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Self-assembled monolayers of 2-(thienyl)hexylphosphonic acid on native oxide surface of silicon fabricated by air–liquid interface-assisted method

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ABSTRACT

A simple, fast, and low-compound-consuming procedure based on the air–liquid interface-assisted method for preparing self-assembled monolayers (SAMs) of organic molecules with phosphonic acid head groups on the native oxide surface of silicon was demonstrated. The SAMs thus prepared were characterized by contact angle measurement, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and atomic force microscopy (AFM). This approach enabled the fabrication of ordered SAMs in a large-area substrate.

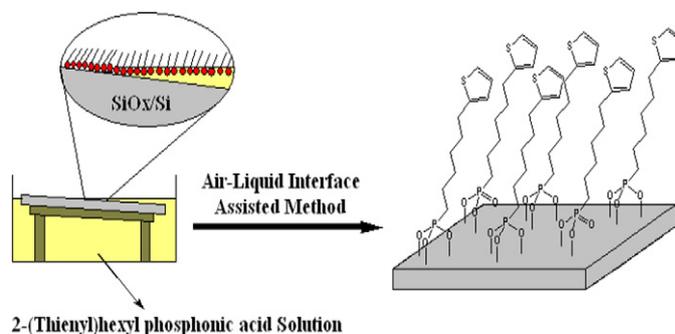
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1. Introduction

Monolayers of amphiphilic organic molecules that form spontaneously on a substrate surface by adsorption from solution are known as self-assembled monolayers (SAMs) and have been extensively studied during the past decade because of their extreme usefulness in surface modification and functionalization. This methodology has numerous potential applications, including adhesion promotion [1,2], microcontact printing [3], chemical/biological sensing [4,5], corrosion resistance [6], and wetting [7]. In the field of SAMs, the Au/thiol system has been investigated extensively because Au is very stable in an atmosphere that will promote the adsorption of thiols onto the Au surface [8] and the adsorptive ability between the thiol group and gold is very strong and highly stable [9]. In addition to Au/thiol systems, organosilicon compounds have been used for many years to generate SAMs on metal oxide substrates [10,11]. Recently, phosphonates or phosphonic acid-bearing molecules have been shown to form ordered SAMs on metal oxide surfaces because the hydroxyl groups on the surface of transition metal oxides, such as titanium oxide, niobium oxide, zirconium oxide, anodized aluminum, and tantalum oxide, are known to interact strongly with phosphonic acids or phosphonates and thus to form relatively stable interfacial bonds [12–14]. However, the literature indicates that phosphonic acid is incapable of forming ordered and compact monolayers on both mica and SiO₂ surfaces [14,15]. Recently, Schwartz and co-workers developed

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Scheme 1. Schematic illustration of preparing self-assembled monolayers of amphiphilic organic molecules on the native oxide surface of silicon by air–liquid interface-assisted (ALIA) method.

a procedure, called T-BAG (tethering by aggregation and growth), in which the aggregation of organophosphonic acid amphiphiles at the air–solvent interface was transferred to the vertically immersed SiO₂ substrate during solution drying, forming compact and ordered monolayers of organic molecules [15]. However, this approach involves a long preparation time. Also, a large change in the solution concentration throughout the preparation process allows micelle formation, which may complicate the aggregation pattern of organic molecules at the air–solvent interface, limiting their ability to form compact SAMs on a large-area substrate.

This work describes a simple procedure for fabricating SAMs of organophosphonic acid amphiphile on the native oxide surface of silicon via an air–liquid interface-assisted (ALIA) method, as in Scheme 1.

2. Materials and methods

2.1. Synthesis of 6-(2-thienyl)hexylphosphonic acid (THPA)

To a 250-ml one-necked round-bottom flask that contained 2-bromothiophene (6 g, 36.8 mmol) was added 50 ml tetrahydrofuran (THF). The solution was chilled to -78°C with liquid N_2 . Then 1.6 M *n*-BuLi (27.6 ml, 44.2 mmol) was added dropwise via a syringe and stirred for 1 h, followed by the addition of neat 1,6-dibromohexane (11.3 ml, 73.6 mmol) in one portion. After the solution was stirred for 12 h, the reaction was quenched with water and the resulting mixture was extracted with ether. Removal of solvent with a rotary evaporator afforded a yellow crude product. It was then distilled under vacuum (0.5 Torr) at 95°C to give 2-(6-bromohexyl) thiophene as a colorless oil (4.9 g, yield = 54%).

To a suspension of magnesium (1.55 g, 64 mmol) in 40 ml anhydrous diethyl ether was added 2-(6-bromohexyl) thiophene (7.97 g, 32 mmol). After being refluxed at 60°C for 1 h, the solution was slowly purged into a diethyl ether solution containing diethyl chlorophosphate (4.7 ml, 32 mmol) and [1,3-bis(diphenylphosphino)-prapane] dichloronickel (II), Ni(dppp)Cl₂ (0.10 g, 0.18 mmol). The mixture was stirred overnight under reflux and then washed with distilled water. The organic phase was dried over MgSO_4 and filtered and the solvent was evaporated. The obtained crude product was purified by silica gel column chromatography using hexane/ethyl acetate (4:6) as eluent to give 6-(2-thienyl)hexyl diethyl phosphonate as a light yellow oil (2.64 g, yield = 27%).

To a round-bottom flask that contained 6-(2-thienyl)hexyl diethyl phosphonate (2.64 g, 8.68 mmol) and dichloromethane (25 ml) was added bromotrimethylsilane (2.9 ml, 21.7 mmol). The solution was stirred at room temperature for 8 h. Following the reaction, the mixture was subjected to vacuum distillation to remove by-products. Afterward, the colorless residue was stirred with excess methanol for more than 12 h. The solution was then concentrated directly under vacuum to give a white crystalline product (1.8 g, 85% yield). ¹H NMR (ppm, MeOD): δ 1.41–1.46 (m, 4H, CH_2CH_2), 1.62–1.74 (m, 6H, P- CH_2CH_2 and 2-Th-C- CH_2), 2.87 (t, 2H, 2-Th- CH_2), 6.82 (d, 1H, 3-Th-H), 6.92 (dd, 1H 4-Th-H), 7.17 (d, 1H, 5-Th-H). ³¹P NMR (MeOD): δ 30.62. HRMS (ESI) calcd. for 248.06; found 248.0.

2.2. Preparation of self-assembled monolayers of TPHA by ALIA method

The substrate, which contains a thin oxide layer of silicon, was prepared by subsequently sonicating a single-crystal silicon (100) wafer (area 25 cm²) in acetone (15 min), piranha solution (96% H_2SO_4 :35% H_2O_2 = 1:3, 45 min), NH_4OH : H_2O_2 :deionized water = 1:1:5 (30 min), and deionized water (30 min). It was then placed on an adjustable platform, which was horizontally mounted at a tilt angle of 5° in a glass bath that contained a solution of TPHA in ethanol. The highest position of the SiO_x/Si substrate was set below the surface of the solution by about 2 mm. After evaporation of the solvent had caused the level of the solution to fall below the substrate surface, the substrate was removed and heated in an oven at 140°C under N_2 for 20 h. The samples were then sonicated in 0.5 M K_2CO_3 and subsequently in ethanol/water (2:1) for 30 min to remove unbound molecules, before being dried in a vacuum oven at room temperature.

2.3. Characterization

Surface wettability was investigated by measuring the static contact angles using a First Ten Angstroms (FTA 125) contact angle analyzer at room temperature and ambient humidity with water

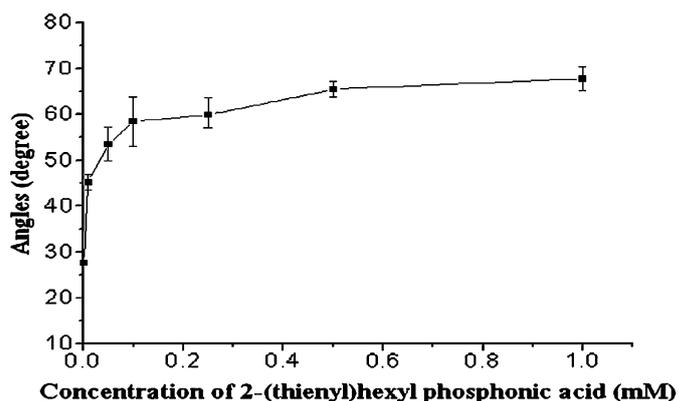


Fig. 1. Static water contact angles of SAMs prepared from different concentrations of 2-(thienyl)hexylphosphonic acid solutions.

as the probe liquid. A 2- μl water droplet was placed on the substrate with a syringe. The angle was obtained by estimating the tangent to the drop at its intersection with the surface, and the average of five measurements was taken for reported contact angles. XPS analyses were performed using a VG Scientific ESCALAB 250 system. Spectra were acquired at a base pressure of 10^{-9} mbar using a monochromatic $\text{AlK}\alpha$ X-ray source operated at 200 W. Fourier transform infrared (FTIR) spectra of SAMs were obtained using a JASCO FT/IR 480 Plus spectrophotometer with an attenuated total reflectance (ATR) accessory. Atomic force microscopy was performed in the tapping mode in air using a Digital Instruments Nanoscope IIIa Multimode atomic force microscope. The nominal force constant of the silicon nitride cantilevers (Nanoprobes Ltd.) was 0.12 N m^{-1} .

3. Results and discussion

Fig. 1 plots the static water contact angles measured on bare SiO_x/Si and TPHA-modified SiO_x/Si surfaces that were prepared using various TPHA concentrations. The results reveal that the water contact angle increased abruptly from 27.6° for bare SiO_x/Si to around 60° as the TPHA concentration increased from 0.05 to 0.25 mM and then leveled off at about 65° at concentrations from 0.5 to 1.0 mM, indicating that the formation of a thin layer of TPHA on top of SiO_x changed the surface from hydrophilic to hydrophobic.

The XPS scan of TPHA-modified SiO_x/Si in the range 50–800 eV yielded P2s and P2p peaks at around 192 and 134 eV, respectively. However, the P2p peak was entirely superimposed by the plasmon loss peak of the silicon wafer. Although the Si-plasmon loss peak at 186 eV interfered with the P2s peak, the two peaks were distinguishable. Accordingly, the P2s peak was selected to analyze TPHA SAMs. The XP spectra of TPHA-treated SiO_x/Si , displayed in Fig. 2, indicate that the intensity of the P2s peak decreased dramatically upon treatment with the K_2CO_3 solution and the ethanol/ H_2O mixture, revealing that the washing step can efficiently remove unbound TPHA. Moreover, the binding energy of P2s shifted from 192.4 to 191.8 eV, implying that the phosphonic acid head group was chemically bonded to the SiO_x surface. A similar result has been reported for the SAMs of octadecylphosphonic acid on an oxide-covered silicon coupon [16].

The FTIR spectra of bulk TPHA and the TPHA-modified SiO_x/Si substrate are shown in Fig. 3. Upon the adsorption of TPHA onto SiO_x , the signal in the region $3300\text{--}3600 \text{ cm}^{-1}$, corresponding to the O–H group in TPHA, disappeared, revealing that the adsorbed phosphonate groups were deprotonated. The absorption bands at 1003 and 950 cm^{-1} , corresponding to the asymmetric and symmetric stretching vibrations of the P–O group, respectively, were

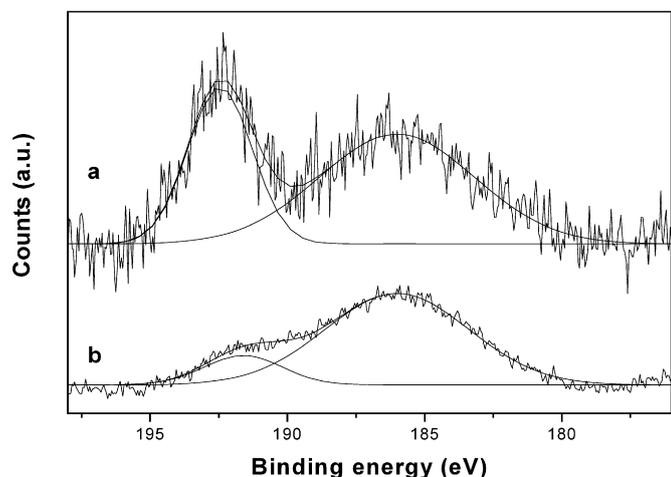


Fig. 2. The P2s signals in the XPS spectra of 2-(thienyl)hexylphosphonic acid SAMs on SiO_x/Si (a) before and (b) after the washing process.

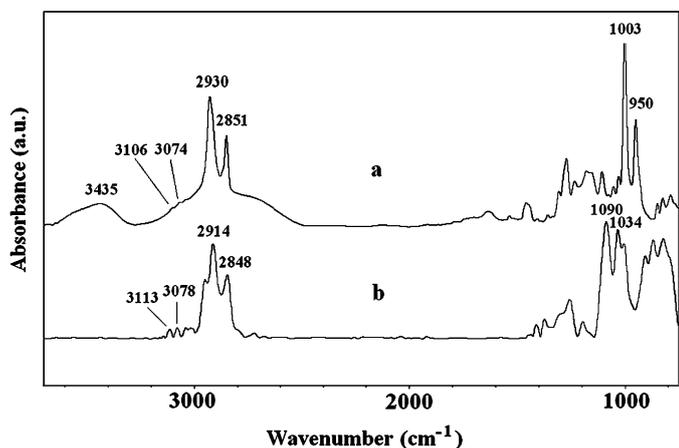


Fig. 3. ATR-FTIR spectra of (a) 2-(thienyl)hexylphosphonic acid and (b) the SAMs of 2-(thienyl)hexylphosphonic acid on SiO_x/Si.

broadened and shifted to 1090 and 1034 cm⁻¹. These observations suggest the formation of P–O–Si bonds via a condensation reaction between the anion of the deprotonated acid and the surface oxide or hydroxide groups of SiO_x [17]. The frequencies of methylene stretching have been demonstrated to be useful for determining the extent of alkyl chain ordering of SAMs [18]. The vibration bands that are attributed to the methylene asymmetric and symmetric stretching at 2930 and 2851 cm⁻¹, respectively, are shifted to 2914 and 2846 cm⁻¹, implying that the methylene chains in THPA, adsorbed onto the native oxide surface of silicon, were staggered in all-*trans* configurations. The ALIA approach takes advantage of the high concentration of amphiphile molecules adsorbed onto the air-liquid interface and the gradual transfer of those molecules onto the SiO₂ surface during the drying process, forming compact SAMs.

The quality of the SAMs was evaluated using atomic force microscopy (AFM). Fig. 4 presents AFM images of bare silicon native oxide (left) and the THPA SAMs that were prepared from 0.5 mM (middle) and 1.0 mM (right) THPA solutions. The scan size and Z range of all images were set to 1 × 1 μm and 3 nm, respectively. The silicon oxide substrate and THPA SAMs that were prepared from the 0.5 mM solution have very smooth surfaces with root-mean-square roughness (*R*_{rms}) values of approximately 0.11 and 0.12 nm, respectively. Although the surface roughness of SAMs increased slightly to 0.14 nm as the concentration of THPA solution increased slightly to 1.0 mM, many particles and some pinholes with an average diameter of about 20 nm appeared all over the surface, probably because the THPA aggregates formed in the more concentrated solution.

The thickness of the SAMs was determined from the difference between the heights of the film surface and the base of the pinhole, observed using AFM; it was determined to be about 1.04 nm. Additionally, the angle of tilt between the adsorbed THPA molecules and the surface normal vector was calculated from the arccosine of the ratio of the film thickness (1.04 nm) to the length of the molecule (1.63 nm), which was estimated from data in the literature [15,19]. The angle was determined to be around 50°. This value slightly exceeds that of the octadecylphosphonic acid that was adsorbed onto SiO₂ (40°) [20] and mica (46°) [21], possibly because the terminal thiophene ring was larger and the polymethylene backbone in THPA was shorter than those in octade-

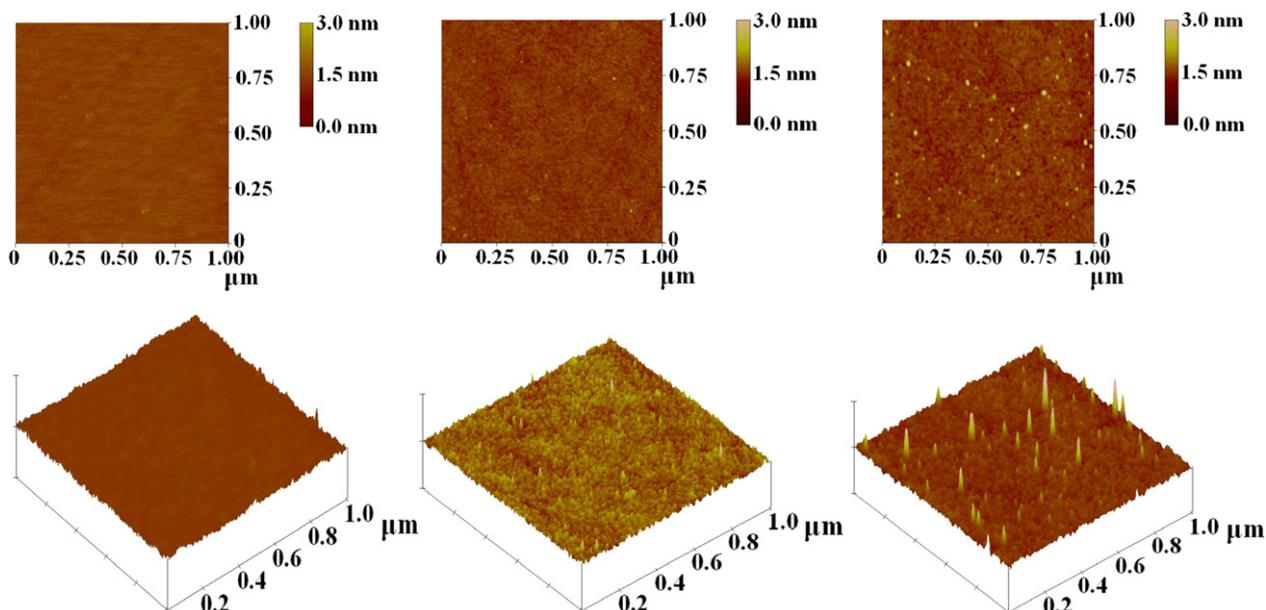


Fig. 4. AFM images (above: height, below: 3D) for pure silicon native oxide (left) and SAMs prepared from 0.5 mM (middle) and 1.0 mM (right) of 2-(thienyl)hexylphosphonic acid solutions.

cylphosphonic acid, thus reducing the van der Waals force among the alkyl chains.

The surface loading of monolayers that formed on the native oxide surface of silicon was determined gravimetrically using a quartz crystal microbalance (QCM). A quartz wafer with gold electrodes on its surface (196 mm²) was sputter-coated with a thin layer of SiO_x that was grown with self-assembled monolayers of THPA by the ALIA method and then washed with K₂CO₃ solution, following the procedure described above. The mass of SAMs was determined from the change of the QCM-measured resonant frequency before and after THPA deposition. It was found to be 47.4 ng, which is equivalent to an occupied area per molecule of 17.0 Å². These values indicate that the THPA on SiO_x/Si prepared by the ALIA method has a packing density similar to that of the octadecylphosphonic acid on SiO₂/Si (18.5 Å²) [15] and 6-(3-thienyl)hexanethiol on gold-coated Si(111) wafers (15.2 Å²) [22].

4. Summary

Smooth and homogeneous self-assembled monolayers of 2-(thienyl)hexylphosphonic acid on the native oxide surface of silicon were prepared by the air–liquid interface-assisted method. The thus-prepared SAMs were packed in an orderly manner with an all-*trans* configuration, and adhered firmly to the substrate surface. This new method is very simple and fast and requires a small amount of solution, and is therefore suited to large-area SAMs fabrication.

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