

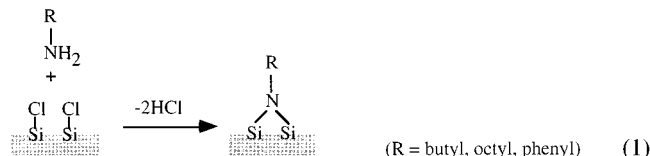
Assembly of Organic Molecules on Silicon Surfaces via the Si–N Linkage

W. F. Bergerson, J. A. Mulder, R. P. Hsung, and X.-Y. Zhu*

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

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The attachment of organic molecules to silicon surfaces is of interest for a number of future technologies. For example, molecules may serve as active components in hybrid molecule/silicon electronic devices^{1a} and as a lubrication layer in silicon-based microelectromechanical systems (MEMS).^{1b} There have been recent reports on Si surface attachment chemistry, including (i) hydrosilation between alkenes or alkynes with hydrogen-terminated Si,² (ii) the reaction of metal organic reagents with Cl-terminated³ or clean Si surfaces,⁴ and (iii) cycloaddition reactions on clean Si(100) in which the Si=Si surface dimer reacts with C=C or C=C–C=C to form 4- and 6-membered rings, respectively.^{5,6} These assembly processes have various advantages and shortcomings. For example, the cycloaddition reaction can yield well-ordered organic layers but requires clean Si(100) in ultrahigh vacuum (UHV) environment. The use of organolithium or Grignard reagent may not be compatible with some semiconductor processes where metal contamination of the surface should be avoided. The hydrosilation process yields dense organic layers, but it only works in the solution phase and reaction rates are relatively slow. All the above methods are based on the covalent Si–C linkage, which puts restrictions on the possibility of surface chemistry. Here, we report a novel approach for the efficient assembly of organic molecules on silicon using the Si–N linkage. It is achieved by reacting amine with chlorinated silicon surfaces to form an organic layer, as demonstrated in eq 1. This reaction



is sufficiently general for the assembly of a variety of functional organic molecules on silicon surfaces in both vacuum environment and solution phase. Ideas for the assembly chemistry presented here can be traced to well-known processes in the atomic layer growth of silicon oxide and nitride.⁷

The assembly reactions were carried out on two types of surfaces: clean Si(100) and porous Si in both UHV and solution phase. The clean Si(100)–(2 × 1) surface was prepared by heating a native oxide covered surface in UHV environment to above 1250 K. It was exposed to a saturation dose of Cl₂ in UHV at 300

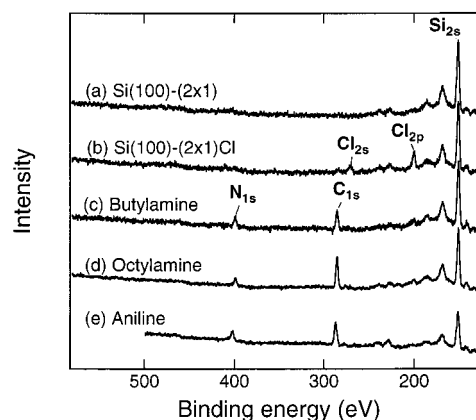


Figure 1. X-ray photoelectron spectra (XPS) for (a) clean Si(100)–(2 × 1), (b) Si(100)–(2 × 1)Cl, (c) C₄H₉N/Si(100), (d) C₈H₁₇N/Si(100), and (e) C₆H₅N/Si(100). The main peaks are labeled on each spectrum. The weak features at ~230 eV are from a small Ta clip used to attach a thermal couple to the Si sample. The Mg K α X-ray (1253.6 eV) was from an anode source (VG) operated at 200 W. Photoelectrons were detected by a hemispherical analyzer (VG100) with a pass energy (PE) of 100 eV. The binding energy scale was referenced to the substrate Si_{2p} peak (not shown) at BE = 99.3 eV.¹¹

Table 1. Ratios of Si_{2p} XPS Intensity between Each Surface Assembly and Clean Si(100)

<i>I</i> / <i>I</i> ₀ (Si _{2p})	C ₄ H ₉ N/Si(100)	C ₈ H ₁₇ N/Si(100)	C ₆ H ₅ N/Si(100)
expt	0.69 ± 0.07	0.67 ± 0.07	0.60 ± 0.06
calcd	0.75	0.59	0.66

K to form the monochloride Si(100)–(2 × 1)Cl surface,⁸ which was subsequently transferred to a high-vacuum reactor attached to the UHV chamber and exposed to amine molecules at a gas pressure of 1 × 10^{–2} Torr and a surface temperature of 450 K. A typical reaction time of 2 h converts over 95% of surface chlorine to organic molecules. The sample was transferred back to UHV for surface analysis by X-ray photoelectron spectroscopy (XPS).

Figure 1 shows a set of XP spectra for (a) clean Si(100)–(2 × 1), (b) Si(100)–(2 × 1)Cl, and the surface after attachment reactions with (c) butylamine (C₄H₉NH₂), (d) octylamine (C₈H₁₇NH₂), and (e) aniline (C₆H₅NH₂). After reaction with RNH₂ for 2 h, the Cl peaks become negligible while the C_{1s} and N_{1s} peaks appear. This result points to the near completion of the attachment reaction. Vibrational analysis of the surface assembly showed the absence of N–H stretch (see below). Based on stoichiometry, we believe the resulting organic layer corresponds to a surface coverage of 0.5 ML (molecule to surface Si atom ratio) with each molecule attached to the surface possibly via bonding to two silicon atoms, as illustrated in eq 1. This coverage is also consistent with XPS analysis, namely the depletion of substrate Si photoelectron intensity upon molecular layer formation. Table 1 compares experimental intensity ratios with predictions by using a simple atomic layer model in which each overlayer attenuates photoelectron intensity escaping from the underlying layer based on the following equation:⁹

$$I_i = I_{i-1}(1 - \theta) + I_{i-1} \cdot \theta \cdot \exp\left(-\frac{d_i}{\lambda \cos \alpha}\right) \quad (2)$$

where *I*_{*i*} and *I*_{*i*–1} are the substrate photoelectron intensities escaping from the *i*th and (*i*–1)th atomic overlayer, respectively. *I*₀ is the intensity from the clean surface; θ is the coverage of the atomic layer. θ is 0.5 for all atomic layers in the alkylamine assemblies, and for the first (N), second (C), and fifth (C) atomic

* To whom correspondence should be addressed: zhu@chem.umn.edu.
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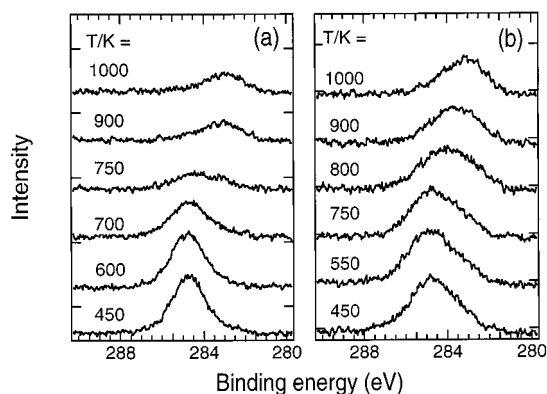


Figure 2. Panel a: C1s region of the XP spectra for the octylamine assembled surface, $C_8H_{17}N/Si(100)$, taken after the surface had been annealed at the indicated temperatures. Panel b: C1s region of the XP spectra for the aniline assembled surface, $C_6H_5N/Si(100)$, taken after the surface had been annealed at the indicated temperatures. The spectra were recorded at a surface temperature of 300 K under the same conditions as in Figure 1, except for PE which was set at 50 eV.

layers in the aniline assembly, and 1.0 for the third (C) and fourth (C) layers in the aniline assembly. The overlayer thickness, d_i , is simply chosen as the atomic diameter (1.4 and 1.3 Å for C and N, respectively). A universal mean free path of $\lambda = 18$ Å is used for the Si_{2p} photoelectron.¹⁰ The angle of detection is $\alpha = 50^\circ$ (from surface normal). Considering the simplicity of the model and the estimated experimental error range of $\pm 10\%$, the agreement between measurement and calculation is satisfactory. We note that, in the absence of detailed knowledge on the structure and ordering of the surface assemblies, the above analysis should only be considered semiquantitative.

The binding energy (BE) of the N_{1s} peak from all surface assemblies is 396.6 ± 0.2 eV. This binding energy corresponds to that of nitride species (396–398 eV; 397.4 eV for bulk silicon nitride) and is much lower than the typical value of ~ 399 eV for amine molecules.¹¹ The C_{1s} binding energy in the surface assembly is 284.7 ± 0.1 eV, as expected for hydrocarbons.¹¹ These binding energies provide strong support for the proposed mechanism in which the molecule is attached to the surface via the Si–N linkage. This conclusion is also consistent with well-established surface chemistry in the adsorption of NH_3 on silicon surfaces⁸ and in the atomic layer growth of Si_3N_4 .⁷

The thermal stability of the surface assembly is studied in UHV by recording XP spectra after annealing the surface at various temperatures. For N_{1s} , both peak position and intensity change only slightly upon heating. More significant change is seen in the C_{1s} region. Figure 2 shows annealing series of C_{1s} for octylamine and aniline assembled on Si(100). For the octylamine assembly (panel a), while the position of C_{1s} remains constant between 450 and 600 K, there is a small decrease in peak intensity. More significant decrease in intensity is seen above 600 K, indicating a loss of carbon-containing species from the surface upon heating. The remaining alkyl chain decomposes on the surface above 750 K, as evidenced by the shift in BE toward 283 eV, typical for carbides,¹¹ with increasing temperature.

The aniline assembled surface is thermally more stable than the alkyl layer, panel b of Figure 2. The XP spectra remain identical from 450 to 750 K, indicating no chemical change in this temperature window. A decrease in peak intensity and a shift in peak position are only seen at temperatures above 750 K.

We have also carried out the amination reaction on porous silicon. The porous silicon samples were prepared by using the

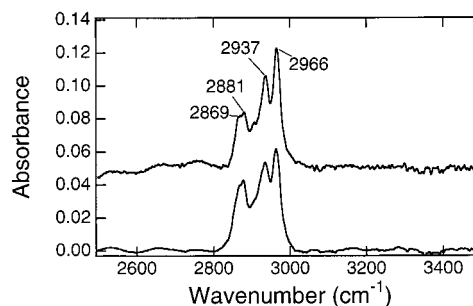


Figure 3. Transmission FTIR spectra for butylamine assembled on the chlorinated porous silicon surface. The surfaces were obtained from gas–surface reactions (upper) and solution-phase reactions (lower). The intensities of the two spectra have been normalized. The main peaks are 2966 and 2937 cm^{-1} for asymmetric C–H stretches in $-CH_3$ and $-CH_2-$, respectively, and 2869 and 2881 cm^{-1} for symmetric C–H stretches in $-CH_3$ and $-CH_2-$.

standard anodization procedure.¹² For the gas–solid assembly reaction, the hydrogen-terminated porous silicon sample is transferred to the UHV chamber. After heating to >900 K in UHV to desorb surface hydrogen, the sample is subject to the two-step chlorination and butylamine assembly reaction under conditions identical with those for Si(100) outlined above. The sample is then removed from UHV and characterized by transmission Fourier Transform Infrared (FTIR) spectroscopy under ambient conditions.

For solution-phase assembly, the hydrogen-terminated porous silicon sample was chlorinated in deoxygenated chlorobenzene at 100 °C for 1 h by using PCl_5 as a chlorine source and a catalytic amount of benzoyl peroxide as a radical initiator.^{3a} The chlorinated silicon sample was then immersed in deoxygenated butylamine at 80 °C for 24 h. At the end of the reaction, the sample was thoroughly rinsed with CH_2Cl_2 and dried on a vacuum pump (1 mmHg) before being characterized by FTIR. Figure 3 compares the FTIR spectra of butylamine assembled on porous silicon by using the gas–surface (upper) and the solution-phase (lower) assembly methods. Both give C–H stretch peaks (2869, 2881, 2937, 2966 cm^{-1}) characteristic of the butyl group. The absence of the N–H stretch peak (~ 3300 cm^{-1}) provides strong support for the proposed reaction mechanism in which the N atom is a bridge between two surface silicon atoms. Also seen consistently in these FTIR spectra are peaks at 1460 and 1220 cm^{-1} (not shown in Figure 3), which are the CH_2-CH_3 stretching frequency and the tertiary C–N stretching frequency, respectively. This further supports the notion that the N atom is likely bonded to two Si atoms on the surface, eq 1.

FTIR taken after air-exposure did not show significant change. XPS taken after the alkyl surface assemblies on Si(100) have been exposed to air also showed no significant change in N_{1s} or C_{1s} peaks. These point to the chemical stability of the organic layer.

In conclusion, a simple chemical approach is presented for the covalent assembly of organic molecules on silicon surfaces via the robust Si–N linkage. This is achieved by the efficient reaction between an amine functional group and a chlorinated Si surface. The N anchor is believed to be a bridge between two surface Si atoms. The resulting organic layer is thermally stable. The method demonstrated here is generally applicable for the assembly of a variety of functional organic molecules under vacuum environment or in solution phase.

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