$_3$; this peak could not be resolved on the oxidized silicon surface because of the intensity of the nearby Si–O–Si asymmetric stretch. The intensities of the Si–N–Si modes increase, with the symmetric Si–N–Si stretch at 800 cm$^{-1}$ becoming more apparent. These changes indicate that monolayer desorption occurs in a manner similar to that of monolayers on oxidized silicon surfaces (i.e., through C–C bond cleavage), and hence, must be bonded to the Si$_3$N$_4$ surface in a similar manner.

D. Significance of cross linking

To probe the importance of head group cross linking, an ODMS-derived monolayer was prepared on both oxidized silicon and Si$_3$N$_4$. Because the ODMS precursor has only one chlorine atom per alkyl chain, the head groups cannot cross link as the trichlorosilane precursors can; at most, they are able to dimerize. Also, infrared (IR) studies of methylchlorosilane adsorption on silica found that trimethylchlorosilane adsors more readily than does methyltrichlorosilane; that is, the species which forms fewer Si–OH bonds adsorbs more readily. Thus, it is expected that the ODMS precursor would form surface bonds more readily than OTS-type precursors. XPS spectra of OTS [Fig. 3(a)] and ODMS [Fig. 3(b)] monolayers on SiO$_2$ show a much smaller increase in the carbon peak intensity for the ODMS-coated surface than for the OTS-coated surface. The intensity of the oxygen peak is greater for the ODMS-coated surface because there is less carbon present to attenuate the oxygen signal. Furthermore, the contact angle of the ODMS-coated surface is only 80°, compared to 112° for OTS-coated surfaces. These observations indicate that the cross-linking bonds play an important role in monolayer formation. The XPS spec-

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**Fig. 2.** HREEL spectra of BTS-coated Si$_3$N$_4$ (a) without annealing; (b) after annealing to 720 K; (c) after annealing to 750 K; and (d) after annealing to 785 K.

**Fig. 3.** X-ray photoelectron spectra of (a) OTS-coated SiO$_2$, (b) ODMS-coated SiO$_2$, and (c) ODMS-coated Si$_3$N$_4$. Each sample was etched with HF before being placed in the monolayer solution.
trum of ODMS-coated Si$_3$N$_4$, shown in Fig. 3(c), indicates that the monolayer formation is even poorer than on oxidized silicon, an observation that is supported by its lower water contact angle of 70°. These results are consistent with the fact that, compared to the oxidized silicon surface, the Si$_3$N$_4$ film has fewer Si–OH groups with which the chains can bond. At the same time, however, OTS-based monolayers can be formed on Si$_3$N$_4$ which are equivalent, as indicated by XPS and the contact angle, to those formed on oxidized silicon. These observations suggest that the formation of alkylsiloxane monolayers is more heavily dependent on the ability to form cross-linking Si–O–Si bonds than bonds between the chains and the surface.

IV. DISCUSSION

Previously, it has been suggested that an adsorbed water layer plays a key role in alkylsiloxane monolayer formation. An IR study of the formation of alkylsiloxane monolayers on a silica surface showed that few, if any, chain–substrate bonds form between hydrolyzed OTS and the silica surface. In another study, it was found that for an untreated gold surface, one which would not have a water layer, monolayer formation was poor. By oxidizing the gold surface, however, through 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 bonding between the chains and the substrate is not necessary for forming high-quality films.

The present work further supports this picture. Oxidized silicon surfaces have about $5 \times 10^{14}$ Si–OH groups per cm$^2$. The XPS spectrum of the Si$_3$N$_4$ surface [Fig. 1(a)] shows that very little oxygen is present on this surface; thus, even if all of the observed oxygen is associated with OH groups, the density of reactive silanol sites with which the chains can bond is low and few if any chain–substrate bonds should be formed. Yet XPS, contact angle, and HREELS thermal stability results indicate that a well-ordered monolayer is formed that is similar to those formed on SiO$_2$. These observations demonstrate that bonding to the underlying substrate is not the primary mechanism for monolayer formation; cross linking must be of primary importance [see Fig. 4(a)]. The Si$_3$N$_4$ surface is hydrophilic, as indicated by the water contact angle of $<30^\circ$. Since the Si$_3$N$_4$ surface was exposed to room air before immersion in the monolayer solution, a layer of water is expected to be present on this surface prior to monolayer deposition. The water layer allows cross linking to occur between adjacent head groups. In contrast, on a Si(100) surface containing the same amount of oxygen, high-quality monolayers could not be formed. Even with 1 ML of oxygen, this surface has a relatively high water contact angle; thus, a layer of water would not be expected on this surface, hindering the formation of cross-linking bonds.

The ODMS-coated surfaces further demonstrate the importance of cross linking. In an earlier study, trimethylchlorosilane was found to adsorb more readily on silica than does methyltrichlorosilane. Based on this result, one might expect ODMS to adsorb more readily on the surface than OTS. However, with the possibility of forming only one Si-OH group per chain, the ability to cross link is greatly reduced [see Fig. 4(b)]. If monolayer formation were primarily determined by chain–substrate bonds, then the ODMS precursor molecule should result in monolayers that are equivalent to those resulting from OTS. XPS and contact angle data show that monolayer formation is quite poor, thus highlighting the significance of cross linking. The ODMS-derived monolayers are slightly better on oxidized silicon than on silicon nitride, most likely because of the higher density of silanol groups on the oxide surface.

In summary, alkylsiloxane self-assembled monolayers have been formed on Si$_3$N$_4$ surfaces. The monolayers are found to be very similar to those formed on oxidized silicon, both in their initial formation and their thermal stability. The formation on Si$_3$N$_4$, on which the density of silanol groups is low, indicates that bonding to the surface does not play a significant role in the chemistry of formation, thus pointing to the importance of cross linking. The poor quality of ODMS-derived monolayers, in which cross linking is not possible, confirms the importance of cross-linking bonds.

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