Arrays of Chemomechanically Patterned Patches of Homogeneous and Mixed Monolayers of 1-Alkenes and Alcohols on Single Silicon Surfaces**

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We have previously demonstrated a facile, chemomechanical method of simultaneously functionalizing and patterning silicon with single organic monolayers by scribing it while it is wet with 1-alkenes,[1] 1-alkynes,[1] and 1-haloalkanes.[2] Here we show that this method can be extended to create individual surfaces that have different monolayer coatings in distinct and precisely controlled regions (Figure 1). Like microcontact printing, this technique allows multiple, patterned, surface features to be prepared with ease. To create these arrays a Si surface is 1) wet with a reactive compound, 2) scribed in a specific region with a computer-controlled diamond-tipped rod, 3) rinsed with a solvent, and 4) dried. This process is then repeated, without moving the Si surface from its original position, to create monolayer coatings in regions distinct from the first. With this technique we have prepared arrays of functionalized, scribed regions on single Si surfaces of a) the homologous series of 1-alkenes from 1-pentene to 1-octadecene (a more extensive study than was previously reported[1]), b) a series of alcohols (providing the first direct evidence for the bonding of alcohols to scribed Si), and c) a series of mixed monolayers on scribed Si from two 1-alkenes or from a 1-alkene and an alcohol (this is the first report of mixed monolayers on scribed Si). Our motivation for studying mixed monolayers is to be able to more easily create surfaces with more than one functional group, or with diluted functionality, as has been demonstrated with mixed monolayers of thiols on gold.[3] Our desire to study the reactivity of alcohols and other functional groups with scribed silicon stems from our interest in developing it as a substrate for the creation of advanced materials.

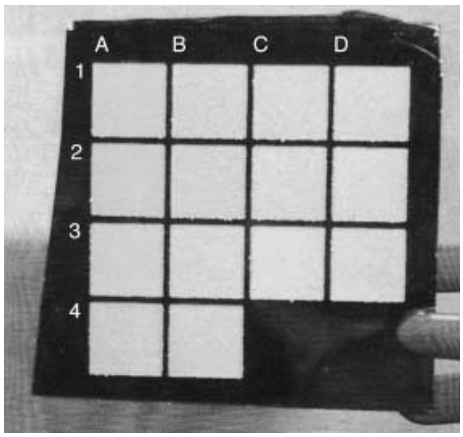

Figure 1. Scribed patches (0.8 × 0.8 cm each) on Si containing the homologous series of 1-alkenes from 1-pentene (A1) to 1-octadecene (B4).

As before,[1, 2] the preparations described herein were performed in the air without any special treatment or degassing of chemicals. The time required to prepare, analyze (especially trends), and chemically modify arrays on single surfaces is much less than that required for the same number of coatings on individual surfaces because some experimental clean-up and analysis steps can be carried out on all array elements simultaneously. In addition, the ability to create surfaces with different monolayer coatings in precisely controlled regions should prove technologically valuable, for example, in creating single surfaces to perform multiple bioassays. Finally, the principles demonstrated herein should allow the preparation of functionalized patterns with smaller features.

We proposed[1, 2] that scribed and unpassivated[4] Si react similarly with 1-alkenes, 1-alkynes, and 1-haloalkanes to yield monolayers that are tethered through C–Si bonds, and that these monolayers are structurally similar to those prepared from hydrogen-terminated Si.[1, 2, 5] Here we propose that scribed and unpassivated Si react similarly with alcohols (and water), which bind to different crystal faces of unpassivated Si through cleavage of O–H bonds to form Si–O and Si–H species.[6–8] A fraction of the chemisorbed alcohols undergo further fragmentation on Si(111)-(7 × 7) to form Si–C bonds.[5, 6] These results suggest that Si–O, Si–H, and perhaps Si–C bonds are formed by scribing Si with alcohols and that the chemisorbtion may be complex.

Other related methods of modifying surfaces include scribing hydrogen-terminated silicon with an AFM tip in the air to produce silicon oxide,[9] grinding silicon in the presence of reactive chemicals to produce coated silicon particles,[10] nanoshaving monolayers of thiols on gold while they are immersed in a solution containing a thiol different from the one in the monolayer,[11] micromachining monolayers on gold with a scalpel blade or a carbon fiber followed by immersion in a thiol solution,[12] and mechanically scratching surfaces to partition fluid-supported membranes.[13]

Figure 2 shows X-ray photoelectron spectroscopy (XPS) data and water contact angle measurements from arrays of individually functionalized patches prepared from 1-alkenes on single Si surfaces. The increasing C1s/Si2p XPS signals, which are in good agreement with previously published results from single patches on single surfaces,[1] and the increase in water contact angles up to the 1-undecene-derived surface indicate an increased carbon loading on the surface. The

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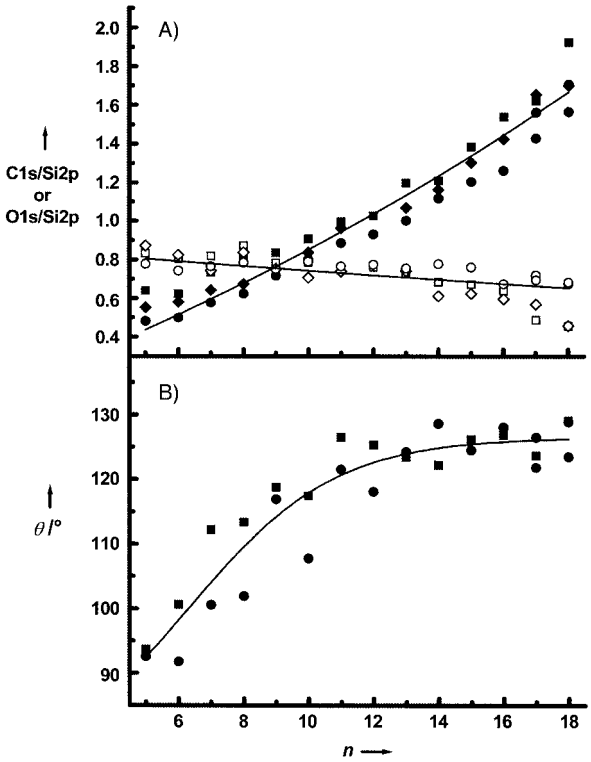

Figure 2. XPS (C1s/Si2p: solid symbols; O1s/Si2p: open symbols) and water contact angle measurements (θ) from arrays of patches prepared from 1-alkenes of different chain lengths (n: 1-alkene chain length, 1-pentene to 1-octadecene). Each symbol type represents data from a different array. Each point in (B) represents the average of two contact angle measurements made on either side of a 10-μL drop placed on the scribed surface. The solid lines are guides to the eye.

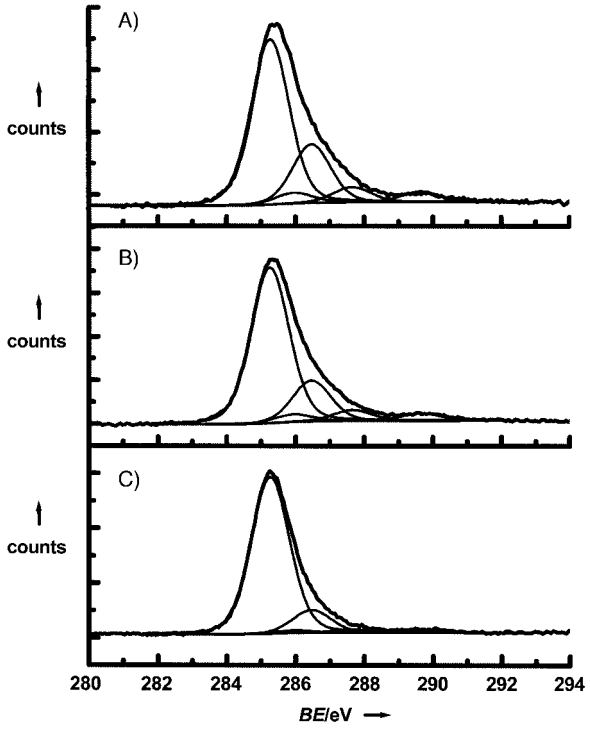

Figure 3. High-resolution XPS C1s narrow scans as a function of electron binding energy (BE) for patches on a silicon surface scribed in the presence of A) 1-propanol, B) 1-butanol, and C) 1-octanol along with peak-fitting results. The area ratios of the two low binding energy peaks to the other peaks are (average of two measurements, errors are half the distance between data points) 2.5 ± 0.5:1, 3.0 ± 0.3:1, and 6.8 ± 1.3:1 for 1-propanol, 1-butanol, and 1-octanol, respectively. All peak widths were fixed at 1.31 eV, which was the value found for the large, unshifted component in the 1-octanol spectrum. The binding energies for the peaks in the fits were set at 285.26, 285.96, 286.47, 287.66, and 289.66 eV. The peak at 285.96 is attributed to the carbon atom secondarily shifted by the presumed carboxyl carbon atom at 289.66 eV.

change in contact angles can be attributed, in part, to an increasingly thick hydrocarbon film which acts as a hydrophobic barrier between the more polarizable silicon substrate and water droplets. The similar water contact angles from patches prepared from 1-undecene to 1-octadecene suggest that their outer few Ångstroms are the same. Analogous wetting behavior was observed for thiols on gold.[11] We attribute the high values of and variation in our water contact angles to surface roughness (CH_3-terminated monolayers from long-chain adsorbates on planar substrates have advancing water contact angles of $111-115^\circ$.[14, 15]) The O1s/Si2p ratio as determined by XPS decreases with increasing chain length of the 1-alkene. This result is consistent with greater attenuation through increasingly thick organic films of less energetic O1s photoelectrons compared to more energetic Si2p photoelectrons[16] from surfaces with constant oxygen levels at their Si–hydrocarbon interfaces.[1, 2]

Arrays of patches or single patches on individual silicon surfaces both yielded the same results by XPS for silicon scribed with alcohols. These spectra show that 1) there is an approximately linear increase in carbon loading with increasing alkyl chain length, as was found for alkenes,[1] alkynes,[1] and alkyl halides,[2] (see Supporting Information and Figure 2) and 2) high-resolution C1s narrow scans (Figure 3) indicate carbon atoms chemically shifted to higher oxidation states. The chemically shifted components show approximately the expected fraction of the total area for one carbon atom in each alkyl chain bonded to one or more oxygen atoms. Surfaces prepared by scribing silicon under 1-propanol, 1-butanol, and 1-octanol were also analyzed by time-of-flight/secondary ion mass spectrometry (TOF-SIMS). The resulting positive and negative ion spectra provide strong evidence for the formation of the expected surface species with three, four, and eight carbon atoms, respectively. Indeed, the 1-propanol-derived surface produces significantly higher levels of $C_3H_7^+$, $C_3H_7OSi^+$, $C_3H_5O^-$, and $C_3H_7O^-$ ions than the surfaces derived from 1-butanol and 1-octanol. Similarly, the 1-butanol-derived surface yielded higher levels of $C_4H_9^+$, $C_4H_9OSi^+$, $C_4H_7O^-$, and $C_4H_9O^-$ ions and the 1-octanol-derived surface higher levels of $C_8H_{15}O^-$ and $C_8H_{17}O^-$ than the other surfaces (see Supporting Information).

Figure 4 shows XPS and wetting data from arrays of mixed monolayers on scribed Si prepared from binary solutions of 1-decene and 1-octadecene. As expected, the C1s/Si2p ratio increases with increasing concentration of 1-octadecene in solution. However, in contrast to mixed monolayers of thiols on gold, which often show a strong preference for the adsorption of one thiol over another,[17] the C1s/Si2p data are fairly linear over the concentrations of 1-octadecene studied. This observation suggests that kinetics, rather than thermodynamics, govern monolayer formation on scribed Si.

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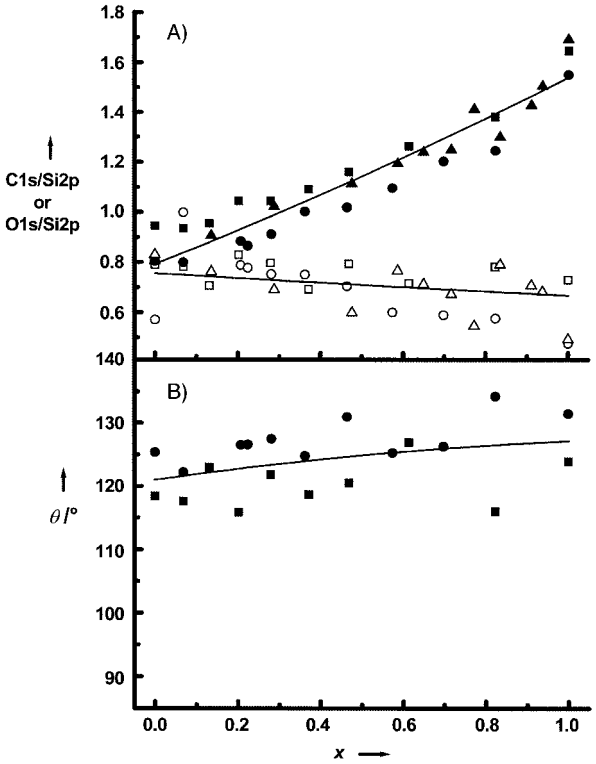

Figure 4. XPS (C1s/Si2p: solid symbols; O1s/Si2p: open symbols) and water contact angle measurements (θ) from arrays of patches prepared from binary solutions of 1-decene and 1-octadecene (x: mole fraction of 1-octadecene). Each symbol type represents data from a different array. Each point in (B) represents the average of two contact angle measurements made on either side of a 10-μL drop placed on the scribed surface. The solid lines are guides to the eye.

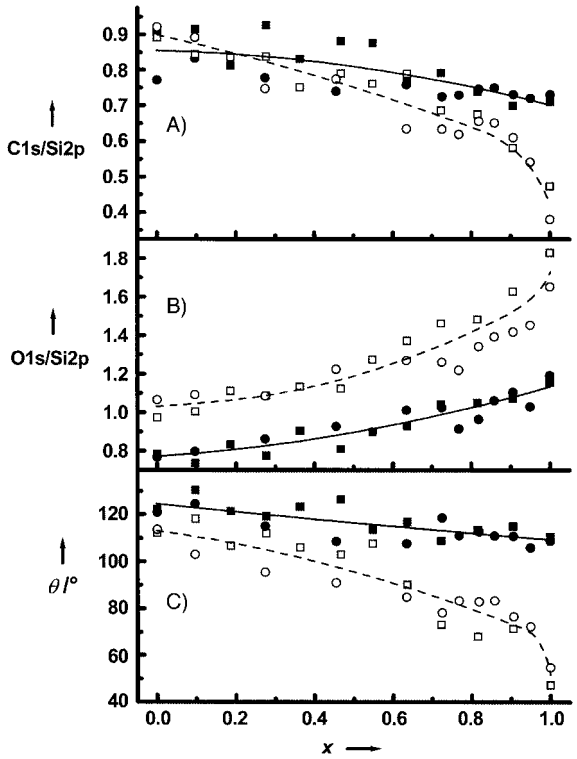

Figure 5. XPS and water contact angle data (θ) for two arrays of patches prepared by scribing under binary solutions of 1-decene and 1-decanol (x: mole fraction 1-decanol) before (solid symbols) and after (open symbols) a stability test (1 h in boiling 0.1 M H_2SO_4). Each symbol shape represents data from a different array. The lines are guides to the eye.

We again attribute the decrease in the O1s/Si2p data to photoelectron attenuation through increasingly thick hydrocarbon films. As expected, the water contact angle data (Figure 4B) suggest there is a small increase in the hydrophobicity of these surfaces as the mole fraction of 1-octadecene in solution increases.

Figure 5 shows XPS and wetting data for arrays of mixed monolayers on single Si surfaces prepared from binary solutions of 1-decene and 1-decanol. XPS and wetting data show there is a decrease in the amount of surface carbon and water contact angles as the mole fraction of 1-decanol increases. (1-Haloalkanes also have lower C1s/Si2p ratios than 1-alkenes with the same number of carbon atoms.[1, 2]) The increase in the amount of surface oxygen shown in Figure 5B is consistent with higher surface concentrations of chemisorbed alcohols.

To better understand the stability of these new materials the arrays were immersed in boiling 0.1 M H_2SO_4 for 1 h. After this stability test (open symbols) the concentration of carbon on the surface decreases at higher solution concentrations of 1-decanol (>30%), the surface oxygen concentrations of all of the patches increase (with the greatest increase at highest concentrations of 1-decanol in solution), and the water contact angles decrease (the greatest decrease is again at higher solution concentrations of 1-decanol). These results, especially the large changes in the properties of the 100% 1-decanol-derived patches, are consistent with a model of hydrolyzable Si–O bonds holding the alkyl chains from 1-decanol and unhydrolyzable Si–C bonds tethering alkyl chains from 1-decene. The contact angle data and residual carbon (by XPS) of 100% 1-decanol monolayers suggest that hydrolysis of the monolayer is incomplete under these conditions or that some of the alcohol molecules bind to the surface through C–Si bonds. Adventitious carbon would also influence these results. In addition, the data in Figure 5 point to some general oxidation of all of the Si–monolayer interfaces during the stability test.

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Synthesis of Very Thin 1D and 2D $CdWO_4$ Nanoparticles with Improved Fluorescence Behavior by Polymer-Controlled Crystallization**

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Nanosized building blocks with lower dimensionality, such as nanotubes, nanowires, nanorods, and ultrathin nanoplatelets have recently experienced a heightened interest.[1–9] These systems with at least one restricted dimension offer opportunities for investigating the influence of size and dimensionality on optical, magnetic, and electronic properties.[2] They can also be used as one component for a nanocomposite material to significantly improve the material properties.[8] Recent efforts have focused on the development of new synthetic routes for preparing nanorods, nanowires, or nanotubes with uniform sizes and aspect ratios, for example, nanorods/nanowires of $BaCrO_4$,[3] CdSe,[4] metal nanorods: Cu,[5a] Fe,[5b] Ag,[5c,d] Au,[6] FeOOH,[7] and vanadium oxide nanotubes (VO_x-NTs).[9] A family of long semiconductor-oxide nanobelts with widths of 30 to 300 nanometers and width-to-thickness ratios of 5 to 10 was successfully synthesized by simply evaporating the desired commercial metal – oxide powders at high temperature.[2b] The formation of a 2D $BaCrO_4$ nanorod monolayer assembly using the Langmuir – Blodgett technique was also reported,[10] and 2D wurtzite ZnS nanosheets were fabricated by a solution-based template method.[11]

Recently, tungstate materials have attracted much interest because of their luminescence behavior, structural properties, and potential applications.[12] Cadmium tungstate ($CdWO_4$) nanocrystals with a monoclinic wolframite structure are interesting because of their high average refractive index, low radiation damage, low afterglow, and high X-ray absorption coefficient;[13] they can be used, for instance, as an X-ray scintillator.[14, 15] Other tungstates with Scheelite structure MWO_4 (M = Ca, Ba, Pb) also display interesting excitonic luminescence, thermoluminescence, and stimulated Raman scattering (SRS) behavior.

To date, the procedure regarded as optimal to prepare $CdWO_4$ nanorods is a hydrothermal process at 130 °C.[16] The nanorods of different compositions reported so far generally have rather small aspect ratios (length-to-diameter) of 2 – 10,[17] which results in weak symmetry-breaking surface effects. In addition a reverse micelle templating method has recently been used to synthesize uniform $BaWO_4$ nanorods with diameters of 5 nm and aspect ratios of about 150 by using barium bis(2-ethylhexyl)sulfosuccinate [$Ba(AOT)_2$] micelles, which are treated with NaAOT microemulsion droplets containing sodium tungstate (Na_2WO_4).[17] The large excess of surfactants as well as the very low concentration throughout synthesis, however, could restrict the applicability of this procedure.

Herein, we present a facile aqueous-solution route for the synthesis of extremely thin 1D and 2D $CdWO_4$ nanoparticles with controlled sizes (length, width, thickness) by using a combination of the double-jet injection of simple inorganic reactants and double-hydrophilic block copolymers (DHBCs) as crystal-growth modifiers.

DHBCs have been introduced as very efficient inhibitors and crystal-growth modifiers[18] and have already shown their potential for the morphosynthesis of calcium carbonate, barium sulfate, calcium phosphates, and zinc oxide crystals.[19] To differentiate between the influence of process parameters and the chemical influence of the DHBCs, $CdWO_4$ was crystallized in a set of experiments in the absence of polymer. The X-ray diffraction (XRD) pattern in Figure 1a demonstrates that well-crystallized $CdWO_4$ particles can be easily synthesized at room temperature, which can be indexed as monoclinic wolframite structure with unit cell parameters $a = 5.029$, $b = 5.859$, $c = 5.074$ Å (JSPDS Card: 14-676). The sharper nature of the diffraction peaks 100, 200, and 002 suggests possible preferential orientation along these directions. In addition, the 010 diffraction peak is very weak and broadened, which indicates that the thickness direction will be along the *b* axis, which was confirmed by high-resolution (HR) TEM results.

The corresponding TEM image in Figure 2a shows very thin, uniform $CdWO_4$ nanorods/nanobelts with lengths in the range of 1 – 2 μm and a uniform width of 70 nm along their entire length (aspect ratio of about 30). No different contrast was observed, which suggests the perfect growth of the nanoparticles and uniform thickness. Large scale, lower-

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