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Fabrication of Octadecyl and Octadecanethiolate Self-Assembled Monolayers on Oxide-Free Si(111) with a One-Cell Process

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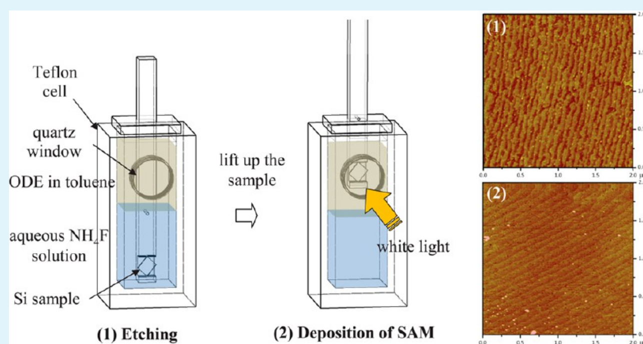
Supporting Information

ABSTRACT: Self-assembled monolayers (SAM) of 1-octadecene (ODE) and 1-octadecanethiol (ODT) were deposited on an oxide-free Si(111) surface with a one-cell method. The etching and SAM deposition of Si(111) were performed in one cell containing immiscible solutions in two layers: an aqueous solution of NH_4F and a toluene solution of organic SAM precursors (ODE and ODT). To remove surface Si oxides, the Si(111) surface was initially etched in the lower layer of NH_4F solution. The Si as etched was subsequently moved directly to the upper solution of the precursors for deposition of the SAM under illumination of white light. This one-cell approach avoids the Si surface, as etched, coming in contact with the atmosphere, so eliminating oxidation and contamination. The ODE and ODT SAM were characterized with measurements with an atomic force microscope (AFM) and X-ray photoelectron spectra (XPS). The resulting ODE SAM was more stable than the ODT SAM and exhibited satisfactory resistance to oxidation under the ambient atmosphere. The ODT SAM prepared with this one-cell method exhibited a resistance to atmospheric oxidation better than with a two-cell method.



KEYWORDS: *silicon, self-assembled monolayer, octadecene, octadecanethiol*

■ INTRODUCTION

The deposition of organic self-assembled monolayers (SAM) on Si surfaces is much investigated because of its prospective application in molecular electronic devices and field-effect transistors.[1,2] A SAM of insulating organic nature (e.g., long-chain hydrocarbon) is an alternative to SiO_2 to serve as a gate dielectric in an ultrathin-film transistor.[3−5] These organic layers find applications also in chemical and biochemical sensing as matrices into which guest molecules insert and, more importantly, as insulating layers.[6,7] In addition, the organic SAM covalently bonded to Si has been demonstrated to serve as the photoresist layer in vacuum ultraviolet lithography.[8] Accordingly, these SAM are further designed with tunable properties, providing unique processing advantages for device fabrication on a Si substrate.[6,9−12]

Various wet chemical methods have been developed for the manufacture of SAM possessing desired chemical and physical properties on oxide-free Si substrates.[6,13−15] The deposition of a SAM on an oxide-free Si substrate involves two fundamental reaction steps: in the first step, the native Si oxides are removed from the surface with an etching solution (e.g., $HF_{(aq)}$ or $NH_4F_{(aq)}$), and subsequently, the Si surface as etched becomes terminated with hydrogen; in the second step, the H-terminated Si substrate is immersed in a solution of SAM precursors to graft covalently an organic monolayer onto the surface.[16] These two steps have been conventionally implemented in two separate cells in a sequence, but the H-terminated Si surface becomes thereby inevitably exposed to the atmosphere between the two reaction steps. The Si surface thus becomes subject to contamination and oxidation in the atmosphere during the period of the sample transfer.[17,18] The properties of SAM could vary markedly with the chemical structures of the initial Si substrates. For example, the electrical transport across a SAM deposited on a Si substrate is sensitive to surface oxidation at the SAM/Si interface.[19] The presence of surface oxides can yield an incomplete SAM because the grafting reaction occurs only on the H-terminated region of the Si substrate. An immediate and careful sample transfer in a clean atmosphere is, accordingly, an essential requirement for the fabrication of organic SAM of satisfactory quality onto the oxide-free Si surface. Our study is to demonstrate a possible method, which prevents the air-sensitive etched substrate from the atmospheric exposure before the preparation of SAM.

Among various organic precursors for deposition of SAM, 1-alkene and 1-alkanethiol have been demonstrated to be tethered to the Si surface upon photochemical activation.[16,20−27] The alkyl SAM, which bonded directly to the Si surface, exhibited excellent surface passivation in the aspects of

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chemical and physical properties.[15,28−31] The densely packed SAM proved to protect the Si substrate from oxidation in the ambient atmosphere.[11,32−34] The alkanethiolate SAM could be deposited on the oxide-free Si surface via the formation of a S−Si bond under thermal activation and irradiation, but the alkanethiolate SAM on Si exhibited less chemical durability and packing density than alkyloxyl SAM.[24,35] The resistivity of SAM to atmospheric oxidation is an important consideration for their practical utility in semiconductor devices that are exposed to air during manufacturing processes.

From the present work, we report the one-cell deposition of 1-octadecene (ODE, $CH_3(CH_2)_{15}CH{=}CH_2$) and 1-octadecanethiol (ODT, $CH_3(CH_2)_{17}SH$) SAM on oxide-free Si(111) under illumination with white light (comprising UV and visible light). The etching reaction and deposition of the SAM were implemented in a reaction cell containing two immiscible solutions: an aqueous solution of NH_4F as the lower layer and an organic (toluene) solution of ODE or ODT as the upper layer. The Si(111) sample was placed initially in the lower solution of NH_4F to etch the surface native oxides. The etched Si sample was subsequently lifted to the toluene solution of ODE or ODT in the upper solution and irradiated with white light to activate the grafting reaction. NH_4F is insoluble in toluene and is thus expected not to interfere with the deposition of a SAM. This one-cell process hence eliminates the chance of contamination and oxidation on the Si surface, as etched, during a sample transfer. The resistance of the prepared SAM to atmospheric oxidation was examined with X-ray photoelectron spectra (XPS) measurements.

■ EXPERIMENTAL SECTION

Materials. 1-Octadecene (Acros, 96%) and 1-octadecanethiol (Aldrich, 95%) served as precursors for the SAM deposition, without further purification. The *n*-type Si(111) wafer (thickness 300 μm, P-doped, 1−10 Ω cm, Virginia Semiconductor Inc.) was cleaved into rhombic chips (length ~1.0 cm) as substrates for SAM deposition. Before use, the Si chips were cleaned in ultrasonic baths of acetone, ethanol, and deionized water (>18.0 M Ω·cm) in sequence and further treated in a piranha solution to remove the residual particles. The Si sample was subsequently rinsed thoroughly with deionized water and dried with blown N_2 gas.

Preparation of SAM on Si(111) with the One-Cell Process. The one-cell deposition of SAM was performed in a Teflon cell, shown in Figure 1, which is equipped with a silica window to transmit white light for photoinduced deposition. The Teflon cell was placed in a homemade glovebox that was filled with dry N_2 gas. The aqueous solution of NH_4F (40%) was added to the cell, which was purged with N_2 for 1 h to eliminate oxygen dissolved in the solution. As previously reported, the solvent was more suitable when its molecular shape was more unlike that of the deposited SAM, and for the preparation of alkyl SAM, aromatic solvents were better than linear alkanes.[11,36] Toluene was thus chosen as the organic solvent for ODE and ODT in this work. The toluene solutions of ODE (1.0 M) and ODT (1.0 M) were also purged with Ar gas for 20 min before use.

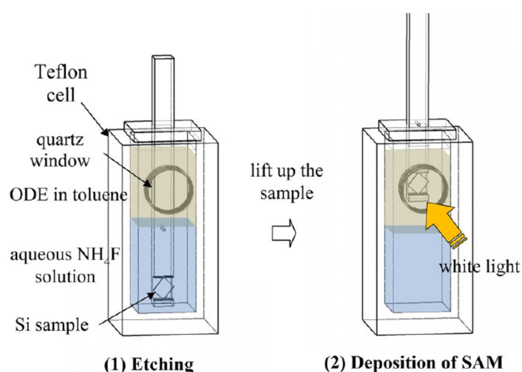

Figure 1. Schematics of a Teflon cell for photoinduced deposition of a SAM.

In the one-cell process, the cleaned Si sample was fixed onto a Teflon holder and immersed into the NH_4F solution. The prepurged toluene solution of ODE or ODT was slowly added to the Teflon cell. The aqueous solution of NH_4F and the toluene solution of ODE or ODT are immiscible and formed a two-layer system; the toluene solution is the upper layer. The Si sample was initially etched in NH_4F solution for 20 min to remove native oxides from the surface. The sample was subsequently lifted slowly into the upper layer and irradiated with white light. A mercury arc lamp (LPS250, PTI) provided this light; a water filter was mounted to attenuate infrared radiation that might heat the sample and solution. After deposition of a SAM, the Si sample was abundantly rinsed with toluene, ethanol, and deionized water and subsequently dried with flowing gaseous N_2. After the deposition of a SAM, the Si sample was sonicated in toluene, ethanol, and dichloromethane to remove residual adsorbates and then dried with blown N_2 gas for subsequent measurements.

Characterization of a SAM on Si(111). The vibrational spectra of freshly etched and SAM-deposited Si(111) surfaces were measured with an infrared interferometer (DA 8.3, Bomen) in attenuated-total-reflection mode (ATR-IR). The sample was pressed onto the germanium crystal of a single-reflection ATR accessory (VariGATR, Harrick), of which the angle of incidence of the IR light was set at 65° from the surface normal. XPS were measured using a hemispherical energy analyzer (Phiobos 100, Specs) in a vacuum chamber maintained at 5×10^{-10} Torr; as a source of X-ray excitation, an Al anode was operated at 15 kV and 20 mA. The hydrophilic property of the deposited SAM was examined on measurement of the water contact angle with a goniometer (Firsttenangstroms FTA32) and fitting software (Video 2.1). The thicknesses of deposited ODE and ODT SAM were measured with an ellipsometer (EP3, Nanofilm). In the ellipsometric measurement, the angle of the incident light (λ_{He-Ne} = 632.8 nm) was 70° from the surface normal, and the polarization angle was set to 45° from the surface. These reflection measurements were typically repeated at least five positions across the deposited organic layer to ensure the reproducibility and to obtain the average thickness of a deposited SAM. The refractive indices of Si and the organic layer were fixed at 3.85 and 1.5, respectively, to derive the thicknesses of the deposited ODE and ODT SAM. Atomic force microscope (AFM) images were recorded (MultiMode SPM system, Veeco DI) with AFM tips (type fpN 01, NIIFP). To examine the surface morphology and roughness, we recorded AFM images of deposited organic layers with the tapping mode.

■ RESULTS AND DISCUSSION

To remove completely the native oxides, the Si(111) surface was initially etched in the aqueous solution of NH_4F for 20 min. The freshly etched Si surface was terminated with hydrogen, according to the measured infrared spectra (Figure S1 in the Supporting Information). Figure 2a shows a typical AFM image of an Si(111) surface as obtained after etching in NH_4F solution for 20 min. The stripes on the AFM image are associated with atomic steps on the Si(111) surface.[25,37,38] The H-terminated Si(111) surface exhibited smooth terraces (average width ~70 nm) with an atomic step (~0.3 nm). The Si(111) surface was deposited with ODE by the one-cell method under illumination of white light (50 mJ/cm^2). Figure 2b−d presents AFM images of a Si(111) surface deposited with ODE for varied duration of illumination. The stripes attributed to surface atomic steps were smeared at the initial deposition (20 min), because ODE molecules were grafted onto the surface. The covalent grafting of 1-alkene onto the H-

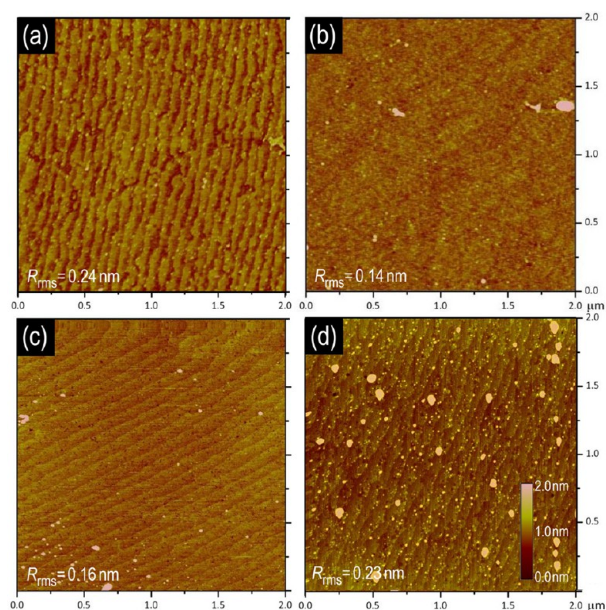

Figure 2. AFM images (tapping mode) of Si(111) surfaces after the SAM deposition in toluene solution of ODE (1.0 M) with the one-cell method under illumination with white light (50 mJ/cm^2) for (a) 0 min, (b) 20 min, (c) 60 min, and (d) 120 min.

terminated Si surface has been described with the mechanisms of radical chain reactions and generation of hole/electron pairs.[6,14,21] According to the former mechanism, the grafting reaction is initiated with formation of a Si radical that is formed via photodissociation of the H−Si bond. The latter mechanism is applied mainly to explain the photoinduced reaction that occurs with visible light.

As shown in Figure 2, the root-mean-square roughness (R_{rms}) slightly decreased upon the initial duration of deposition. According to the ellipsometric measurement, the thickness of the ODE layer increased with increasing duration of deposition during the initial period of deposition (Table S1 in the Supporting Information). The stepped morphology was clearly retained with R_{rms} = 0.16 nm after deposition for ∼60 min, indicating that a complete ODE monolayer was deposited on the Si(111) surface. The average thickness of the deposited ODE was ∼2.0−2.1 nm, corresponding to a monolayer of ODE rather than a multilayer.[39,40] Conversely, the surface morphology became rougher at 120 min (Figure 2d), because the prolonged illumination of white light caused the cleavage of the C−H and C−C bonds of the deposited ODE. As a result, polymerization might be initiated to form small aggregates on the surface, especially at the edges of surface steps. It is also likely that alkene molecules underwent polymerization in toluene solution and subsequently deposited onto the surface.

Figure 3 displays the AFM images of a Si surface deposited with ODT with the one-cell process for various durations. Similarly to ODE, the Si substrate exhibits a temporal evolution of morphology during light-induced deposition of ODT. The stepped morphology disappeared in the initial period and recovered after deposition for 90 min, indicating that a complete ODT monolayer was obtained. According to AFM data, the resulting ODT SAM had R_{rms} = 0.14 nm, which is comparable to that of the ODE SAM. The ellipsometric measurements indicated that the thickness of the complete ODT SAM was ∼2.2 nm (Table S2 in the Supporting Information). The feature of a stepped surface is not observed for an ODT layer obtained by deposition for 150 min as shown in Figure 3c. The thickness of deposited SAM decreased to become 1.2 nm. The C−S bond of alkanethiol was much more vulnerable to cleavage than the C−C and C−H bonds of an alkyl chain under UV activation.[41] For prolonged illumination of white light, a portion of the deposited ODT molecules further underwent photoinduced dissociation of the C−S bond, which might result in the desorption of octadecyl chains from the deposited ODT SAM.

That ODE and ODT molecules became grafted onto Si(111) was confirmed on measurement of vibrational spectra. Figure 4

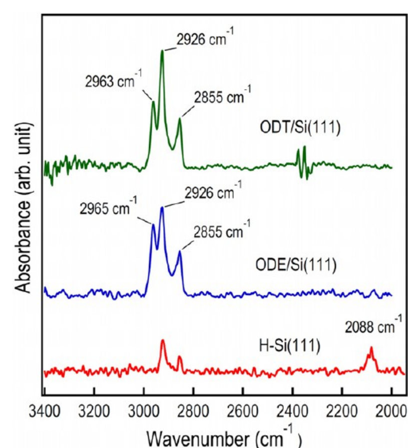

Figure 4. ATR-IR spectra of the Si(111) surface before and after deposition of ODE and ODT SAM with the one-cell process.

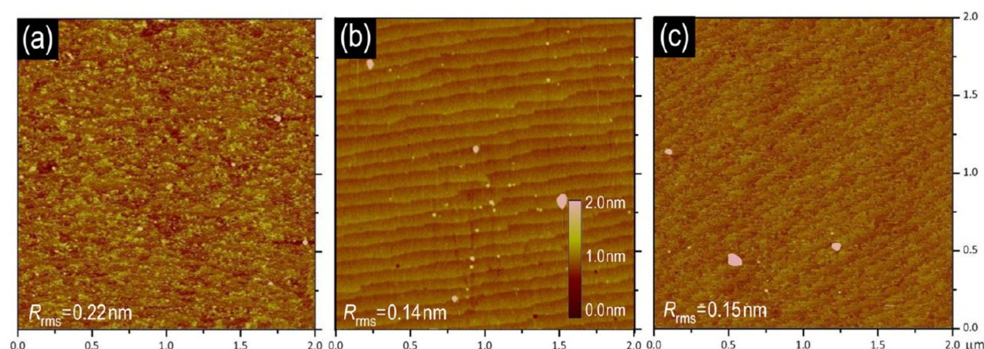

Figure 3. AFM images of Si(111) surfaces on which were deposited ODT in the one-cell process under illumination with white light for (a) 30 min, (b) 90 min, and (c) 150 min.

shows the ATR-IR spectra of ODE and ODT SAM deposited on Si(111) with the one-cell process. The line at 2088 cm^{-1} associated with the Si−H stretching mode disappeared after the deposition of SAM onto the Si surface. Three distinct lines were observed in the range between 2800 and 3000 cm^{-1} and are attributed to CH_2 and CH_3 groups in their asymmetric (ν_a) and symmetric (ν_s) stretching modes.[29,37,38]

As a measure of surface hydrophobicity, the water contact angles were recorded for the Si(111) before and after light-induced deposition of ODE and ODT with the one-cell process. The water contact angle was 86° for Si(111) as etched and increased to greater than 100° upon the deposition of ODE and ODT SAM (Figure S2 in the Supporting Information).[24,35,42] The contact angles of ODE and ODT SAM deposited on Si with the one-cell process are nearly the same as those obtained with the two-cell process. The ODE and ODT SAM exhibited a hydrophobic property because of the terminal methyl group ($-CH_3$). The measurement of the water contact angle thus provided additional evidence for the grafting of ODE and ODT onto the Si(111) surface.

To identify the elemental composition of deposited SAM on Si(111), we recorded X-ray photoelectron spectra. Figure 5 shows a comparison of XPS before and after deposition of ODE and ODT SAM on Si(111) with varied duration for the one-cell deposition. A distinct signal appears at ∼285 eV on the deposited surface, which corresponds to the C 1s signal for the grafted ODE and ODT molecules. The intensity of the signal at 99.8 eV associated with the Si substrate was attenuated on deposition of ODE and ODT SAM. The intensity of C 1s relative to Si 2p for ODE and ODT SAM increases with increasing duration of deposition (Tables S3 and S4 in the Supporting Information). Two additional XPS signals were observed at 163.2 and 164.4 eV for the surface on which ODT was deposited, which are attributed to S $2p_{3/2}$ and $2p_{1/2}$ signals, respectively (Figure S3 in the Supporting Information).[24]

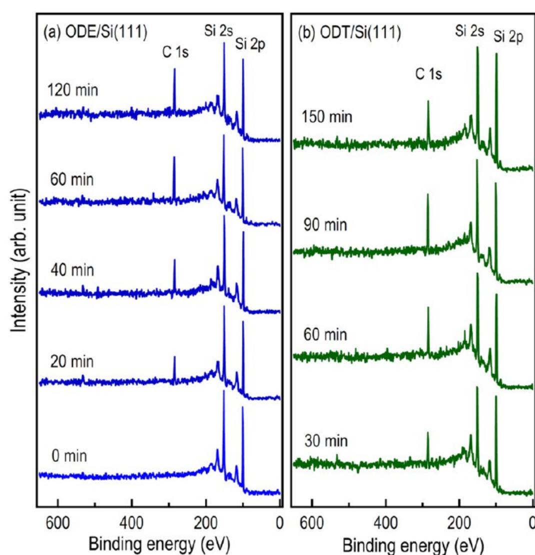

Figure 5. XPS of Si(111) surfaces on which were deposited with (a) ODE and (b) OTD with the one-cell method for varied duration.

For the deposition of ODE, the intensity of C 1s increased with increasing duration of deposition and became almost saturated at 60 min, at which a complete ODE monolayer was grafted onto the surface, consistent with the AFM data shown in Figure 2. Nevertheless, the intensity of the C 1s signal attained a maximum at ∼90 min for the deposition of ODT and slightly decreased with prolonged deposition because the C−S bond of a deposited ODT molecule was subject to photochemical dissociation. The signal of O 1s at ∼530 eV is much smaller than that of Si 2p for all samples, indicating that the Si surface is nearly free of oxidation after the deposition of SAM. During the SAM deposition, the etched Si surface was directly moved into the solution of SAM precursors without exposure to the atmosphere.

We tested the chemical stabilities of the ODE and ODT SAM by measuring XPS upon exposure of the SAM to the ambient atmosphere. Figure 6a shows XPS of Si 2p for the Si(111) surfaces, on which were deposited ODE molecules for varied durations with the one-cell process and which were subsequently exposed for one day to an ambient atmosphere. A broad signal appeared at ∼104 eV for the Si sample as etched upon exposure to the atmosphere, which was due to surface Si oxides (Si^{+}, Si^{2+}, Si^{3+}, and Si^{4+}), because the H-terminated surface was susceptible to oxidation (Figure S3 in the Supporting Information).[32] The intensity of Si 2p assigned to Si oxides decreased on increased duration of SAM deposition. The spectrum of Si 2p for the Si surface on which ODE was deposited for 60 min is nearly the same as that obtained for the freshly etched Si surface, indicating that the surface was densely covered with a complete ODE SAM and protected from atmospheric oxidation.

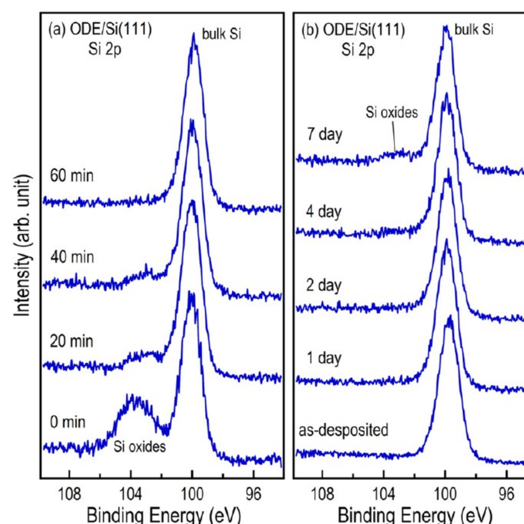

Figure 6. XPS of Si 2p for (a) Si surfaces on which was deposited ODE for varied duration and exposed to the atmosphere for 1 day and (b) a Si surface on which was deposited an ODE SAM with the one-cell method and exposed to the atmosphere for varied duration.

The chemical durabilities of complete ODE and ODT SAM prepared with the one-cell method were compared on exposing these SAM under ambient conditions. Figure 6b shows XPS of Si 2p for a Si(111) surface on which was deposited an ODE SAM for 60 min and which was then exposed to air for varied duration. The ODE SAM showed an insignificant alteration after exposure to the atmosphere for four days, and the intensity of the Si 2p signal due to Si oxides increased only slightly after exposure for seven days. The temporal evolutions of XPS spectra of Si 2p for the ODE SAM prepared by the one-cell method are similar to those obtained with the two-cell

method after atmospheric exposure (Figure S5 in the Supporting Information). This result indicates that the ODE SAM exhibits an effective resistance to atmospheric oxidation. Figure 7a shows XPS of Si 2p for a Si(111) surface on which

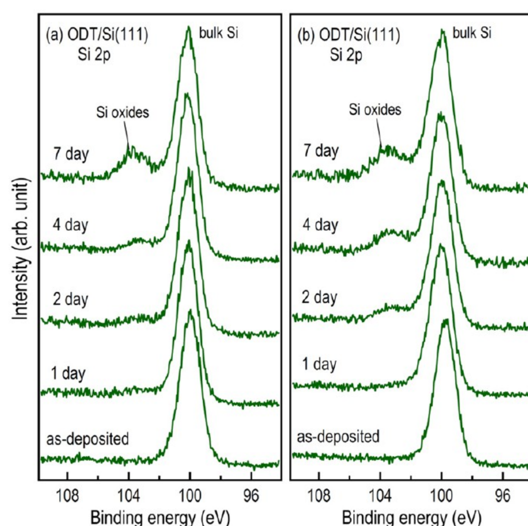

Figure 7. Comparison between XPS of Si 2p for the Si surfaces on which were deposited ODT SAM with the (a) one-cell and (b) two-cell methods, respectively, and exposed to the atmosphere for varied duration.

was deposited an ODT SAM for 90 min and which was exposed to air for varied duration. For the same period of atmospheric exposure, the ODT-deposited Si surface showed a greater intensity of Si oxides than the ODE-deposited one. This observation indicates that the ODE SAM exhibited a passivation layer on Si(111) to oxidation superior to that of the ODT SAM. The C−Si bonded SAM on an oxide-free Si silicon exhibited greater resistance than that with the S−Si bond, similar to the results obtained for the Ge surface.[43,44] This observation might result from the fact that the C−Si bond (318 kJ/mol) is stronger than the S−Si bond (293 kJ/mol).[45] In addition, the C atom bound to the Si surface can not access d-orbitals to extend the electronic configuration of the octet for oxidation.[43]

For comparison, Figure 7b shows XPS of Si 2p for a Si(111) surface on which was deposited an ODT SAM with the two-cell method and which was subsequently exposed to the atmosphere for a varied duration. After the same atmospheric exposure, the Si 2p signals of Si oxides were larger for a Si surface deposited with an ODT SAM with the two-cell method than with the one-cell method (Table S5 in the Supporting Information). This observation indicates that the one-cell preparation provided a quality of ODT SAM superior to that of the two-cell method. The difference between ODT SAM prepared by the one-cell and two-cell methods is more significant than that observed for ODE SAM. The advantage of the one-cell process is that an etched Si surface is transferred into the organic solution for the subsequent deposition of ODT without exposure to the atmosphere. As a result, the possibility of forming Si oxides at the SAM/Si interface is greatly diminished and a SAM on an oxide-free Si is formed of superior quality than with the two-cell process.

CONCLUSION

Our approach to deposit ODE and ODT SAM on Si(111) involves the use of one cell containing two immiscible solutions. The sample was directly transferred from the aqueous etching solution into the organic solution of the SAM precursors. This process avoided exposure of the clean Si surface as etched to the atmosphere and eliminated contamination and oxidation, providing a Si substrate free of oxide for the subsequent step of the SAM deposition. The ODE SAM prepared with the one-cell method exhibited satisfactory resistance to atmospheric oxidation. Our data show also that the ODT SAM prepared with the one-cell method exhibited a resistance to oxidation greater than with the two-cell method. This strategy of utilizing a two-layer solution in one cell via appropriately chosen solvents might be applicable to the fabrication of other functionalized molecular layers on various substrates.

ASSOCIATED CONTENT

Supporting Information

IR spectrum of a H-terminated silicon, XPS spectrum of S 2p for an ODT SAM, XPS spectra of Si 2p for an ODT SAM for varied atmopheric exposures, and the tables of ODE and ODT SAM thickness. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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