

Formation of Organic Monolayers on Hydrogen-Terminated Silicon Surfaces *via* Silicon–Carbon Bond: Effect of Terminal Groups on Stability

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Introduction

Aryl-terminated alkyl self-assembled monolayers (the so-called σ - π SAMs) on silicon can function as thin film organic field effect transistors (OFET) since the alkyl (σ -bonded) part of the SAMs will act as the gate insulator while the terminal aryl groups (the π -electron moieties) can act as the active organic semiconductor. OFET based on such σ - π SAMs have been fabricated [1, 2] successfully. With π -moieties such as phenyl, retinol and pyrene large in-plane conductivities have been achieved without any hampering of the insulating behaviour in the perpendicular direction [1]. So for example, the ratios between the parallel and perpendicular conductivities ($g_{\parallel} / g_{\perp}$) for these moieties are of the order of $10^6 - 10^9$ when measured at room temperature. In addition, reasonably high charge carrier mobilities can be obtained. Mobilities of $\sim 0.05 \text{ cm}^2 / \text{V s}$ and on-off current ratios $> 10^5$ have been demonstrated with pyrene-terminated SAMs on Si [2].

Of the many functionalization procedures that exist in the literature, Grignard reagents have been reported to yield more densely-packed, thermally and chemically stable SAMs [3]. In the case of σ - π SAMs the additional inter-chain π - π stacking [2] between the terminal aryl groups affords much greater rigidity and higher packing density in these SAMs. A consequence of the dense structure is that the susceptibility to oxidation in both the SAMs and the underlying substrates is minimized. Examples of aromatic SAMs that have been shown to be contaminant-free for extended periods include 4-mercaptobiphenyl on GaAs(100) [4], 1,1'-biphenyl-4-thiol on GaAs(100) [5], 4, 4'-terphenyl-substituted alkanethiols on gold and silver substrates [6], and biphenyl-4-ol and p-terphenyl-4-ol on hydrogenated Si(111) [7].

In this paper we report on the formation of 3-phenylpropyl SAMs on hydrogen passivated porous silicon using phenylpropyl Grignard reagent. We also report results of octyl SAMs on hydrogen passivated Si(100), firstly to show the dens SAMs that can be obtained on a flat silicon surface using the Grignard reagent method, and secondly to compare the effect the non-aromatic CH_3 - terminal group will have on the chemical stability of the SAMs.

Experimental

Preparation of hydrogen-terminated Si(100) (H:Si(100)) and porous silicon (H:pSi). The H-terminated surfaces were prepared immediately prior to the functionalization step. In the case of Si(100) (p-type, 1–10 $\Omega \text{ cm}$) the samples were cleaned in a *piranha* solution (concentrated H_2SO_4 and 30% H_2O_2 in 3:1 v/v ratio) at 90 °C for 20–30 minutes followed by copious rinsing with MilliQ water. This was followed by etching in 5% HF solution for 1 minute, which removes the native oxide and leaves the surface hydrogen terminated. Note this surface is hydrophobic and emerges dry from the HF solution, an observation that was used to confirm the successful preparation of the H:Si(100) on a routine basis. The porous silicon samples were prepared from Si(100) wafer (p-type, 1–10 $\Omega \text{ cm}$) by electrochemical etching in ethanolic HF solution, followed by rinsing with a number of solvents. Prior to the functionalization step, the native oxide layer was removed first, as for Si(100) described above. The sample was then etched in 5 % HF in ethanol, followed by rinsing with ethanol.

FT-IR spectroscopy was used to confirm that the surface was hydrogen terminated. The H:Si(100) and H:pSi samples were dried under a stream of dry argon and then immediately transferred to the Schlenk reaction flasks containing the de-oxygenated Grignard reagent. The transfer of the silicon pieces into the Schlenk flask was performed under a continuous flow of dry nitrogen to prevent oxidation of the silicon samples.

Preparation of Grignard Reagents. A 1.5 M solution of 3-phenylpropylmagnesium bromide ($C_6H_5(CH_2)_3MgBr$) in THF was prepared from 1-bromo-3-phenylpropane. The octylmagnesium bromide (2.0 M solution in diethyl ether) was purchased from Aldrich, and was used as received

Functionalization of H:Si(100) and H:pSi with Grignard reagents. The freshly prepared H:Si(100) (H:pSi) sample was placed in the Schlenk tube containing ~20 mL of deoxygenated octylmagnesium bromide in diethyl ether (phenylpropyl magnesium bromide in THF) and the solution was warmed to 30 °C (70 °C) and maintained at that temperature under a dry nitrogen atmosphere, for at least 16 hours. The functionalized sample was then washed at room temperature with 1% solution of acetic acid in diethyl ether, MilliQ water and finally in dichloroethane. It was then dried under a stream of dry nitrogen.

Characterization Techniques. X-ray photoelectron spectra were recorded on a VG Scientific EscaLab 220IXL spectrometer with a monochromated Al K α source (1486.6 eV) using a pass energy of 20 eV on a concentric hemispherical analyzer. FT-infrared spectra were recorded using a Thermo Nicolet Avatar 370 FT-IR spectrometer, and measurements were made in the diffuse reflectance mode (in both specular and off-specular geometry) with a resolution of 4 cm⁻¹. Water contact angle measurements were conducted using a Ramé-Hart Imaging System, and were made only for octyl SAMs. Measurements of equivalent, advancing and receding angles were performed using MilliQ water under ambient conditions. All three angle measurements were made at different locations on the surface so as to check the homogeneity of the SAMs.

Results and Discussion

Phenylpropyl SAMs on Porous Silicon. XP spectrum taken over the C 1s region (Figure 1(a)) shows a single symmetrical peak at a binding energy of 285.1 eV which is attributed to the carbons in the SAMs. Note it was not possible to distinguish between the aromatic and aliphatic carbons in the SAMs at the resolution used in the study. However, we see a small peak at 292 eV binding energy, which is attributed to the $\pi \rightarrow \pi^*$ transition due to the presence of benzene ring in the SAMs [8].

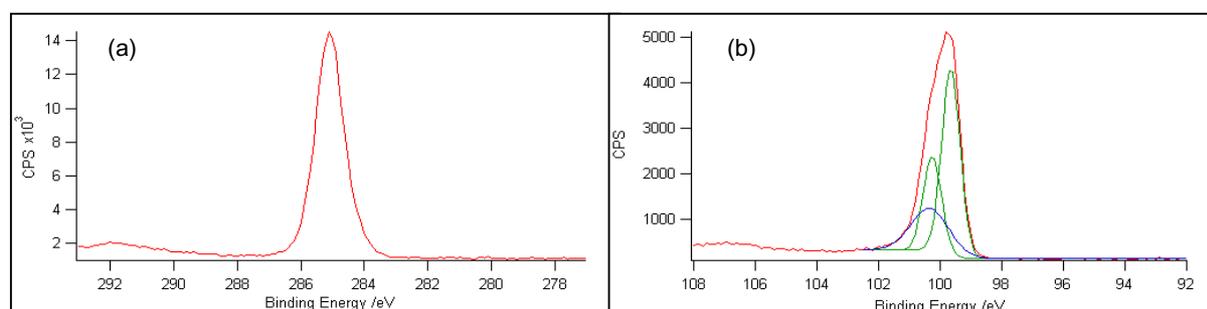


Figure 1: XP spectra of phenylpropyl SAMs on hydrogen terminated porous silicon, (a) C 1s region, (b) Si 2p region with the fits to spin orbit split $2p_{1/2}$ and $2p_{3/2}$ to the substrate peak plus the unresolved chemically shifted Si 2p peak due Si-C bond formation are also shown.

No evidence for adventitious or oxidized carbon exists in the spectrum. The spectrum in Figure 1 (b) shows an asymmetrical Si 2p peak, which can be deconvoluted into the

spin-orbit split $2p_{3/2}$ and $2p_{1/2}$ components to yield binding energy values at 99.7 and 100.3 eV, respectively. The broad feature at 100.8 eV is the unresolved chemically shifted Si 2p peak mainly due to the formation of Si-C bonds between the SAMs and the silicon surface. Of noteworthy is the absence of the chemically shifted Si 2p feature due to the surface SiO_2 , expected at ~ 102 eV binding energy. This suggests that oxidation of the surface silicon atoms either during or after the functionalization step did not occur.

Infrared spectrum of the same surface taken in the $4000 - 400 \text{ cm}^{-1}$ range (not shown) showed all vibrational features associated with the phenylpropyl SAMs, plus peaks associated with Si-H bonds. We observed aromatic (=C-H) antisymmetric (3066 cm^{-1}) and symmetric (3029 cm^{-1}) stretches; the corresponding aliphatic C-H stretches at 2924 and 2848 cm^{-1} respectively; aromatic C=C stretch at 1606 and 1495 cm^{-1} ; H-C-H deformation in CH_2 at 1450 cm^{-1} ; aromatic C-H deformation at 700 cm^{-1} . The Si-C stretch at 610 cm^{-1} was observed as a small peak in the spectrum. The presence of peaks at 2090 and 908 cm^{-1} , due to SiH_x ($x = 1, 2, 3$) and Si-H stretches, respectively, [9] suggests that not all Si-H bonds are converted to Si-C bonds during functionalization. The absence of the Si-O asymmetric and symmetric stretches, expected at 1106 and 517 cm^{-1} , respectively, arising from Si-O-Si or Si-O-C bonds, confirmed no oxidation of the Si-H of the Si-C bonds had occurred either during or after functionalization, showing that the phenylpropyl SAMs formed is robust.

Octyl Self-Assembled Monolayers on Si(100). The C 1s spectrum in Figure 2(a) shows a single peak at 284.9 eV binding energy. This peak is symmetrical, which suggests that adventitious carbon or oxidized carbons are minimal, and hence the peak intensity is entirely due to the aliphatic carbons in the octyl SAMs. The Si 2p spectrum presented in Figure 2(b) shows a much more defined $2p_{3/2}$ and $2p_{1/2}$ spin-orbit splitting than the porous silicon sample due to the higher crystallinity in the Si(100) substrate. However, no chemically shifted Si 2p feature due to the Si-C bond formation is discernible in this case, which we attribute to the lower coverage of the octyl overlayer achievable on this flat Si(100) surface. The broad feature centred at ~ 102 eV is due to the chemically shifted Si 2p feature due to the surface SiO_2 , and its peak intensity relative to the bulk Si 2p is approximately 11%. The XP spectrum taken over the O 1s region (not shown) showed a single peak at 532.2 eV binding energy.

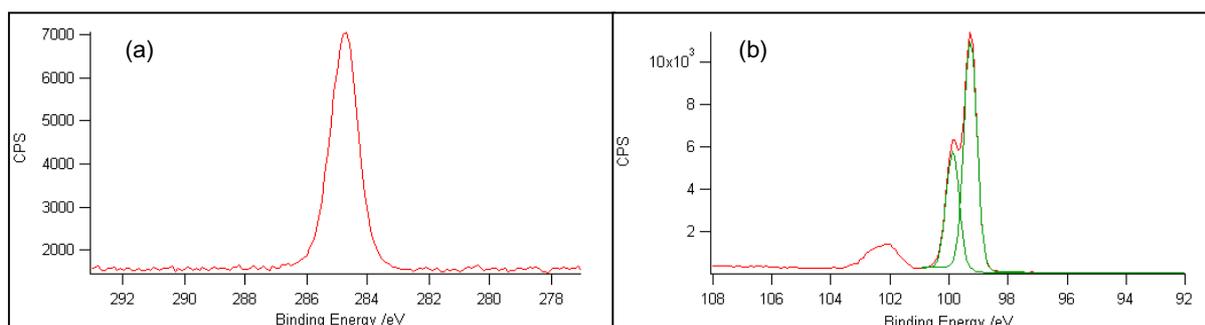


Figure 2: XP spectra of octyl SAMs on hydrogen terminated Si(100), (a) C 1s region, (b) Si 2p region with the fits to spin orbit split $2p_{1/2}$ and $2p_{3/2}$ to the main peak also shown.

Contact angle measurements yielded an average equivalent angle of $99 \pm 3^\circ$, higher than the untreated / oxidized silicon value of 72° (Figure 3), and which is higher than the $93 \pm 2^\circ$ value reported for decyl SAMs on Si(111) [10]. This value suggests the octyl SAMs is highly hydrophobic, and hence possesses a high packing density, and that the terminal methyl groups are exposed more than the methylene units in the chains. Although a dense octyl SAM layer is formed some oxidation of the surface still occurs, and we believe the unreacted Si-H bonds provide sites for oxidation rather than the Si-C bonds.

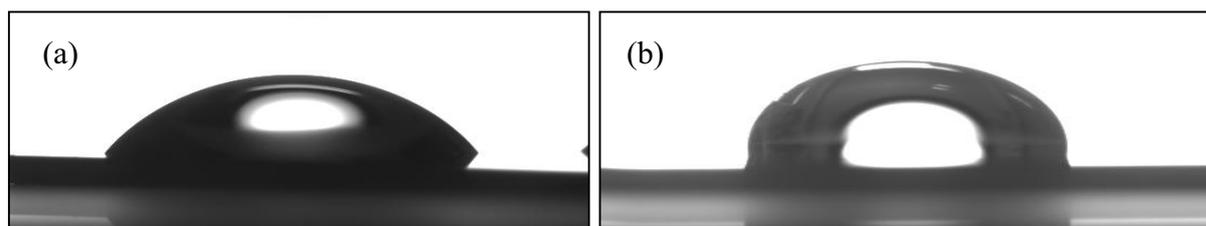


Figure 3: Water contact angle images on (a) untreated / oxidized Si(100), (b) Octyl SAMs formed on hydrogen terminated Si(100).

While further quantification of the SAMs surface coverage and the morphologies is warranted, for example by X-ray reflectivity measurements, the very high water contact angle obtained for octyl SAMs on Si(100) suggests a dense surface layer. However, IR measurements of the phenylpropyl SAMs show that Si–H bonds still remain after the functionalization step implying the coverage to be less than 1 ML, and we expect a similar scenario for octyl SAMs on Si(100). This observation was not entirely unexpected as the bulky octyl / phenylpropyl chains of the SAMs cannot be accommodated on the neighbouring silicon atoms due to steric hindrance effects [10]. Oxidation of the unreacted Si–H bonds on Si(100) occurs, not by direct attack of the Si–H bond but more likely via back-bond oxidation involving the bulk silicon–silicon bond in $\text{Si}=\text{SiH}_2$, as shown previously in a study which investigated the reactivities of hydrogen terminated Si(100) and Si(111) [11]. The fact that the surface becomes oxidized in the case of octyl SAMs and not in the case of phenylpropyl SAMs suggests that the terminal groups (CH_3 - vs phenyl- (C_6H_5 -)) play a major role in controlling the chemical reactivities of the two SAMs. The octyl SAMs with its non-bulky methyl terminal group in essence exhibits an open structure and exposes the unreacted Si–H bonds more to the moisture and oxygen in the atmosphere than the phenylpropyl SAMs. In the latter SAMs the added intermolecular forces of attraction between the phenyl terminal groups via π - π interactions yields a more rigid, highly oriented and a much less open structure and hence the oxidation of the silicon atoms is minimized. This observation is consistent with the previous investigations of aromatic SAMs on GaAs(100) [4, 5], Si(111) [7], and gold and silver surfaces [6] noted above.

Conclusions

Phenylpropyl and octyl SAMs were successfully formed on hydrogen terminated silicon surfaces from the respective Grignard reagents in a one-step functionalization procedure under mild conditions. These SAMs were characterized by XPS, FT-IR and contact angle measurements. It was found that the phenylpropyl SAMs with the terminal phenyl groups were chemically more stable, not undergoing oxidation upon exposure to atmosphere.

References

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