

Tailor-Made Functionalization of Silicon Nitride Surfaces

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Silicon nitride (Si_3N_x) is well-known for outstanding properties such as its mechanical hardness, chemical inertness, and high electrical resistivity.¹ These properties are used in a wide variety of applications. In contrast, the surface properties of Si_3N_x are still poorly defined and usually also changing over time. This situation significantly hampers the large-scale use of Si_3N_x in a variety of applications, such as microsieves. The way out is to provide a well-controlled and stable surface modification to Si_3N_x . While this was problematic up to now,² this paper presents the first surface modification of Si_3N_x via the covalent attachment of a well-defined organic monolayer onto hydrogen-terminated (H-terminated) Si_3N_x . In addition, preliminary data on its further functionalization are provided.

Such desirable flexible functionalization has been achieved on other, related surfaces, such as silicon. Over the past decade, a variety of methods has been developed to covalently attach organic monolayers to Si surfaces, by thermal^{3,4} mild photochemical⁵ or chemomechanical means.⁶ For example, reaction of 1-alkenes or 1-alkynes with H-terminated Si surfaces allows for the construction of tailor-made surfaces and have provided, e.g., the covalent attachment of DNA fragments⁷ and fragile carbohydrates.⁸ In contrast, modification of the Si_3N_x surface is largely limited to the functionalization of native SiO_2 that is present as a poorly defined, thin layer on Si_3N_x surfaces. For example, this procedure is used in the modification of Si_3N_x AFM tips to obtain specific substrate interactions.^{9,10} Other examples on Si_3N_x include a poorly defined monolayer of 1-octadecene (static water contact angle $\theta = 83^\circ$)¹¹ and a carboxylic acid-functionalized monolayer via the N-alkylation of an ω -bromoalkanoic acid.¹² However, no reaction analogous to the reaction of H-terminated Si with alkenes or alkynes has been reported on HF-treated Si_3N_x .

Low-stress silicon-enriched Si_3N_x surfaces (1 cm², 200 nm thickness) were deposited on polished silicon wafers using low-pressure chemical vapor deposition. The slightly higher than stoichiometric Si/N ratio may direct the chemistry of Si_3N_x towards the chemistry of silicon, e.g., H-termination by treatment with HF solutions and monolayer attachment. X-ray Photoelectron Spectroscopy (XPS) measurements show the presence of Si, C, N, O, and F in solvent-cleaned but unetched Si_3N_x (see Supporting Information).¹³ Prolonged exposure to HF leaves the nitride layer largely intact: almost complete removal of oxygen is observed, while there are no significant changes in the N signal (XPS data; see Figure 1). In addition, X-ray reflectivity measurements indicate no observable change in the Si_3N_x layer thickness upon etching.

The static water contact angle θ was found to increase from $\sim 20^\circ$ to $\sim 60^\circ$ after 2 min etching with 2.5% HF solution, indicating the formation of the less polar Si–H bonds. The presence of N (partially as NH and NH₂ sites at the surface) makes θ for the H-terminated

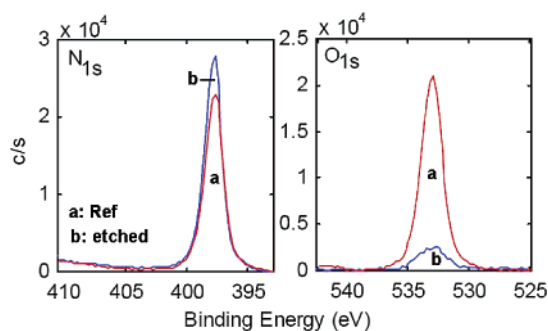


Figure 1. N_{1s} and O_{1s} XPS spectra of Si_3N_x before (a) and after (b) etching in 2.5% HF for 2 min.

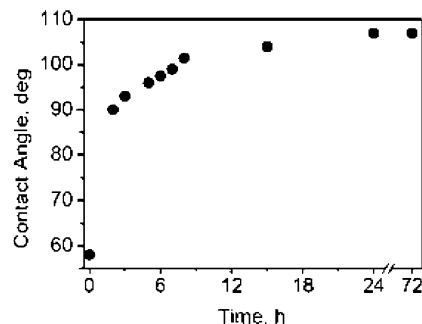


Figure 2. Variation of the static water contact angle θ of a 1-hexadecene-derived monolayer on Si_3N_x as a function of reaction time.

Si_3N_x surface lower than that obtained for H-terminated Si surfaces.³ The residual amount of oxygen that is observed after etching is at least partially due to deeply embedded atoms that cannot be removed upon etching but which are therefore not expected to be reactive at the surface.^{3,14}

Organic monolayers on this H-terminated Si_3N_x surface were prepared by placing the wafer in refluxing solutions of 1-alkene or 1-alkyne (0.4 M) in mesitylene¹⁵ or in neat 1-alkene at 165 °C.^{3a} The effect of the reaction time on the quality of 1-hexadecene monolayers on Si_3N_x , as studied by measuring θ is shown in Figure 2.

Stable and almost densely packed monolayers are obtained after ~ 24 h reaction time ($\theta \sim 107^\circ$). This is much better than that obtained without HF etching ($\theta \sim 83^\circ$),¹¹ which we attribute to the formation of reactive Si–H bonds at the surface upon HF etching. Modification of the Si_3N_x surface is much slower than Si modification under similar circumstances (~ 2 h),¹⁵ but θ is only a few degrees lower (vide infra).

Support for monolayer formation also comes from XPS C_{1s} spectra that show a clear increase in the amount of carbon upon modification after different time intervals (Figure 3). The C_{1s} signals due to the alkyl chain are not resolved from Si–C bond formation (284.9 and 283.1 eV, respectively).¹⁶ The shoulder at 286.9 eV that

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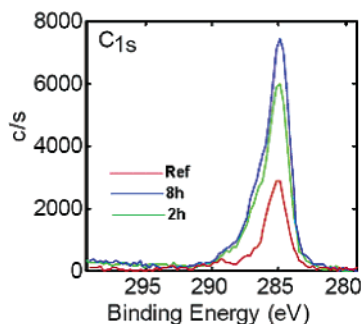


Figure 3. XPS C_{1s} spectra of Si_3N_x before (reference spectrum) and after monolayer attachment of 1-hexadecene, for 2 and 8 h, respectively.

Table 1. Water Contact Angle θ of Different Monolayers

compound (concentration)	$\theta \pm 1^\circ$
$CH_2=CH-C_{20}H_{41}$ (0.4 M)	102
$CH_2=CH-C_{16}H_{33}$ (neat)	107
$CH_2=CH-C_{16}H_{33}$ (0.4 M)	104
$CH_2=CH-C_{14}H_{29}$ (neat)	107
$CH_2=CH-C_{14}H_{29}$ (0.4 M)	106
$CH_2=CH-C_{12}H_{25}$ (0.4 M)	105
$CH_2=CH-C_{10}H_{21}$ (0.4 M)	106
$CH\equiv C-C_{16}H_{33}$ (0.4 M)	104
$CH\equiv C-C_{14}H_{33}$ (0.4 M)	103
$CH_2=CH-(CH_2)_8CO_2CH_2CF_3$ (0.4 M)	85

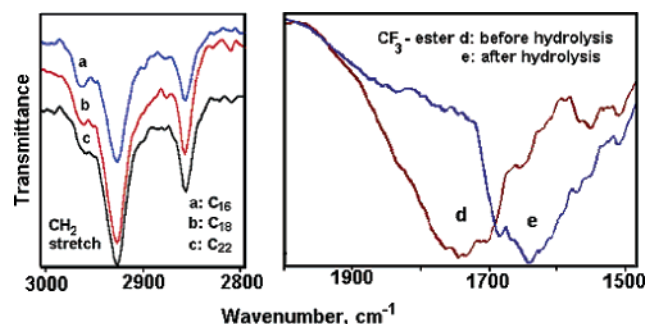


Figure 4. IRRAS data of modified Si_3N_x . (Left) CH_2 vibrations after reaction of Si_3N_x with different 1-alkenes. (Right) $C=O$ vibrations after reaction of Si_3N_x with $CH_2=CH-(CH_2)_8CO_2CH_2CF_3$, before (d) and after (e) hydrolysis.

appears only for modified Si_3N_x is likely due to N–C bond formation.¹⁶ No precise indication of the ratio of N–C and Si–C bond formation can be given at this stage, but both these data strongly support covalent monolayer attachment.

Increase of the 1-alkene concentration to neat reaction mixtures yields a rise of θ by 1° – 2° to $\sim 106^\circ$ – 107° (Table 1; 24 h reaction time), which points to the formation of an almost densely packed hydrophobic monolayer. This packing is no indication for high ordering in this case, as shown by infrared reflection absorption spectroscopy (IRRAS, 1 cm^{-1} resolution). IRRAS yields peaks corresponding to antisymmetric and symmetric CH_2 vibrations at 2926 and 2856 cm^{-1} , respectively (see Figure 4). These spectra strongly support the presence of a well-defined monolayer. In addition, they also point to a significant degree of disorder in these monolayers, as the peak at 2926 cm^{-1} resembles that obtained for CH_2 in isotropic media (2928 cm^{-1}) rather than that obtained in crystalline media (2914 cm^{-1}).^{5b} We attribute this disorder partially to the surface roughness of HF-etched Si_3N_x surfaces^{12,17} and likely also to a slightly diminished packing density of the monolayer.

Finally, functionalization of these monolayers has been shown via the attachment of a trifluoroethanol-ester derived alkene ($CH_2=CH-(CH_2)_8CO_2CH_2CF_3$). Attachment shows in IRRAS the

appearance of a $C=O$ stretching vibration at 1740 cm^{-1} , characteristic for the ester functionality. Hydrolysis of this moiety under basic conditions (0.25 M potassium *tert*-butoxide in DMSO) reduced θ from 88° to 44° . This was also visible in the IRRAS spectrum, which yields a shift of the $C=O$ stretch frequency from 1740 to 1640 cm^{-1} (Figure 4, right). Stability of the alkyl monolayer under these circumstances was shown by a near-constant intensity of the CH_2 stretching vibrations.

In conclusion, H-terminated Si_3N_x surfaces can be modified with a covalently attached organic monolayer upon reaction with 1-alkenes or 1-alkynes. These monolayers can undergo further functionalization, for example, via standard ester chemistry, similar to the case of modification of $Si^{4b,15}$. This opens up new entries to the controlled functionalization of Si_3N_x surfaces, as, e.g., present in microsieves or AFM tips. Such studies are currently in progress in our laboratories.

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Supporting Information Available: IRRAS, contact angle, and XPS data of etched and modified Si_3N_x . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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