

Bonding Self-Assembled, Compact Organophosphonate Monolayers to the Native Oxide Surface of Silicon

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Abstract: A new method is described to prepare strongly bonded, compact monolayer films of alkyl- or arylphosphonates on the native oxide surface of Si (SiO_2/Si). This method is illustrated for octadecyl- and α -quarterthiophene-2-phosphonates. For both cases, AFM shows comprehensive coverage of the SiO_2/Si surface. The thickness of the continuous film of 4TP/ SiO_2/Si was measured both by AFM and by X-ray reflectivity to be ca. 18 Å. Direct gravimetric analysis shows surface coverage by α -quarterthiophene-2-phosphonate to be about 0.66 nmol/cm², which corresponds to molecular packing in the film close to that of crystalline α -quarterthiophene. Coverage by octadecylphosphonate was ca. 0.90 nmol/cm², corresponding to a cross-sectional area of about 18.5 Å²/molecule, consistent with close-packed alkyl chains.

Widespread interest in attaching organics to the surface of semiconductors such as Si^{1-3} derives in part from possible applications in devices,⁴ including sensors and thin film transistors. In the latter context, several requirements have been enunciated,⁵ including contacting the organic directly to the gate dielectric, as well as having constituent molecular order, film homogeneity, and film density. Simplicity of film formation might also be a practical consideration. Remarkably few unique approaches to Si surface derivatization, however, have been reported. Prominent among these are metal complex catalyzed² or radical-induced hydrosilylation⁶⁻⁸ of unsaturated organics. Yet these techniques are inappropriate where direct bonding to a Si oxide coating (SiO_2/Si) is required⁵ because they involve H-terminated Si,⁹ and the first step in preparing H-terminated Si is to remove the oxide coating, usually with HF. Electrochemical methods^{10,11} or reactions with Grignard or lithium reagents also require H-terminated Si,¹² although halogen-terminated Si can also be used with organometallics.¹³ Direct attachment of organics to SiO_2/Si can be accomplished, though, by silanization,^{14,15} but this method suffers from the low surface

OH group content of the Si surface oxide.^{16,17} Indeed, comprehensive Si surface coverage by silanization derives from amorphous siloxane polymerization, and the degree of siloxane cross-condensation depends critically on the water content of the deposition solvent,¹⁵ attaining structural order in such films could be problematic.

We now report the first examples of self-assembled organic monolayers (SAMs) bound directly to the native oxide surface of Si. SAMs of organophosphonic acids can be prepared easily on SiO_2/Si using a new, simple technique performed under ordinary laboratory conditions, with minimum reaction control. Heating these SAMs yields dense organophosphonate films bonded to the SiO_2/Si surface. Monolayer films of both aliphatic and aromatic phosphonates can be bound to SiO_2/Si by this method. The process we report herein parallels self-assembly on the native oxide coatings of pure Ti or Ti-6Al-4V,^{18,19} but is conceptually new for surface treatment of SiO_2/Si : No pretreatment of the native oxide is necessary,²⁰ film growth is not limited by surface OH content, and densely packed surface-bound monolayer films can be obtained.

Growing an organophosphonate film on SiO_2/Si by self-assembly is a straightforward process: The substrate is held vertically in a solution of the corresponding organophosphonic acid below its critical micelle concentration (CMC),²¹ and the

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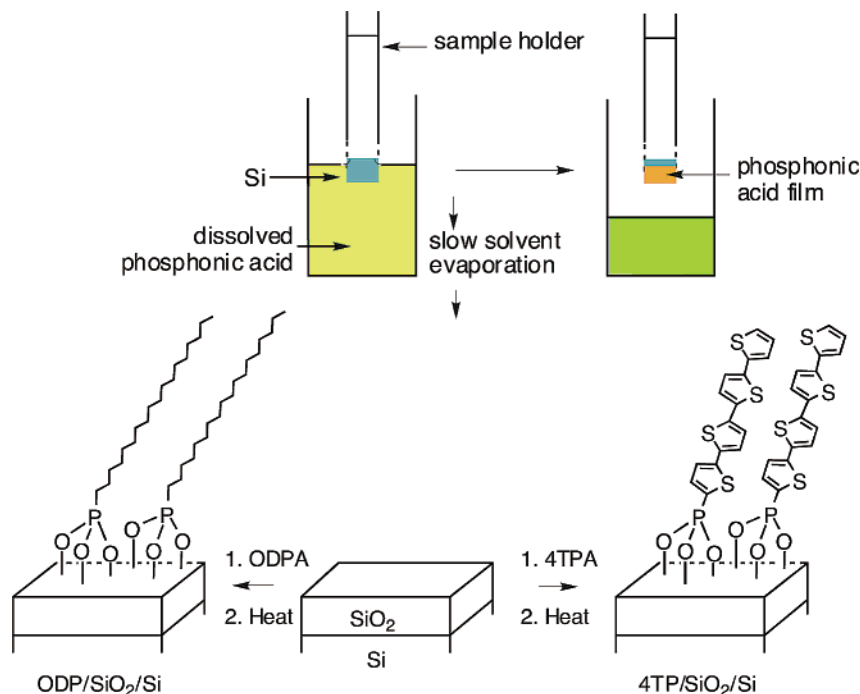


Figure 1. The T-BAG setup and chemical reactions; colors shown for 4TPA.

solvent is allowed to evaporate slowly. As the meniscus slowly traverses the substrate (Figure 1), the organophosphonic acid is transferred to the surface in inverse analogy to Langmuir–Blodgett methods, but without application of pressure.²² Our procedure might benefit from some organized aggregation of the dissolved organophosphonic acid amphiphile at the air–solvent interface; thus, we have nicknamed this deposition method “T-BAG” (tethering by aggregation and growth). The T-BAG SAM of the phosphonic acid can be removed from the SiO₂/Si surface by “carbonate rinse”, but a monolayer remains bonded to that surface, even after vigorous sonication, if the ensemble is first heated at 140 °C, which converts the surface-adsorbed phosphonic acid ($\nu_{\text{PO}} \approx 1250 \text{ cm}^{-1}$) to surface-bound phosphonate ($\nu_{\text{PO}} \approx 1100 \text{ cm}^{-1}$).^{18,19,23}

Experimental Section

General. Bithiophene (2T; Aldrich) and octadecylphosphonic acid (ODPA; Alfa Aesar) were used as received. THF (EM Science) was distilled over Na and stored under argon. Semiconductor grade single-crystal silicon (100) samples were cut from a single wafer into 8 mm × 8 mm coupons. These coupons were cleaned by sonication in acetone (15 min) followed sequentially by immersion in boiling “piranha” solution (3:1 30% H₂O₂:98% H₂SO₄) for 45 min, rinsing with distilled/deionized water, immersion in “buzzard” solution to remove traces or residual organics (1:1 30% H₂O₂:38% HCl) at 80 °C for 15 min, and then a final rinsing with distilled/deionized water (18.2 MΩ; MilliQ). *Note: Take care in preparing the “piranha” and “buzzard” solutions, because they can detonate when contacted by organic compounds. We used cold (0 °C) H₂O₂ to prepare these solutions to minimize frothing.* Si samples thus treated were hydrophilic, were dried in a stream of dry N₂, and were used immediately. AFM analysis of films was done using a Digital Instruments Multimode Nanoscope IIIa SPM equipped with silicon tips (Nanodevices Metrology Probes; resonant frequency, 300 kHz; spring constant, 40 N/m) in tapping mode. Quartz crystal microbalance (QCM) measurements were made using a home-built

Ward oscillator and 10 MHz, AT-cut quartz crystals (ICM) equipped with SiO₂/Si-coated (1000 Å Si/100 Å Cr/1000 Å Au undercoat) electrodes. IR spectra were obtained using a Midac Model 2510 spectrometer equipped with a Surface Optics Corp. specular reflectance attachment.

α-Quarterthiophene. α-Bithiophene (2T; 1.03 g; 6.2 mmol) was dissolved in a mixture of 20 mL of methanol and 20 mL of acetonitrile in a 50 mL three-necked flask. Distilled water (5 mL) was then added, and air was bubbled through the solution via a sparging tube. A condenser was fitted to the three-necked flask, and 190 mg of PdCl₂ (1.1 mmol; 0.18 equiv) was added slowly to the solution. The reaction mixture was stirred and was monitored by TLC (using 3:1 hexane:dichloromethane as eluant). As the reaction proceeded, α-quarterthiophene (4T) and Pd black precipitated, and some 2T was carried out of the reaction vessel by the air stream. When the supply of α-bithiophene was nearly exhausted (by TLC, after about 7 days), the reaction mixture was filtered; any unreacted α-bithiophene could be removed by washing the dark red precipitate with methanol. 4T was isolated as bright yellow crystals by sublimation (170 °C, 1 mTorr; 480 mg, 1.45 mmol; 135% based on PdCl₂, 47% based on 2T; ¹H NMR [400 MHz, acetone-*d*₆]: δ [H2] 7.07–7.11, *J*_{H1H2} = 5.2 Hz, *J*_{H2H3} = 3.4 Hz; [H4, H5] 7.21–7.26, *J*_{H4H5} = 3.5 Hz; [H3] 7.29–7.32, *J*_{H2H3} = 3.3, *J*_{H1H3} = 1.1 Hz; [H1] 7.42–7.46). The yield of 4T could be increased to 357% (based on PdCl₂) by addition of 1 equiv (based on Pd) of benzoquinone to assist in the reoxidation of Pd(0).²⁴

α-Quarterthiophene-2-(diethylphosphonate), 2. Sublimed α-quarterthiophene (255.0 mg; 0.7727 mmol) was dissolved in 20 mL of dry, distilled THF, and the solution was cooled to –50 °C under dry N₂. A solution of *n*-butyllithium in hexane (Aldrich; 0.60 mL of a 2.5 M solution; 2 equiv) was added quickly via syringe, and the reaction mixture was allowed to stir at –50 °C for 2 h. (Using 2 equiv of *n*-butyllithium is necessary because of the low solubility of 4T at –50 °C as compared with that of 2-lithioquarterthiophene; using 1 equiv of *n*-butyllithium gives 50% dilithiated 4T and 50% unreacted 2T.) The color of the reaction mixture changed from chrome yellow to dark brown as lithiation proceeded. Diethylchlorophosphate (0.135 mL; 1.2 equiv; Aldrich) was then added. The reaction mixture became dark orange and was allowed to stir at –50 °C for 2 h; it was then slowly

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warmed to room temperature and stirred for 8 h. The solvent was removed, and the resulting solid was extracted with methylene chloride. The product was separated by column chromatography (silica) using increasing proportions of ethyl acetate in hexane. Elution of a yellow solution with 40% ethyl acetate in hexane (the second yellow material eluted overall) yielded orange-brown α -quarterthiophene-2-(diethylphosphonate) (**2**) which was contaminated with a small amount of 4T (73 mg; 30%; $^1\text{H NMR}$ [acetone- d_6]: δ 2.03 [m, $-\text{OCH}_2\text{CH}_3$, 6H], 4.05–4.18 [m, $-\text{OCH}_2\text{CH}_3$, 4H], 7.08–7.11 [dd, H8, $J_{\text{H8H9}} = 5.13$ Hz, $J_{\text{H7H8}} = 3.63$ Hz], 7.23–7.26 [d, H2, $J_{\text{H1H2}} = 3.87$ Hz], 7.28–7.31 [dd, H5, H6, $J_{\text{H5H6}} = 2.14$ Hz], 7.31–7.33 [dd, H7, $J_{\text{H7H9}} = 1.13$ Hz], 7.37–7.42 [m, H3, H4], 7.44–7.47 [dd, H9], 7.52–7.57 [dd, H1, $J_{\text{H1P}} = 8.21$ Hz]. $^{31}\text{P NMR}$: δ 10.7. HRMS: MW calc'd for $\text{C}_{20}\text{H}_{19}\text{O}_3\text{PS}_4$, 465.9955; found 465.9947). Ester **2** was hydrolyzed to **1** using 2 M HCl in ethanol at 70 °C for 3 days. The reaction mixture was cooled to 0 °C and centrifuged, and then triturated with cold methanol and dried in vacuo (1 mTorr) to give dark orange 4TPA (**1**; 62 mg; nearly quantitative). It was not possible to determine the CMC for **1** because of its low solubility; a saturated solution of **1** in THF at room temperature is approximately 0.73 mM.

Phosphonate Film Preparation: “T-BAG” Preparation of Octadecylphosphonate/SiO₂/Si. An 8 mm \times 8 mm coupon of Si cleaned as described above was held vertically using a small clamp in a solution of octadecylphosphonic acid (ODPA; 1 mM in THF) in a 50 mL beaker (see Figure 1). The solvent was allowed to evaporate slowly over 3 h, until the level of the solution fell below the Si sample. Under these conditions, the concentration of the ODPA in the remaining solution increased by about 30%, but was still below its CMC of ca. 100 mM.²¹ The treated Si sample was then removed from its holder and was heated at 140 °C in a simple glass tube for 2 days to bond the SAM to the SiO₂/Si as octadecylphosphonate (ODP). Any multilayer ODPA was removed by sonication in 0.5 M K₂CO₃ in 2:1 ethanol/water (“carbonate rinse”) typically for 20 min, followed by extensive rinsing with distilled/deionized water. Samples were then dried in a stream of dry N₂. It is important to note that extensive loss of surface phosphonate material occurs if coupons are carbonate-rinsed prior to heating. As well, extended rinsing (> 2 h) will begin to dissolve the SiO₂/Si from under the film, perhaps through attack at the film edges. Copiously rinsing Si samples with pure THF or with 5% dry triethylamine in THF also removes most, but not all, multilayered material, as determined by AFM.

α -Quarterthiophene-2-phosphonate/SiO₂/Si. Yellow-green solutions of 4TPA were made by dilution of a stock solution of 4TPA in 50 mL of THF (0.73 mM, 15 mg). The diluted solutions (0.143 mM; 0.01 mM; 0.0025 mM) were then passed through a 0.2 μ PTFE syringe filter before use. Si samples were treated with the solutions of 4TPA as described above, except that heating was done under N₂ to prevent oxidation of the quarterthiophene moieties.²⁵

Quartz Crystal Microbalance (QCM) Measurements. Ten megahertz AT-cut quartz crystals equipped with SiO₂/Si electrodes were “carbonate rinsed”, rinsed again with distilled water, and then evacuated (10⁻² Torr) until a constant baseline frequency \pm 2 Hz was measured for three successive rinse/evacuation cycles. SAMs of the phosphonic acid were grown on these crystals using the T-BAG method, in which the crystal was suspended vertically in the deposition solution (0.05 mM ODPA; 0.0025 mM **1**) using a small alligator clip attached to one of the binding posts of the crystal mounting so as not to damage the crystal itself. Following passage of the solvent meniscus over the QCM crystals, solvent was allowed to evaporate, and the crystals were then heated at 140 °C for 2 days to form the bound phosphonate film. They were then rinsed gently by pipetting first a solution of “carbonate rinse” and then distilled water alone, followed by water evaporation (10⁻² Torr, 2 h). Several rinse and dry cycles were performed in this way until a constant frequency (\pm 2 Hz) was recorded. It is not advisable to

rinse the crystals with sonication, because this can lead to electrode delamination or loosening of the epoxy which fixes the electrode binding wires. Accordingly, T-BAG procedures used more dilute solutions on QCM substrates than on the more robust Si coupons, to minimize multilayer formation. The T-BAG sequence of deposition, heating, and rinse was repeated until electrode surface coverage asymptoted; close to 90% of this final value could be attained with only one cycle of treatment. Gravimetric surface coverage by the phosphonate SAM was determined using the Sauerbrey equation for double-sided quartz crystal microbalance measurements,²⁶ and areal coverage was obtained by dividing this value by the AFM-determined surface roughness factor, 1.3.

X-ray Reflectivity. X-ray experiments were done at the National Synchrotron Light Source (NSLS) using beam line X10b (Exxon) with wavelength $\lambda = 0.087$ nm. Measurements were performed in reflectivity mode ($\Theta - 2\Theta$), resulting in a momentum transfer, q_z , along the surface normal ($q_z = 4\pi/\lambda \sin\Theta$). A simple NaI detector was used, and receiving slit sizes within the scattering plane were 0.6 and 0.8 mm for sample and detector slit, respectively. Rocking scans were performed at different angles to verify the background level. The observed rocking width (fwhm) of these scans was resolution-limited to 0.03°. The background was kept low by side-ways clamping of the Si wafer substrates, which resulted in efficient isolation of the incident beam from any other material. Analyses of films of 4TP bonded to chemically reoxidized Si (HNO₃ oxidation of H-terminated Si; rms roughness 0.21 nm) were performed in air, and both rinsed and unrinsed samples of 4TP/SiO₂/Si were used. Data were analyzed using a freely available program based on the Parratt formalism (dynamical scattering). Various parameterizations for electron density profiles (n) were used to model reflectivity from the organic layer (slab profile with rounded edge and graded electron density profile).

Results and Discussion

AFM analysis of a film of ODP formed on SiO₂/Si using the T-BAG method (1 mM ODPA in THF) followed by heating showed comprehensive surface coverage with rms roughness (0.26 nm) comparable to that of the underlying surface (Figure 2a; 0.21 nm), as is expected for a surface bound monolayer. This conformity contrasts with silanized surfaces, where film structure is not defined by the underlying substrate but rather results from cross-polymerization; silanized surfaces can appear smoother or rougher than ODP/SiO₂/Si according to the silanization conditions employed.¹⁵ A pinhole was found in the film of ODP/SiO₂/Si (by extensively searching over 900 μm^2) which allowed the film thickness to be measured (1.8 nm). This thickness is slightly less than that of a comparable film grown on the native oxide surface of Ti (2.2 nm)¹⁸ and is consistent with monolayer formation with the phosphonate alkyl chains (estimated length 2.5 nm) arranged at an average tilt angle of 40°, as is observed on mica.²⁷ In addition to peaks for bound phosphonate,^{18,23} the IR spectrum of ODP/SiO₂/Si (Figure 2c) showed $\nu_{\text{CH}_2\text{antisym}} = 2914$ cm⁻¹ (indicative of alkyl chain order²⁸) and $\nu_{\text{CH}_2\text{sym}} = 2845$ cm⁻¹.

Surface loading of monolayers formed on SiO₂/Si was determined gravimetrically using a QCM.¹⁹ Because our film growth procedure requires periodically removing the QCM crystal from the oscillator, for example, for deposition of films, baking, and rinsing, we calibrated the oscillator periodically (after 30 min warm) using a set of reference crystals. QCM

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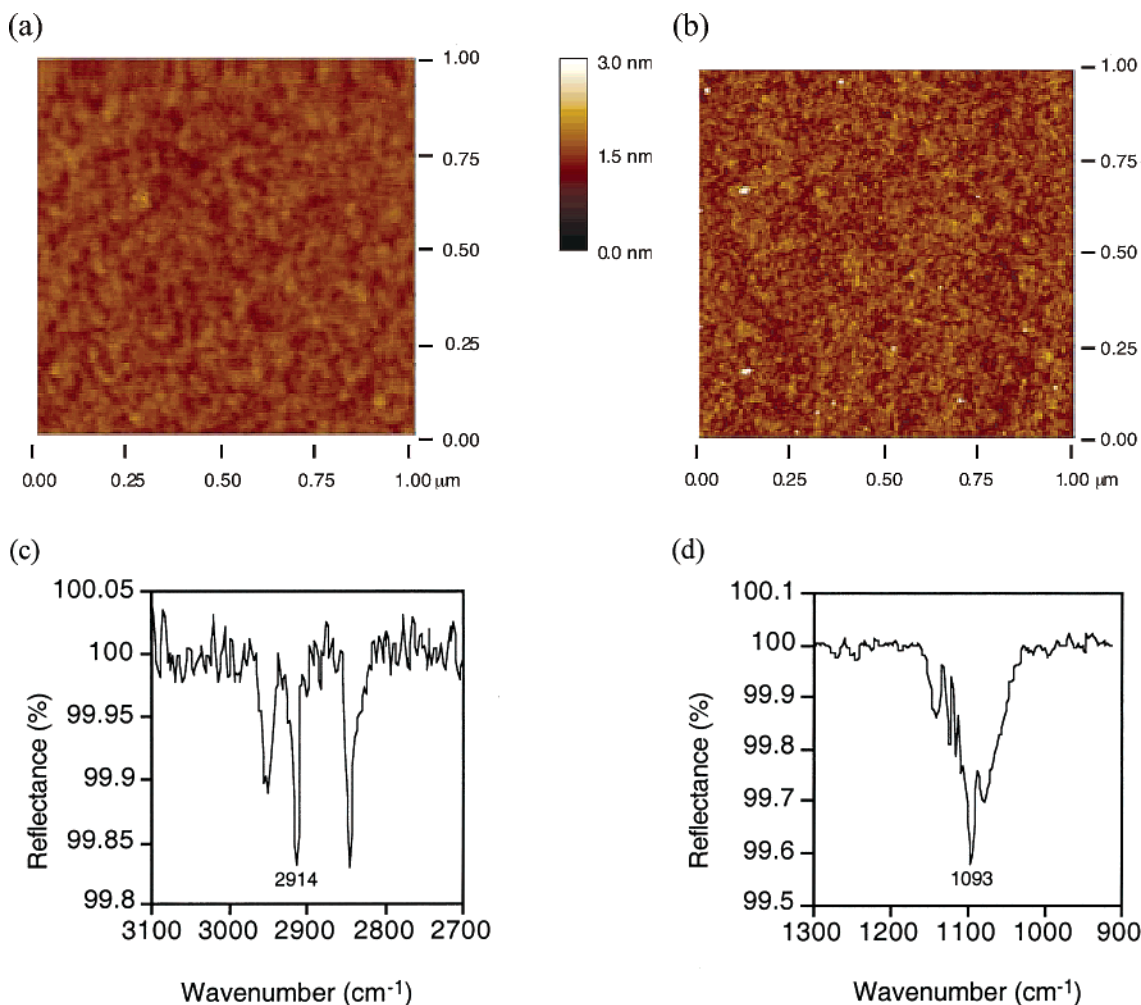


Figure 2. AFM images of (a) the clean Si native oxide surface (rms roughness 0.21 nm); (b) octadecylphosphonate/SiO₂/Si (rms roughness 0.25 nm), from 1.0 mM deposition solution; IR spectra of (c) octadecylphosphonate/SiO₂/Si, aliphatic region; (d) phosphonate region.

measurement of a film of ODP grown on SiO₂/Si from 0.05 mM ODPA in THF by one T-BAG cycle showed surface coverage to be 0.82 ± 0.02 nmol/cm², about 75% of that measured for octylphosphonate on the Ti native oxide. This loading corresponds to an area per molecule of 20.2 ± 0.4 Å², which is slightly more densely packed than octadecylphosphonic acid/mica.²⁷ A QCM measurement following two T-BAG cycles gave a surface coverage of 0.90 ± 0.02 nmol/cm², which corresponds to an area of 18.5 ± 0.4 Å²/molecule, close to the value of 18.6 Å²/molecule for close-packed aliphatic chains.²⁹

α-Quarterthiophene (4T) prepared according to literature procedures^{30–32} was contaminated with byproducts that were difficult to separate and which complicated subsequent phosphonation steps. In response, we developed a new and simple method to prepare 4T which is based on palladium-assisted coupling of bithiophene. Oxygen serves as the ultimate oxidant, and water is the only byproduct. Quarterthiophene could be obtained in good yield and was pure as indicated by ¹H NMR. We have also synthesized α-sexithiophene from α-terthiophene

in 152% yield (based on PdCl₂, 71% based on 3T) using this method.

α-Quarterthiophene-2-phosphonic acid (4TPA, **1**) was prepared from 4T by adaptation of a known procedure³³ and was used for film formation on SiO₂/Si by the T-BAG method. AFM showed that a comprehensive monolayer of α-quarterthiophene-2-phosphonate (4TP) was formed on SiO₂/Si (Figure 3a) when the film was grown from a 0.14 mM solution of **1** in THF. Section analysis (Figure 3b) based on the 4TP/SiO₂/Si film edge indicates its thickness to be 2.0 ± 0.2 nm. Because the estimated length of 4TP is approximately 1.9 nm, this film thickness suggests only a small deviation, if any, of the 4T moiety from vertical.³⁴ Surface loading of 4TP/SiO₂/Si prepared from three T-BAG cycles (0.0025 mM solution of **1** in THF) was measured by QCM¹⁹ to be 0.66 ± 0.03 nmol/cm² (Figure 4). This corresponds to a molecular cross-sectional area of 25.1 ± 0.4 Å²/molecule, which is in the range reported for crystalline 4T (23.4–25.6 Å²/molecule, for low and high temperature forms, respectively).³⁵

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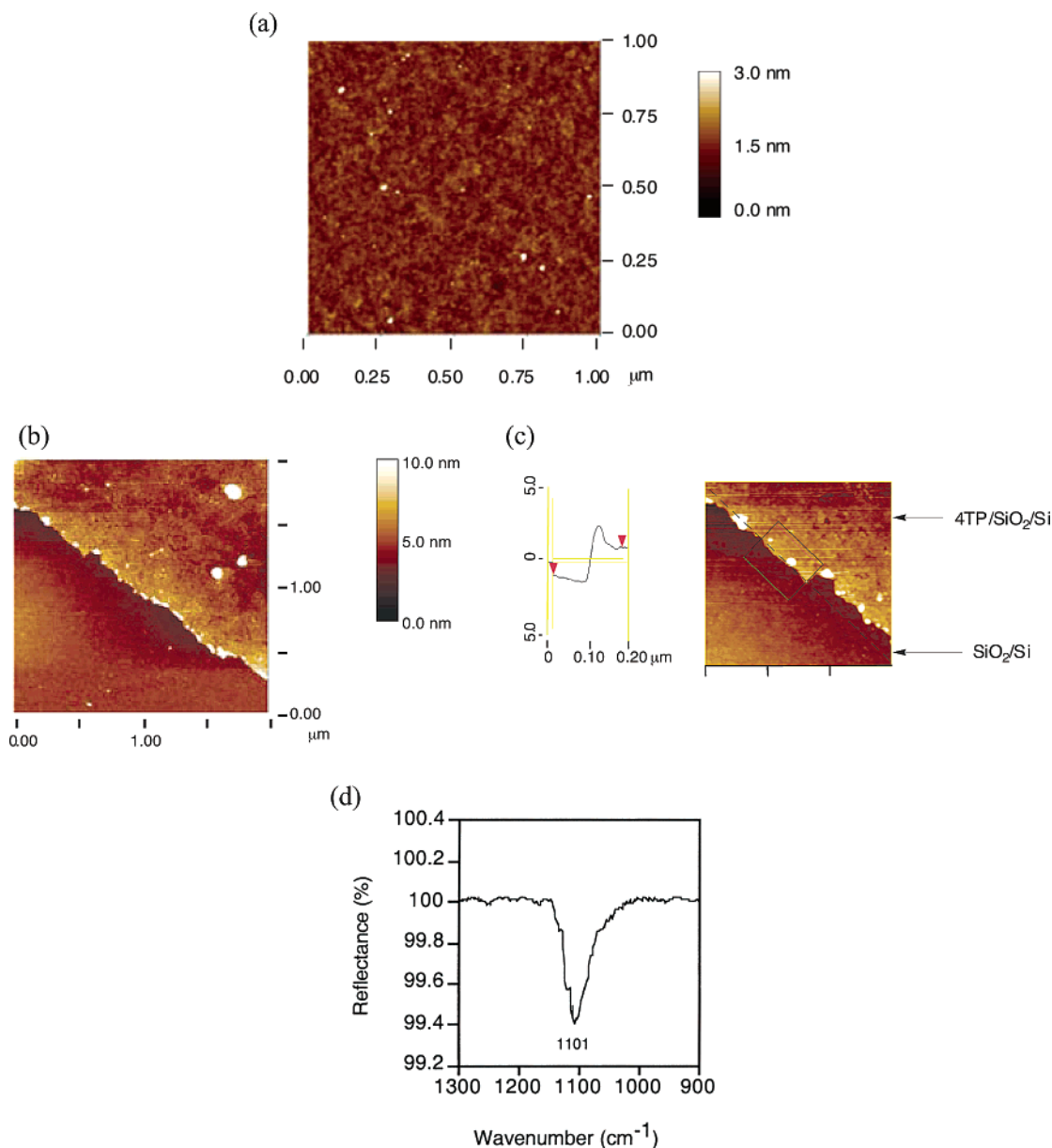


Figure 3. AFM images of (a) the comprehensive monolayer of 4TP/SiO₂/Si; (b) the α -quarterthiophene-2-phosphonate monolayer film edge, from 0.143 mM deposition solution; (c) section analysis of this monolayer film edge; (d) IR spectrum of α -quarterthiophene-2-phosphonate/SiO₂/Si, phosphonate region.

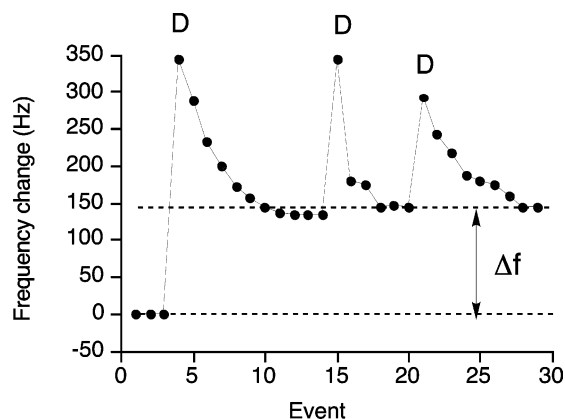


Figure 4. Preparation of 4TP/SiO₂/Si on a QCM crystal. (D) Indicates frequency measurements following each T-BAG deposition step; the unlabeled points indicate frequency measurements following rinsing and solvent removal. The net frequency change (Δf) gives the surface loading of 4TP/SiO₂/Si.

No film formation was observed when a SiO₂/Si substrate was simply immersed in a solution of the phosphonic acid²⁷ at room temperature for 3 days or with heating at 60 °C, even for 2 weeks (Figure 5). Heating in solution or aerosol spraying¹⁸ also failed to give a monolayer film of ODP or 4TP on smooth SiO₂/Si, with or without heating following solvent removal. Instead, these techniques gave uneven surface coatings (by AFM) with regions of multilayer surface deposition. The concentration of a T-BAG deposition solution also has an effect on initial film formation: Films grown from a 0.01 mM solution of 1/THF (followed by heating and rinsing) consisted of small islands of different heights of 4TP on the SiO₂/Si surface (Figure 6a). It is interesting that, even at this submonolayer coverage, some of these islands are also about 2.0 ± 0.2 nm high (Figure 6b). Three T-BAG deposition sequences from this same solution (followed by a final heating step), however, gave a complete monolayer (Figure 6c).

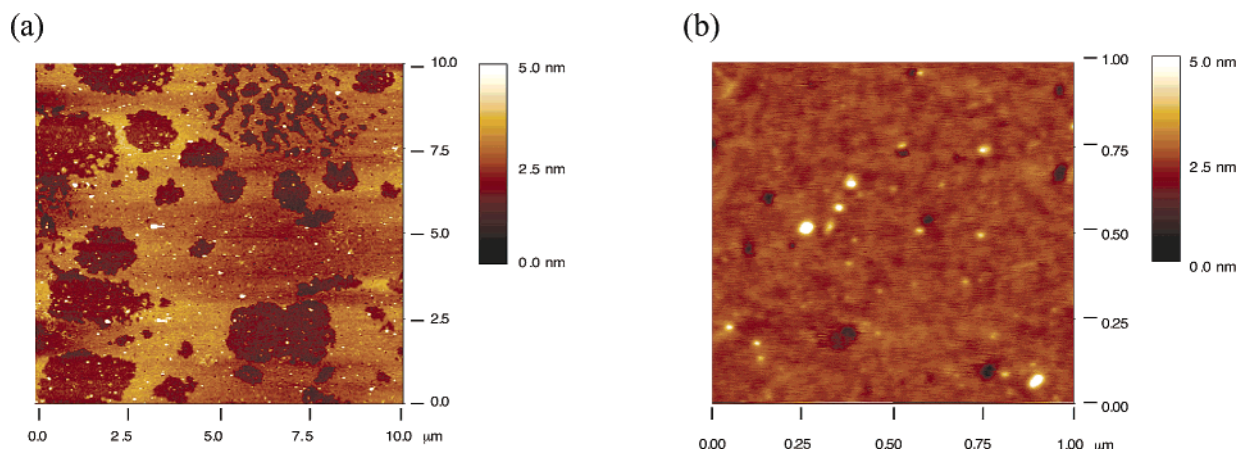


Figure 5. AFM images of (a) α -quarterthiophene-2-phosphonic acid deposited on SiO_2/Si , without heat treatment, then rinsed ($10 \times 10 \mu\text{m}$); (b) close-up view of the film, $1 \times 1 \mu\text{m}$. From the large holes formed in the SAM, it can be seen that 4TP is easily removed from the surface, likely as the corresponding potassium salt by the carbonate rinse. No such effects are observed for the heated films, even after 1 h of sonication in carbonate.

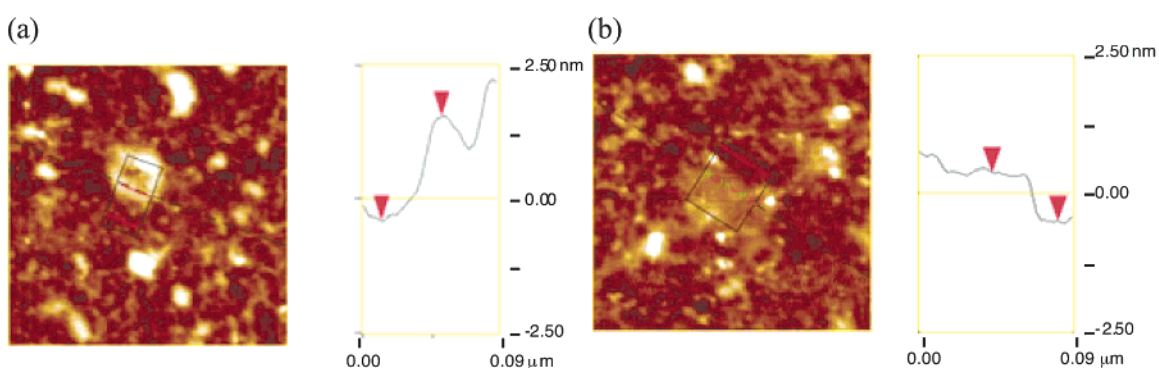


Figure 6. AFM section analysis of (a) island formation of 4TP/ SiO_2/Si , $2.0 \pm 0.2 \text{ nm}$ high, from 0.01 mM deposition solution, one T-BAG cycle; (b) island formation, $1.2 \pm 0.2 \text{ nm}$ high, from 0.01 mM deposition solution, one T-BAG cycle; (c) $10 \times 10 \mu\text{m}$ image of α -quarterthiophene-2-phosphonate deposited on SiO_2/Si , after three T-BAG cycles.

X-ray reflectivities were measured for 4TP/ SiO_2/Si following heating, both before (Figure 7a; \circ) and after rinsing (Figure 7a; \blacksquare), and were plotted against the momentum transfer, q_z .

Intensities were multiplied by q^4 to compensate for overall decay. As shown in Figure 7a, measurements made for the 4TP-covered surface before rinsing show intensity variations in the

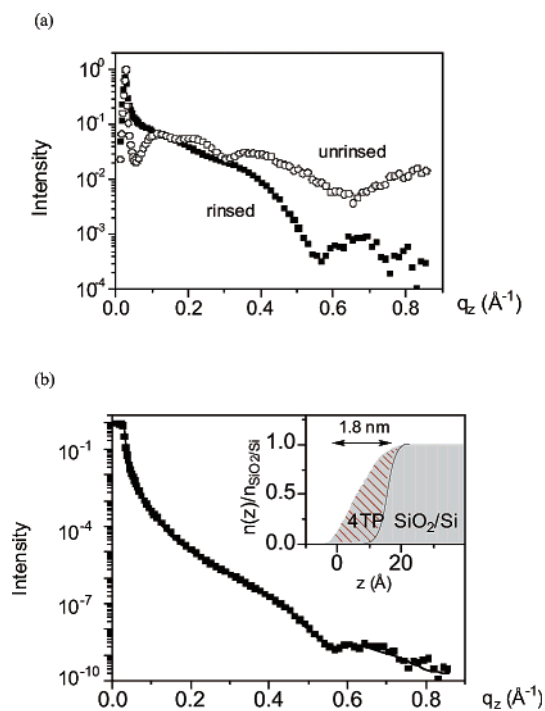


Figure 7. X-ray reflectivity data for 4TP/SiO₂/Si. (a) Rinsed and unrinsed 4TP/SiO₂/Si; (b) carbonate rinsed 4TP/SiO₂/Si. X-ray reflectivity data (○) and fit to the data (—) based on the model function shown in the inset. The gray area represents the clean, dry SiO₂/Si surface (rms roughness 0.21 nm), which has a sharp density profile; the striped area represents the extra electron density due to the film of 4TP on SiO₂/Si.

range $q_z \approx 0.1 \text{ \AA}^{-1}$. These data indicate a structural feature in direct space on the order of about $2\pi/0.1 = 70 \text{ \AA}$, indicative of multilayer formation. Reflectivity data from this multilayered structure could not be modeled. In contrast, reflectivity data

obtained after rinsing (Figure 7b; ■) were well-modeled; the solid line in Figure 7b represents a best fit based on the inset electron density profile (normalized to the density of SiO₂). The striped area in this profile is due to the organic film, which is calculated to be 1.8 nm thick. However, the profile for 4TP/SiO₂/Si is not as abrupt as that for clean SiO₂/Si, which indicates some microscopic disorder within the 4TP film.

We have now demonstrated a new methodology based on the self-assembly for bonding organic monolayers to the native oxide surface of silicon. We have shown films of ODP and 4TP prepared by the T-BAG method to be densely packed; 4T groups are nearly perpendicular to the surface. It may be that the high density of the 4TP film measured is possible because of favorable π -interactions among neighboring units unencumbered by the relatively small size of the phosphonate headgroups. T-BAG is easily accomplished and, because it is carried out on the native oxide of Si, no special pretreatment of the semiconductor is required. Thus, our new surface processing technique is significant in that it provides for easy synthesis of a variety of film types on SiO₂/Si, which may facilitate the study of the physics of microelectronic devices based on Si⁴ where molecular ordering, as well as dense surface coverage, of a surface-bound semiconducting layer is required.⁵

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Supporting Information Available: The ¹H NMR spectrum (400 MHz; acetone-*d*₆) of α -quarterthiophene-2-phosphonate diethyl ester (aromatic region) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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