

A Close-packed, Highly Insulating Organic Thin Monolayer on Si(111)

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A long-chain dialkylated olefin, **2C18** was found to form a close-packed, highly insulating self-assembled monolayer (SAM) on Si(111) via Si–C bond formation. The IR absorption spectra of the **2C18**-SAM show that the alkyl chains are densely packed with an all-*trans* conformation. The threshold voltage to initiate the scanned probe oxidation (SPO) of the **2C18**-SAM-covered Si(111) was ca. 9 V, which is much higher than the previously reported voltages for organic monolayers on Si or SiO₂/Si substrates.

Hydrogen-terminated silicon surfaces (H–Si(111)s) are well known to provide alkyl self-assembled monolayers (SAMs) through robust Si–C bonding¹ under mild conditions such as light irradiation² (Figure 1a). SAMs have great potential to be atomically flat, close-packed,³ thermally,⁴ and chemically⁵ robust, and possess excellent electrical characteristics.⁶ In addition, chemical modification of the organic building blocks, in advance or stepwise, and hierarchical stacking of the functionalized SAMs can be readily performed to control surface functions.^{1,3} Thus, the application of SAMs on Si substrates shows promise particularly as functionalized substrates for electronic devices that require highly insulating SAMs. Although SAMs composed of long-alkyl chains are known to be robust in the voltage range of 2–5 V,^{6,7} SAMs with higher insulating properties have been long-awaited for insulators, gate dielectrics, resistors, and capacitors. Herein, we report a close-packed organic thin monolayer on Si(111) using a dialkylated olefin, **2C18** (Figure 1b), that provides a highly insulating monolayer on Si(111). We also found using a series of precursory olefins (Figure 1b) that chemical structures of alkyl chains employed have a strong correlation with the packing modes of structures on Si(111) in relation to the insulating properties.

A **2C18**-SAM was formed from dialkylated olefin **2C18** on

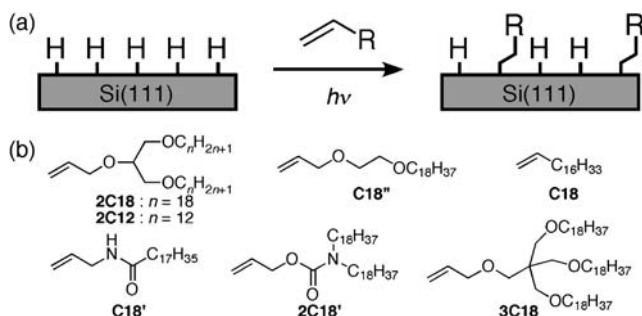


Figure 1. A self-assembled monolayer on Si(111): (a) a schematic representation of alkylation on Si(111); (b) olefins used in this study.

an H–Si(111) under UV irradiation at 254 nm. The water contact angle of the surface reached a maximum of 106° within 30 min, which indicates that the Si(111) was fully covered with hydrophobic alkyl chains.⁸ The topographic images of the **2C18**-SAM-covered Si(111) (**2C18**-Si(111)) observed in the normal AFM mode clearly showed atomically flat terraces and 0.3-nm steps.⁹ No domains larger than tens of nanometer were observed showing that the **2C18**-SAM is homogeneous at the submicrometer scale.

The packing structures of the alkyl chains of the SAMs were determined by transmission IR spectra. In this study, multiple-angle incidence resolution spectrometry (MAIRS)¹⁰ was adopted. In MAIRS, an unpolarized transmitted infrared ray through thin films on a transparent material is collected at different angles of incidence, and the transmittance single-beam spectra are subjected to chemometric spectral resolution to obtain in-plane (IP) and out-of-plane (OP) absorption spectra.¹⁰ In both the IP and OP spectra of **2C18**-Si(111), the symmetric and asymmetric stretching vibrations of the CH₂ groups were observed at wavenumbers assignable to the all-*trans* conformation (Figure S2a).¹⁶ This clearly indicates that the alkyl chains are close-packed and crystalline in **2C18**-SAM. In contrast, absorption peaks for stretching vibrations of the CH₂ groups of **C18**-Si(111) (Figure S2b)¹⁶ were observed at higher wavenumbers compared with those of **2C18**-SAM, which indicates that the alkyl chains display *gauche* conformation in which the alkyl chains are disordered. In addition, the higher wavenumber shifts of the bands in the OP spectrum from those in the IP one indicate that the alkyl chains are bent with a roughly perpendicular stance to the substrate.^{10b,10d,10e}

The tilt angle of the straight alkyl chains of **2C18**-SAM from the surface normal was estimated to be 44 ± 1° from the absorbance ratio of the CH₂ groups in the IP and OP spectra,¹⁰ which shows the thickness of **2C18**-SAM is ca. 2 nm. Furthermore, the 3-dimensional density of the CH₂ groups per unit volume in **2C18**-SAM was calculated from the absorbance of the ν_sCH₂ band to be as large as those of close-packed LB films of 10-layered cadmium stearate on a Ge substrate^{10a} (see Supporting Information).¹⁶ This result is consistent with the observation that alkyl chains in **2C18**-SAM adopt all-*trans* conformation and arranged in a close-packed manner on Si(111).

Although other olefins also exhibited homogeneous SAM structures as observed in the AFM topographic images,⁹ the alkyl chains proved to be more disordered with smaller water contact angles and densities compared with those of **2C18**-SAM (Table S1).¹⁶

The packing efficiency of organic molecules spatially fixed through covalent bonding in Si–C type SAMs on Si(111)s largely depends not only on their structures but also on the

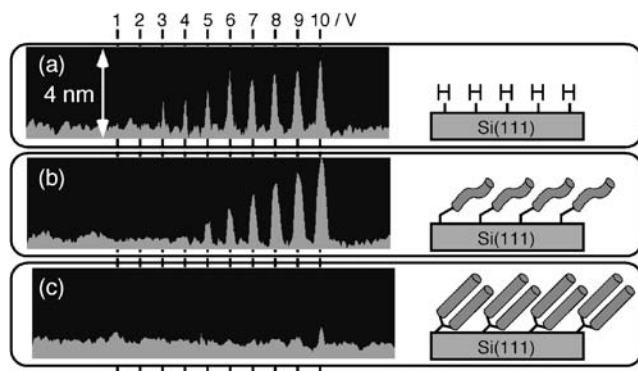


Figure 2. The SPO profiles of (a) H-Si(111), (b) C18-Si(111), and (c) 2C18-Si(111) at 25 °C with 53% humidity.

substrate crystallinity. The two-forked, all-*trans* structures of alkyl chains of 2C18 are well suited to a close packing on Si(111), where the Si atoms are hexagonally arranged¹¹ with an occupancy of 0.128 nm², whereas other olefins with one or three long alkyl chain(s), or two shorter alkyl chains formed disordered SAMs. This explanation is strongly supported by the fact that C18', which is a monoalkyl counterpart of 2C18, formed a disordered SAM. Thus, the number of the alkyl chain(s) in one molecule and the chain length are important factors determining the packing modes of the SAMs.

We conducted scanned probe oxidation (SPO) using a conductive probe AFM to examine the electric properties of the SAMs.¹² In SPO, the electric current flowing from the AFM tip to the substrate through the alkyl SAM oxidizes Si atoms into SiO₂, which results in protrusion in AFM topographic images.^{13,14a} Figure 2 illustrates the SPO profiles of H-Si(111), C18-Si(111), and 2C18-Si(111). To minimize the experimental error, the SPO experiments for the three Si(111)s were conducted successively under the same condition using the same tip. The set of SPO experiments were repeated three times using newly fabricated samples for each time to confirm reproducibility, and finally the same results were obtained. Figure 2 shows that the threshold voltage¹⁴ (U_{th}) for each SAM to initiate the oxidation was 2 V (H-Si(111)), 5 V (C18-Si(111)), and 9 V (2C18-Si(111)). The result of C18-Si(111) is almost the same as Yang's report^{14b} (4 V, on p-type 10–35 Ω cm Si(111), ca. 55% RH, 0.05–1.00 μm/s) and as Pignataro's report¹³ (5.5–6.0 V, on p-type 1.5–4.0 Ω cm Si(100), >80% RH, 30–90 μm/s). The U_{th} values of the other SAM-covered Si(111)s, C18'-Si(111), and 2C18'-Si(111), were all around 5 V, similar to that of C18-Si(111) (Table S1).¹⁶ In marked contrast, 2C18-Si(111) was only slightly oxidized even when 9 V was applied. This value is higher than any other reported values for Si-C type SAMs on Si(111),^{13,14b} and even higher than that of an octadecylsilated SiO₂/Si surface (6.4–6.8 V)¹⁵ that has an insulating SiO₂ layer. The insulating property of 2C18-Si(111) is thus remarkable.

In summary, the molecular structures of the precursory olefins have strong influence on the molecular orientations and physical properties of the SAMs formed on Si(111). Especially, 2C18 with a two-forked, long alkyl chain forms a close-packed, highly insulating 2 nm-SAM. This result will encourage us to apply 2C18-SAM to the insulators of organic thin layer devices, such as organic field-effect transistors. Furthermore, tailored

surface characteristics such as tunable reactivity or biocompatibility can be introduced to the 2C18 backbone, which can lead to functional SAMs and various bottom-up devices.

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- Higher static water contact angles (ca. 110°) of Me-terminated SAMs were reported in the literature (see Ref. 1e). The difference between our data and those in the literature is assumably due to that of the tilt angles of the alkyl chains.
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