

Phenyl-Terminated Self Assembled Monolayers on Si(100) for Low Voltage Transistor Applications

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ABSTRACT

This paper reports on the structural studies of 3-phenyl propyl and 9-benzyloxynonanyl self-assembled monolayers (SAMs) on Si(100). Surface compositional analysis of both SAMs reveal they are robust and do not undergo oxidation over extended periods. Scanning tunneling microscopy reveals that both SAMs exhibit dense layers which is attributed to the π - π stacking between the phenyl rings. The C9 SAMs shows more dense packing with a distance of <0.5 nm between the phenyl rings whereas the C3 SAMs shows a distance of 0.6 nm. The effect of the alkyl chain length on the π - π stacking and density of SAMs is discussed.

Keywords: self-assembled monolayers, scanning tunneling microscopy, silicon, organic thin film transistors.

INTRODUCTION

A key problem with the existing thin film organic field effect transistor is their large operating voltage (> 20 V) due to the relatively thick (>50 nm) gate insulating layer (e.g. SiO₂) which has to date restricted their applications in nano-field effect transistors¹. Efforts to reduce the insulator thickness have not been successful, as silica for example with thickness <5 nm has serious problems with leakage currents due to defect-assisted tunnelling. A solution to this problem is to eliminate oxides as the insulator material and to use alkyl chains in self-assembled monolayers instead. The leakage current through these alkyl chains have been shown to be remarkably low, despite their thickness of only a few nanometers²⁻⁴. Aryl-terminated alkyl self assembled monolayers deposited onto oxide-free silicon, forming dense and stable organic-inorganic nanohybrid architectures, offer promise of transistor with very thin insulator layer. Additionally the aryl terminal groups can be used to direct the growth of the overlayer organic semiconductor eg., pentacene, in a highly controllable

manner to yield highly crystalline material. The end-product is expected to be a transistor that can be operated at low voltages and at the same time will exhibit much higher electron mobilities.

While aryl-terminated have been studied on gold surfaces there are only a limited number of studies of these SAMs on oxidized silicon. There are no studies where the SAMs have been formed onto the silicon via Si-C bond. We have thus commenced structural and thermal studies of aryl-terminated alkyl SAMs, of varying alkyl chain lengths, on hydrogen-terminated Si(100), and in this paper report present key results for 3-phenyl propyl (C3) and 9-benzyloxynonanyl (C9) SAMs.

2 RESULTS & DISCUSSION

The SAMs were formed by the reaction of the corresponding Grignard reagents with the hydrogen-terminated Si(100). The composition and functionalities in the layers were studied using X-ray photoelectron and FT-Infrared spectroscopies while the morphology and surface geometry were studied using scanning tunneling microscopy and X-ray reflectivity measurements.

2.1 3-phenyl propyl SAMs

The water contact angle measured for the 3-phenyl propyl SAMs yielded an angle of $90\pm 3^\circ$, which is much higher than the 45° contact angle on oxidized Si(100), but lower than the 112° contact angle for methyl-terminated octadecyl SAMs⁵ on the same surface.

The XP spectrum of the SAMs was taken over the C 1s and Si 2p regions using a monochromated Al K α X-ray source for compositional analysis. In Figure 1 the C 1s region is presented, and shows a symmetrical peak centred at 284.5 eV with a FWHM of 1 eV. This binding energy corresponds to aromatic and aliphatic carbons, and the

small FWHM suggests that the monolayer is of uniform composition and morphology, with minimum (if any) incorporation of adventitious carbon into the monolayer or oxidation of the alkyl chains occurred during functionalization.

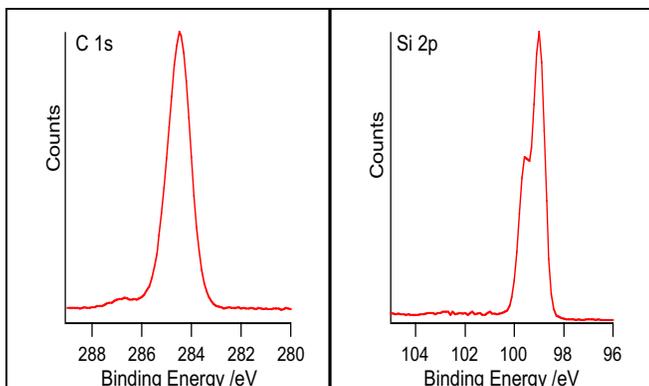


Figure 1: XPS spectra, taken over C 1s and Si 2p regions, of 3-phenylpropyl SAMs on Si(100).

The Si 2p spectrum (Figure 1) shows the $2p_{3/2}$ and $2p_{1/2}$ spin-orbit peaks at 99.0 and 99.7 eV binding energies. The monolayer coverage on the surface means no chemically shifted Si 2p peaks due to Si-C bond formation could be detected. Note also no chemically shifted Si 2p feature due to SiO_2 , expected at ~ 102 eV, is present which suggests that oxidation of the surface silicon atoms either during or after the functionalization step did not occur, similar to our previous investigation of 3-phenylpropyl SAMs on porous silicon.

Infrared spectrum of the SAMs taken in the $4000\text{--}700$ cm^{-1} range (not shown) showed vibrational features associated with the propyl component of the SAMs but not all features associated with the phenyl component were present. Hence we observe the aliphatic anti-symmetric (2924 cm^{-1}) and symmetric (2854 cm^{-1}) C-H stretches, aliphatic antisymmetric H-C-H deformation in CH_2 at 1458 cm^{-1} , C-H in-plane bending mode at 1253 cm^{-1} . Although there is no evidence of modes associated with aromatic anti-symmetric and symmetric C-H stretches, expected in the range 3080 and 3030 cm^{-1} , modes associated with the phenyl ring are present. The ring C=C stretching modes at 1595 and 1381 cm^{-1} , and the out-of-plane ring deformation mode at 820 cm^{-1} are observed.

An STM image, measured in air at room temperature with typical tip-sample bias voltages of up to 1500 mV and tunneling currents up to 100 pA, is presented in Figure 2.

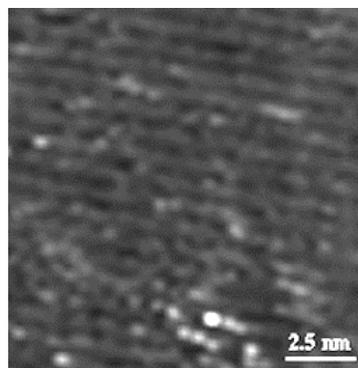


Figure 2: STM image of 3-phenylpropyl SAMs on Si(100).

The low magnification image had shown islands of 3-phenylpropyl SAMs assembly with domain sizes ranging between 20–60 nm. The higher magnification image shows (Figure 2) shows SAMs organized in rows and typical molecular features of a well-ordered monolayer. The STM of hydrogen-terminated Si(100) exhibits rows, and since the functionalization with the SAMs by reaction with Si-H bonds on alternate Si atoms (due to geometrical constraints) then the appearance of rows for SAMs was not unexpected. Line profiles of this image reveal an apparent distance of 0.6 nm between the phenyl rings, suggesting a densely packed monolayer exists, and is smaller than the calculated distance of 7.5 Å, being equal to two Si-Si bond distances of 3.78 Å.⁶ We believe the dense layer is due to some π - π stacking that must exist between the phenyl terminal groups, also observed previously for 18-phenoxyoctadecyl SAMs on oxidized silicon⁷. The 0.6 nm distance is larger than the 3.5 Å distance reported for benzene rings exhibiting π - π interactions in the solid phase⁸. The likely reason for this shorter distance is the absence of any appreciable translation of the SAMs on the surface due to the fixed Si-Si bond distance, which is different from metal surfaces where mobility of species can be appreciable, and combined with the short C3 chain means that the closest between the phenyl rings will be somewhat limited. Analysis of the STM in conjunction with scanning tunneling spectroscopy data also suggests that the alkyl chains are slightly tilted away from the surface normal. However, the fact that the alkyl chain has an odd number of methylene units means that the terminal phenyl groups will have the C1-C4 axis orientated slightly ($\sim 30^\circ$) away from the surface normal⁹. This is consistent with the observation that the aromatic C-H bond stretches in the FT-IR spectrum are absent, the reason being that the C-H bonds in the tilted phenyl ring do not make contributions to the perpendicular component of the molecular dipole, a requirement before any vibrational mode from species adsorbed on atomically-flat surfaces can be detected.

2.2 9-benzyloxynonanyl SAMs

Contact angle measurements of $\sim 80^\circ$ were typically obtained for this SAMs, less than achieved for the shorter phenylpropyl monolayer. The reason for this is that in this case the polarity of the terminal group is enhanced by the presence of the nearby ether linkage ($-\text{H}_2\text{C}-\text{O}-\text{CH}_2-$) which increases hydrophilicity. However, the value is high in comparison to the $\sim 88^\circ$ value obtained for a longer chain phenoxyundecyl SAMs on Si/SiO_x surface¹⁰.

XP spectra taken over the C 1s region of the C9 SAMs showed a prominent peak at 285 eV, attributed to carbons in the phenyl groups and in the alkyl chain not adjacent to the oxygen, and a second peak at 286.5 eV, attributed to the two carbon peaks adjacent to the oxygen. The peak intensity ratio of the 285 eV peak to the 286.5 eV peak is 0.87:0.13, consistent with the composition of the 9-benzyloxynonanyl chain. The Si 2p region, as for 3-phenyl propyl SAMs shows the 2p_{3/2} and 2p_{1/2} spin-orbit peaks at 99.0 and 99.7 eV binding energies, and no evidence of chemically-shifted peak expected at ~ 102 eV had oxidation of the surface had occurred during and following functionalization.

As for the infrared spectrum of the C3 SAMs above the C9 SAMs showed the vibrational characteristics of the aliphatic chain and ring stretching and deformation modes and there was an absence of the aromatic C-H modes. Additionally, peaks at 1057 and 878 cm⁻¹ attributable to C-O-C antisymmetric and symmetric stretches were observed. The aromatic C-H stretch was again not discernible implying that the terminal phenyl groups most probably lie parallel to the surface.

STM image acquired of the C9 SAMs show rows, as for the C3 SAMs, of SAMs layers at low magnification (not shown) and at higher magnification (Figure 3) features due to the terminal phenyl rings become discernible. However the distance between the phenyl rings is smaller than that for the C3 SAMs, being less than 5 nm, confirming that the C9 SAMs has much higher packing density. Basic molecular modeling conducted to determine the actual geometry reveals that of the phenyl rings of the SAMs are tilted away by 30° relative to the alkyl chains¹¹. The alkyl chains, as we show below using the X-ray reflectivity data, are tilted away from the surface normal by 35°. This resting geometry allows the phenyl terminal rings to approach each other more closely and become more parallel to the surface.

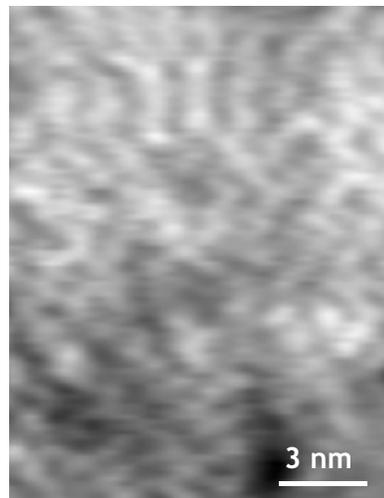


Figure 3: STM image of 9-benzyloxynonanyl SAMs on Si(100).

In order to further characterize the benzyloxynonanyl SAMs X-ray reflectivity measurements were conducted and the data, plotted as normalized reflectivity versus momentum transfer Q_z , are presented in Figure 4. Unlike the smooth Fresnel-like decay obtained for unfunctionalized silicon the C9 SAMs covered surface shows a clear interference minimum at approximately 0.22 Å⁻¹.

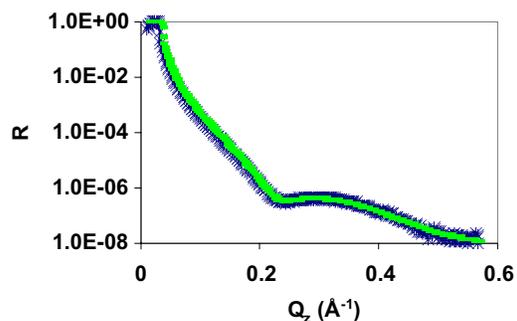


Figure 4: Reflectivity versus Q_z plotted for C9 SAMs

By fitting the reflectivity data to a standard formalism, the film thickness was determined to be 14 Å. Since the calculated length for a fully stretched chain is 18 Å the tilt angle of the alkyl chains in the SAMs is found to be $\sim 35^\circ$, greater than the 15° found in our studies of dodecyl SAMs on oxidized Si(100). The larger tilt angle in the case of benzyloxynonanyl SAMs arises due to its larger terminal group, which forces the SAMs to adopt a more tilted geometry. The calculated molecular surface area for each hydrocarbon chain is 25.2 Å², which is equivalent to 3.97 x

10^{14} alkyl chains / cm^2 of surface. On the Si(100) surface there are 6.78×10^{14} atoms/ cm^2 and hence the SAMs occupy approximately half the surface sites. This observation is consistent with previous studies which have shown that not all possible sites become occupied by alkyl chains because of steric hindrance¹².

3 CONCLUSIONS

This study has shown that phenyl-terminated alkyl SAMs exhibit dense morphology and form large domains on Si(100), when compared to methyl terminated alkyl SAMs of comparable chain lengths. The dense nature of the SAMs is attributable to the additional π - π stacking that can occur between the phenyl rings on adjacent chains. The distance between the phenyl rings depends on the alkyl chain lengths, being shorter in the case of the longer C9 SAMs. This observation suggest that longer chain allows more flexibility to the phenyl rings which subsequently tilts relative to the alkyl chain, which itself is tilted away from the surface normal by 35° . The dense packing of the SAMs ensures that the substrate does not oxidized for extended periods. The high thermal stability means that these SAMs can be used in the fabrication of reliable organic thin film transistor devices.

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