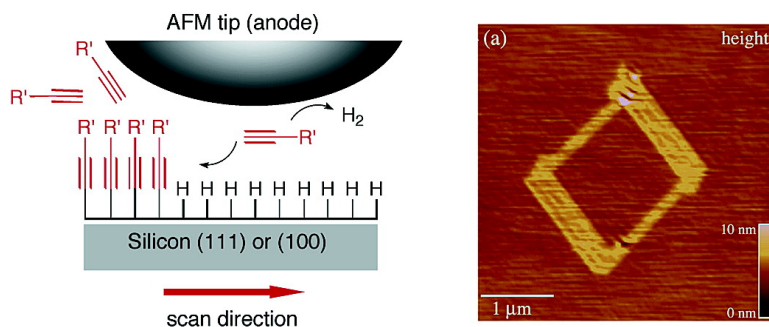**Article**

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Nanopatterning of Alkynes on Hydrogen-Terminated Silicon Surfaces by Scanning Probe-Induced Cathodic Electrografting

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Abstract: The electrochemical cathodic electrografting reaction, previously demonstrated on bulk silicon surfaces, can be patterned on the nanoscale utilizing conducting probe atomic force microscopy (CP-AFM). Alkyne electrografting is a particularly useful chemical technique since it leads to direct covalent attachment of conjugated alkynes to silicon. In addition, application of a forward bias during the reaction renders the surface less sensitive to oxidation and the resulting monolayers are very stable in air and basic aqueous solution. Alkyne monolayer lines can be drawn down to 40 nm resolution using a Pt-coated AFM tip, and the heights of the monolayers scale with the molecular length of the alkyne. The tip is biased (+) and the surface is biased (−) to drive the cathodic electrografting reaction under ambient conditions. The resistance of the monolayers to fluoride, as well as friction force microscopy, indicate that the alkynes are covalently bonded to the surface, not oxide-based, and hydrophobic. The reaction does not work with alkenes, and therefore hydrosilylation is not the primary mode of reaction. Wider lines (300 nm) can be produced using broadened Pt-coated AFM tips. This reaction could be important for the interfacing of conjugated molecules directly to silicon in a spatially controlled fashion.

Introduction

The patterning of monolayers on conducting and semiconducting surfaces has become a central focus of research because of the critical importance of integration of various molecular devices, wires, and other nanoscale components with existing electronic structures.[1−3] To address the issue of integration, there has been an explosion of constructive methods to pattern discrete molecule-based monolayers on the nanoscale and upon conducting and semiconducting surfaces, including nanoshaving and nanografting,[4] Dip Pen Nanolithography (DPN),[5] and related offshoots,[6] soft lithography,[1,2,7] photolithography,[8,9] and other techniques.[10] Interfacing of molecular wires and conducting

polymers directly with silicon through a potentially conjugated linkage could provide a means of hardwiring with integrated circuitry.[11] Covalent attachment of conjugated alkenes, alkynes, and aromatics with silicon through an Si−C bond is an intriguing and potentially useful approach because of the small electronegativity difference between silicon and carbon, the thermodynamic and kinetic stability of this bond, and the potential to avoid the insulating and electronically defective native silicon oxide interface.[12,13] Bulk-scale surface wet chemistries (non-UHV) already developed to link up unsaturated groups with Si−C bonds to various morphologies of hydride-

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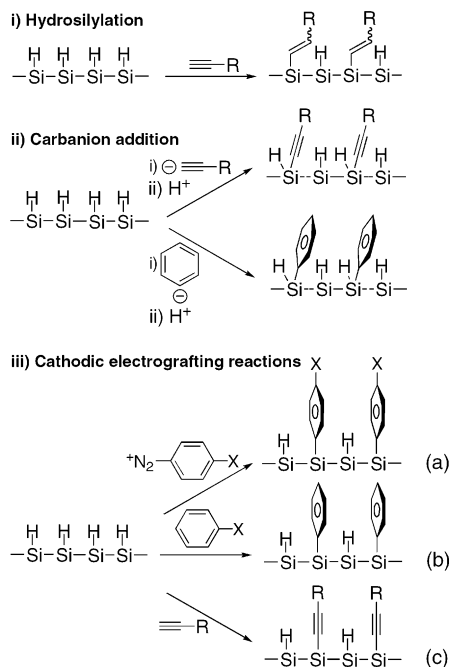(13) Royea, W. J.; Juang, A.; Lewis, N. S. *Appl. Phys. Lett.* **2000**, *77*, 1988.

Figure 1. Wet chemical reactions on hydride-terminated silicon surfaces which result in conjugated alkenes, alkynes, or aromatics bonded directly to the surface through a silicon−carbon bond.
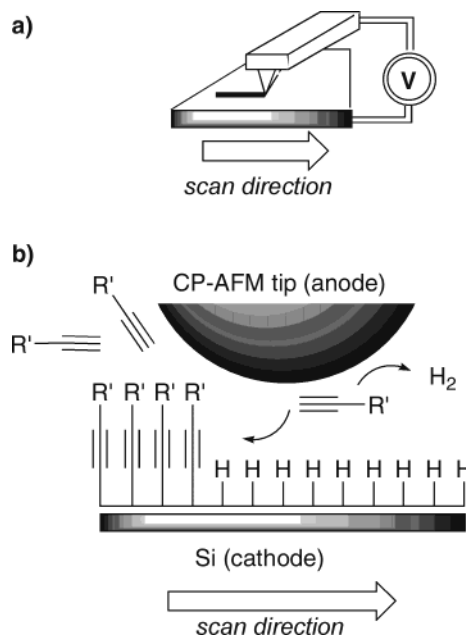

Figure 2. Schematic of the alkyne electrografting reaction mediated on the nanoscale by CP-AFM. (a) A voltage difference is applied across the tip−surface interface; as the tip moves across the surface, lines of the electrografted alkyne are drawn. (b) A forward negative bias is applied to the hydride-terminated surface in the presence of excess alkyne to drive the cathodic alkyne electrografting reaction.

terminated silicon, include hydrosilylation of terminal alkynes leading to alkenyl groups,[14] addition of alkynyl and phenyl carbanions,[15] and electrografting of phenyl diazonium salts,[16] aryl bromides,[17] and alkynes,[18] as outlined in Figure 1.

Integration of organic-based structures and biomolecules directly with silicon in a spatially defined fashion on the nanoscale remains a fundamental challenge in nanoscience. For these silicon surface chemistries to be useful for potential device applications, the reactions need to be performed in a spatially defined manner, with control down to the nanoscale. Previous wet chemical approaches to accomplish constructive patterning of molecules on unoxidized silicon through direct Si−OR or Si−C bonds include microcontact printing of alcohols on Si-(111)−Cl (micron scale),[19] mechanical scribing of Si(111)−H with a diamond scribe or AFM tip in the presence of alkenes (micron nanoscale),[20] photolithographic alkene/aldehyde hydrosilylation (micron scale),[8,21,22] and silyl ester formation[23] on hydride-terminated flat and porous silicon (micron scale). Under UHV conditions, hydrosilylation can be mediated in a spatially defined manner on Si(111)−H through STM-based cleavage of Si−H bonds.[24] The resulting nanoscale domains of silicon-dangling bonds react with alkenes to form alkyl monolayer regions. These surface terminations produce saturated aliphatic functionalities, and thus, we looked to reactions that cleanly lead to potentially conjugated, unsaturated linkages to the surface (Figure 1) through straightforward means.

Through the use of conducting probe atomic force microscopy (CP-AFM), the alkyne electrografting reaction (reaction c, Figure 1) is mediated with a Pt-coated AFM tip on hydride-terminated Si(111) and Si(100) in ambient air. This reaction is of interest because of the ubiquity of alkyne termination in synthesized organic molecular wires[25] and the ease of synthesis and commercial availability of alkyne-containing molecules.[26] Previously published cathodic alkyne electrografting work (macroscale dimensions) utilized an electrolytic solution of dichloromethane and NH_4PF_6, but the close proximity of the tip to the flat hydride-terminated silicon surfaces enables the reaction to proceed in absence of electrolyte.[27] In fact, mac-roscale electrografting, carried out through the superimposition

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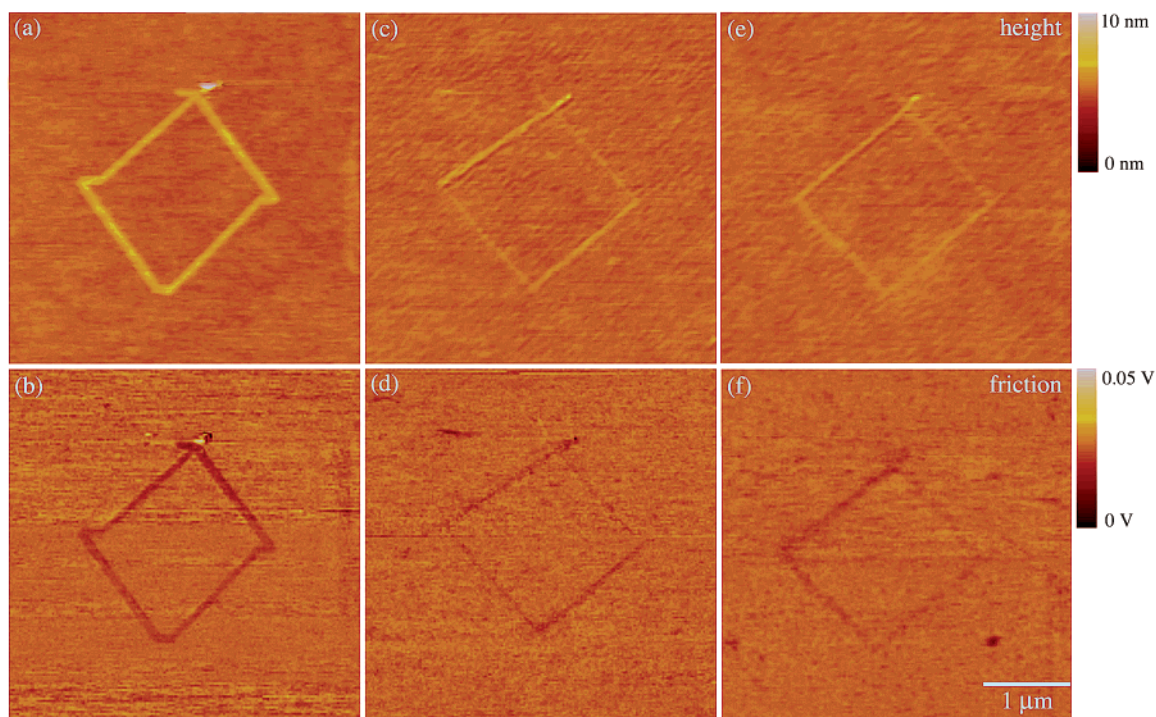
Figure 3. Height- and friction-mode AFM images of three different alkynes electrografted to the surface. Height images of (a) 1-octadecyne, (b) 1-dodecyne, and (c) 1,4-diethynylbenzene on Si(111)−H. Friction images of (d) 1-octadecyne, (e) 1-dodecyne, and (f) 1,4-diethynylbenzene, taken simultaneously with the height images.
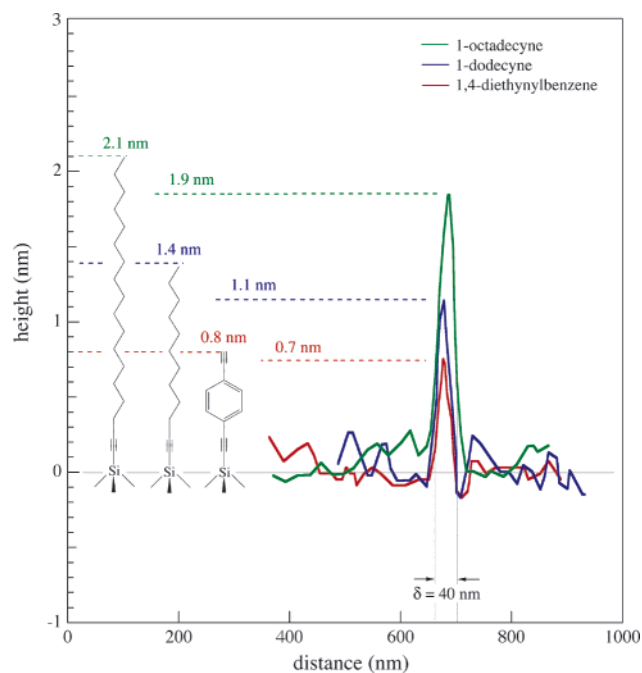

Figure 4. Calculated and experimentally determined height information for the three different alkynes electrografted onto the Si(111)−H surface. The values above each drawing are calculated heights, and those which correspond to the height of the plots are the experimentally determined values.

of two highly doped silicon wafers sandwiching a thin layer of neat alkyne (no added electrolyte), successfully leads to cathodic alkyne electrografting,[28] as determined by ellipsometry and contact angle measurements (Supporting Information). The mechanism has yet to be determined,[18] but the application of

the forward bias to the silicon surface is expected to render the Si−H groups more hydridic or progress further to silyl anions.[17] Reaction of the forward-biased Si−H groups with the relatively acidic alkyne ($pK_a \approx 25-26$) could proceed via direct evolution of H_2 and formation of the alkyne termination in a concerted fashion. Alternatively, in situ generation of silyl anions could deprotonate the alkyne,[29] leading to the alkynyl carbanion that then adds across weak silicon−silicon bonds to yield the final alkyne termination.[17]

The conducting probe AFM procedure is outlined in Figure 2. Lines with diameters of 40 nm can be produced rapidly and reproducibly, with the heights of the monolayers correlating with molecular length, as expected. The cathodic alkyne electrografting reaction has several advantages that render this reaction of interest for both fundamental studies and future applications.[18] Because the reaction is tolerant of a diverse range of chemical functionalities, the interfacial characteristics of the surfaces can be manipulated with extreme precision, allowing for exact and exquisite tailoring. Thus, spatially defined arrays of different surface terminations are possible. Alkynyl termination of silicon leads to surfaces of increased stability with respect to oxidation and aqueous hydrolysis, as shown on bulk-scale hydride-terminated porous silicon.[18] From a synthetic perspective, the applied cathodic bias to the hydride surface during the electrografting reaction lends the surface increased resistance to oxidation.[16] Previous results have shown that oxidation does not occur on Si(100)−H with applied voltages of up to −10 V in ambient air.[30] This result suggested that cathodic alkyne electrografting could be carried out in air. Indeed, we observe no difference between ambient air with humidity levels under

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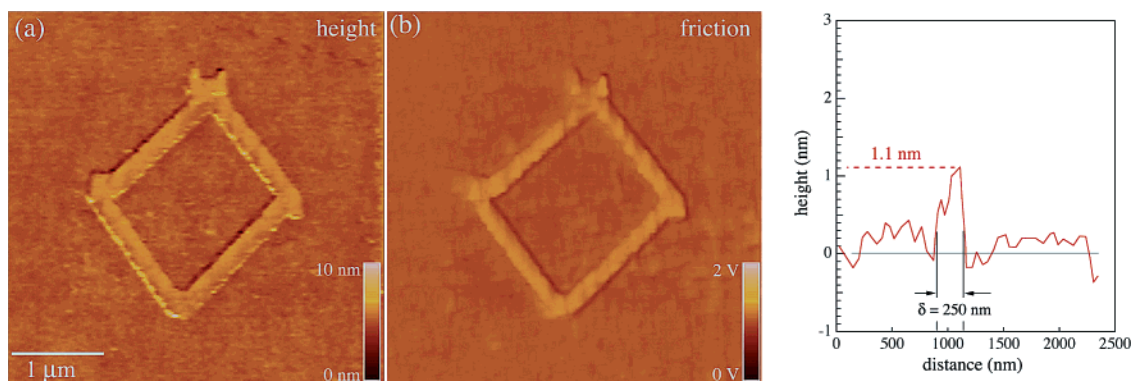
Figure 5. Height (a) and friction (b) AFM images of oxide produced on Si(111)−H under ambient conditions with an applied surface voltage of −6.5 V.

27%, and dry nitrogen. And finally, by extending the cathodic alkyne electrografting reaction to the nanoscale, it is expected to have utility for interfacing molecular electronics and biological molecules directly with silicon, through a potentially conjugated linkage.

Experimental Section

Reagents. Mesitylene (Aldrich) was dried with CaCl$_2$ and distilled from Na under Ar. The mesitylene was then taken into a nitrogen-filled glovebox and passed through neutral dry alumina to remove residual peroxides and water and stored over 4 Å molecular sieves. 1,4-Diethynylbenzene was purchased from TCI, stored in the glovebox, and used as received. 1-Dodecyne (Aldrich) was vacuum distilled, discarding the first 20% of the distillate, and then taken into the glovebox, passed through neutral dry alumina, and stored at −40 °C in the dark. 1-Octadecyne (GFS) was taken into the glovebox, passed through neutral alumina, and stored at −40 °C in the dark. All reagents utilized for silicon wafer cleaning and preparation were strictly semiconductor grade, without exception. Water is 18 MΩ quality from a Millipore system. Highly doped Si(111) (ρ = 0.0011−0.0015 Ω·cm) or Si(100) (ρ = 0.008−0.01 Ω·cm) wafers were purchased from TTI.

Cleaning of Si Wafers and Hydride Termination. Si(111) and Si(100) wafers were cut to size and then cleaned via the RCA procedure.[31] Silicon shards were degreased with commercially available dish soap and then placed into a preliminary cleaning solution of 3:1 parts by volume of hot concentrated H$_2$SO$_4$/H$_2$O$_2$ (aq, 30%) for 30 min. **WARNING: Mixtures of H$_2$SO$_4$ and H$_2$O$_2$ (Piranha solution) will react violently with organics.** In the first treatment, the wafers were placed in a solution of 7:2:1 parts by volume of hot H$_2$O/H$_2$O$_2$ (aq, 30%)/NH$_4$OH (aq, 27%) for 20 min. For the second treatment, the wafers were immersed in a solution of 2:1:8 parts by volume of hot H$_2$O$_2$ (aq, 30%)/HCl (aq, 37%)/H$_2$O for 20 min. After the cleaning process, the wafers were then placed in a 5% HF (aq) solution for 3 min to create the hydride-terminated surface or a degassed 40% NH$_4$F (aq) solution from Transene for 4−6 min.[32] The hydride-terminated surfaces were immediately dipped into water for several seconds. Teflon beakers and forceps were exclusively used in the steps listed above.

Alkyne Electrografting Procedure with CP-AFM. A Nanoscope IIIa and an EG&G Princeton Instruments 273 potentiostat were utilized for electrografting of alkynes on the hydride-terminated silicon surfaces. The humidity needs to be less than 27% for successful electrografting. The tips were noncontact silicon cantilevers coated with platinum (NSC21/Pt) from MikroMash. These tips have a resulting tip curvature radius of less than 40 nm and a cantilever length of ∼290 μm. To "load" the tip with alkyne, the Pt tip was placed in the AFM holder

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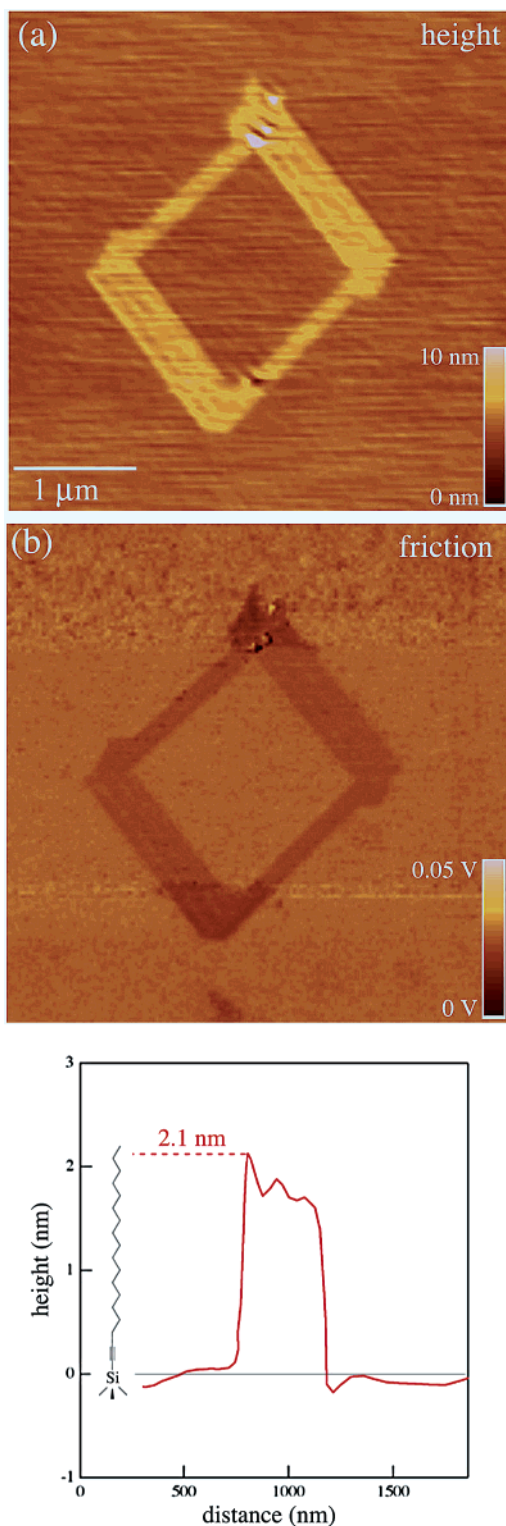
and then put in contact with the liquid alkyne spread on a clean Si-(100) wafer (native oxide) for ∼15 s. The tip was then raised out of the alkyne, and the oxide-coated Si(100) wafer was replaced with the hydride-terminated silicon surface to be functionalized. This approach for "loading" the alkyne is advantageous to spin-coating alkyne over the entire surface since it reduces the amount of residual organics following the reaction/rinsing steps, although we have found the spin-coating method to be successful.

After loading the alkyne on the tip, a low deflection set point of 50 nN (set point = 0.010 V) was utilized to minimize damaging interactions with the surface. A nanoscript was written to control the tip movement and pattern written. The scan rate was set at 0.100 Hz, or a tip speed of 2 μm/s. A potential of −1.0 V was applied to the surface, with the exception of the viscous 1-octadecyne alkyne which requires a higher applied voltage of −2.2 V since it is more difficult to press the tip as close to the surface.

Following the nanolithography, the sample was rinsed with copious amounts of dichloromethane, ethanol, and pentane to remove residual alkyne and physisorbed hydrocarbons. A rinse with 1:1 49% (aq) HF/EtOH can be used to ensure that the observed features are nonchemisorbed and to help clarify the image by removing particularly tenacious hydrocarbons.

Imaging. Imaging was done in lateral force mode to capture topological and friction force images simultaneously. The silicon cantilevers were purchased from MikroMash (NSC21, tip curvature less than 10 nm). Conditions for imaging are as follows: using the E scanner (13 μm maximum dimension image size) the scan angle was changed to 90° for lateral force microscopy mode, with a scan rate of 1.39 Hz (tip velocity of 36.1 μm/s).

Results and Discussion

Briefly, alkyne electrografting was performed in ambient air using a Digital Instruments NanoScope IIIa AFM equipped with an external potentiostat. In each experiment, a standard platinum-coated AFM tip was dipped into the desired neat liquid alkyne or alkyne-containing mesitylene solution for 15 s prior to electrografting. A constant negative potential was then applied to the surface [tip(+)] to generate the desired pattern. A low force of 50 nN was utilized to ensure that the soft Pt tip gently brushed the surface and did not induce mechanical abrasion. Unsaturated carbon−carbon bonds will only react directly with Si(111)−H if a force several orders of magnitude greater is applied.[20] Following completion of the reaction, the silicon wafer was rinsed extensively with dichloromethane, ethanol, and pentane to remove excess alkyne from the surface. To ensure that the silicon features were not oxide-based, the samples could then be rinsed with a 1:1 49% (aq) HF/ethanol solution. Imaging

Figure 4; the heights correspond to an average collected down the entire ~2 μm side of the square figure. The monolayer corresponding to the 1-octadecynyl termination (Figure 3a) is 1.9 nm in height, which is slightly less than the calculated length for 1-dodecynyl termination in an all-trans arrangement of methylene groups (2.1 nm). This indicates that, as would be expected for 16 methylene groups in a small area, the alkyl chains are flexible and most likely disordered and thus appear shorter under the pressure of the AFM tip.[33] The friction mode of the 1-dodecynyl termination is darker than the surrounding silicon hydride, indicating less interaction between the hydrophilic oxide-coated silicon tip and the hydrophobic monolayer.[34] A voltage of −2.2 V was applied to the surface to induce electrografting of 1-dodecyne [tip(+)], and control experiments clearly show that without bias, no monolayer is formed and the surface remains unfunctionalized. In addition, if this bias is applied in absence of alkyne, no apparent oxidation is noted. Alkyne functionalization cannot be detected by AFM if a voltage less than −0.5 V is applied to the surface, even holding the tip in place for extended periods of time, suggesting a minimum required voltage in this vicinity. Concentrated hydrofluoric acid solutions, 1:1 49% HF (aq)/EtOH, do not erase the monolayer pattern, conditions under which silicon oxide rapidly dissolves (vide infra). Alkyne electrografting also functions on Si(100)−H, as shown in the Supporting Information, and thus, substrate orientation is unimportant.

A shorter aliphatic alkyne, 1-dodecyne, was also electrografted, leading to monolayers with a height of 1.1 nm, as compared to the calculated length of 1.4 nm, as shown in Figures 3, b and e. As with 1-octadecyne, the flexible nature of the 10 carbon aliphatic chain leads to a slightly lower height than expected under the force of the tip. In the case of 1-dodecyne, a lower applied surface voltage of −1.0 V could be consistently used because of its lower viscosity, keeping the deflection set point constant.

Electrografting of 1,4-diethynylbenzene, a solid at room temperature, can be carried out in a 0.22 M mesitylene solution with an applied surface voltage of −1.0 V [tip(+)]. Control experiments indicate that mesitylene is suitably inert, as use of neat mesitylene under these conditions does not result in observable deposition of chemisorbed organics on the surface. The 1,4-diethynylbenzene termination on Si(111)−H, as shown in Figure 3c, is 0.7 nm in height, which corresponds closely to the calculated value of 0.8 nm. The calculated and experimentally determined heights are closer with this conjugated bis-alkyne because of its rigidity; compression is less likely under the AFM tip. Line diameter is 40 nm, and the friction mode image of Figure 3f reveals its hydrophobic nature. The successful use of a dilute solution of the alkyne suggests that other solid alkynes can be electrografted and that this technique is not limited to neat liquid reagents.

In absence of alkyne, cathodic electrografting conditions can lead to production of a very thin surface oxide, but only upon application of high potentials to the Si(111)−H surface that are in excess of −6.0 V at 45−50% humidity, as shown in Figure 5.[30] The maximum height observed is ~1 nm, and the friction image reveals a more attractive interaction between the oxide-

Figure 6. Height (a) and friction (b) AFM images of 1-octadecyne electrografted on Si(111)−H using a broad Pt-coated tip.

of the electrografted alkyne monolayers was conducted in lateral force microscopy (LFM) mode using noncontact silicon cantilevers.

Figure 3 shows height-mode images of box-shaped patterns, made up of lines 40 nm wide, drawn with three different alkynes, 1-octadecyne, 1-dodecyne, and 1,4-diethynylbenzene, along with the corresponding friction mode images, on Si(111)−H. The height information, experimental and calculated, is shown in

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coated tip and the surface oxide (lighter colored) as compared to that of the Si(111)−H termination, presumably due to hydrogen-bonding interactions.[34,35] Nanoscale oxide features on silicon formed via AFM and STM techniques in ambient air are generally accomplished with a positive applied surface potential to render the surface more electrophilic; in addition, the intense electric field at the tip produces O⁻ ions which react with surface silicon.[3,36,37] The negative bias has the opposite effect, making the surface less prone to oxidation.[16,30] Rinsing for 15 s with 1:1 49% HF (aq)/EtOH cleanly removes the oxide features produced under forward bias [surface(−)]. Therefore, oxide can be distinguished from organic monolayers via friction force microscopy and fluoride stability tests.

Previous results under UHV have demonstrated that surface hydrides on silicon can be cleaved electrochemically in a homolytic fashion with STM tips, yielding silicon-dangling bonds that subsequently react with alkenes in a hydrosilylation reaction.[3,24] A high applied voltage [surface(+) > 4.5 V], well in excess over the normal potential utilized for alkyne electrografting, is required to cleave the Si−H bond. To test whether the observed monolayers are actually hydrosilylation products, and thus are alkenyl- instead of alkynyl-terminated, 1-dodecene was tested to contrast with 1-dodecyne. Monolayer formation is not observed at the low bias (−1.0 V) applied for cathodic 1-dodecyne electrografting, ruling out hydrosilylation under these conditions.
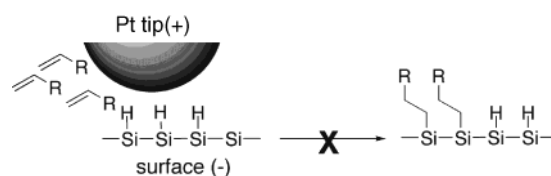
Under bulk, macroscale conditions, either with or without electrolyte[18] (Supporting Information), monolayer formation is not observed with alkenes. These results indicate that alkenes do not adhere to the surface under this set of electrochemical conditions, nor is polymerization observed.

Various approaches have been tested to control line width. The usual tip velocity during the alkyne electrografting reaction is 2 μm/s; holding the tip in place for 5 s does not result in a spot wider than 50 nm, most likely because of the insulating nature of the newly formed alkyne monolayer and the weak electric field distant from the tip.[37] Increasing the applied surface voltage from −1.0 to −2.5 V appears to have little impact on line width for these Pt tips. For wider lines, however, flattened tips result in thicker lines, as shown for a 1-octadecyne line in Figure 6. The lines in this image are about 300 nm wide, showing that line widths may be controlled by varying tip shape.

Conclusions

Cathodic alkyne electrografting, a reaction already demonstrated to function on bulk surfaces, can be carried out on the nanoscale using conducting probe atomic force microscopy (CP-AFM). Three different alkynes of varying length scale the height of the formed monolayers, as would be expected. Difficulties in producing oxide under the negative bias and resistance to fluoride indicate that the organic monolayers are not oxide-based or result in substantial local oxidation. Hydrosilylation is not in operation under these mild conditions since alkenes do not form monolayers. The electronic properties of these potentially conjugated alkynyl structures are presently under investigation. The ability to precisely tailor specific nanoscale domains by chemical functionality is expected to yield new information concerning the potential for interfacing of molecular wires with silicon and for related applications.

Supporting Information Available: Macroscale cathodic electrografting on flat Si(111)−H, AFM images of electrografting on Si(100)−H, and information on oxide line formation (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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