

Hydrolysis Improves Packing Density of Bromine-Terminated Alkyl-Chain, Silicon–Carbon Monolayers Linked to Silicon

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Bromine-terminated alkyl-chain monolayers, bound to oxide-free Si substrates, were prepared by self-assembly. Infrared spectroscopy and atomic force microscopy imply that monolayer packing density improves after hydrolysis, despite an increase in the presence of oxide. The probable reason is that OH-mediated intermolecular H-bonding along the monolayer emerges after hydrolysis and rearranges the molecular components of the insulating layer. Current–voltage and differential capacitance measurements show that also the interfacial electronic properties of these junctions are changed by hydrolysis of the Br groups. This is expressed in an increased effective Schottky barrier height and a decreased junction ideality factor. We correlate the proposed structural changes of the monolayer with the change in the interfacial electronic properties, with the help of the inhomogeneous Schottky barrier height model. The role of oxide in the charge transport through the monolayer is discussed, as well.

Introduction

The ability to control both structure and electronic properties of organic molecules provides a strong incentive to study and design them as electronic components. A basic starting point is the study of molecules or monomolecular layers,^{1–3} where connecting these molecular building blocks to macro-scale electronics remains a major problem.

In the past several years, important progress was made, also in terms of the idea of possible future integration of molecules into Si-based electronics.^{4–7} We can now prepare monolayers of saturated alkyl chains, bound to oxide-free Si substrates through Si–C covalent bonds, that are of sufficiently high-quality and dense enough, to yield well-defined and reproducible semiconductor–organic insulator–metal junctions.^{8–11} The thickness of the insulating layer and, thus, the current passing through the molecules can be controlled by choosing the length of the molecules.^{12,13}

Here we show how to extend in a significant manner the potential of this alkyl chain–Si system. It is applicable by exploiting the ability to modify the terminal groups at the end of the monolayer-forming molecules.^{14,15} Not only are such modifications important for improving our understanding of charge transport through molecules, but also because pure alkyl chains are a very problematic starting material for further synthetic modifications.

We compare here the effect of two different functional groups, bromine (–Br) and hydroxyl (–OH), on the electronic properties of Si/molecules/metal junctions. These functional groups differ in their dipole character¹⁶ and in the interactions between the molecules in a dense monolayer. The message of this paper is 2-fold.

First, modification of the alkyl chain monolayers is expected to change the total dipole of the monolayer, which will affect

the energetics of the semiconductor–insulator interface.² We show that dipole change is expressed in the height of the Schottky barrier (SB) limiting the transport in the semiconductor, as well as in the overall monolayer dielectric properties.¹⁵

Second, the morphology of the layer has a role in the electronics of the junction, as well. We argue that by changing the –Br terminal groups to –OH ones the interactions between the molecules are modified from repulsive, due to steric and electronic (lone pair) reasons, in the Br case, to attractive, via hydrogen bonds between the OH terminal groups. Therefore, the packing of the molecules in the monolayer and, consequently, its homogeneity are likely to be affected, which, in turn, can affect the junction's electronic properties.

Experimental Section

Materials. Wafers of *n*-Si (111), single side polished, with nominal resistivity of 1–20 $\Omega \cdot \text{cm}$ (calculated dopant density $\sim 5 \times 10^{15}$ to $\sim 2 \times 10^{14} \text{ cm}^{-3}$) were purchased from Virginia Semiconductors. Semiconductor grade chemicals were used for cleaning (30% H_2O_2 , 98% H_2SO_4) and etching (40% NH_4F solution) the wafers.

Sample Cleaning and Preparation. Si pieces were cleaned by rinsing with solvents (ethanol, acetone, and ethyl acetate) and dried under a stream of N_2 . Subsequently, the pieces were immersed in piranha solution (98% H_2SO_4 :30% H_2O_2 , 3:1, *v/v*) at 90 °C for 1 h, rinsed with copious amounts of MilliQ (18 M Ω) water, and etched in deoxygenated 40% NH_4F solution for 10 min. This treatment (immersion in piranha solution, rinsing with water, and etching in NH_4F) was done twice.

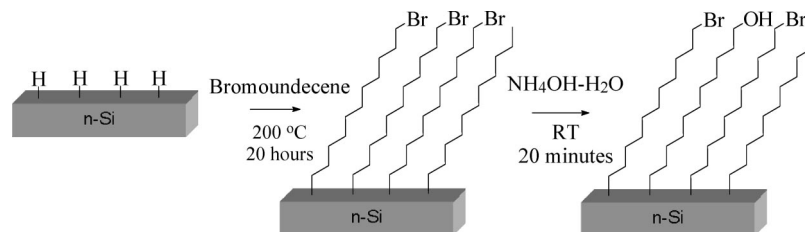
Monolayer Preparation. The CH_3 -terminated alkyl chain monolayers were prepared on freshly etched *n*-Si, as described previously.¹⁰

Br-terminated alkyl monolayers were prepared by immersing freshly etched wafers in neat 11-Br-1-undecene (96%, Alfa Aesar) under Ar and heated to 200 °C for 16–20 h. Beforehand, 11-Br-1-undecene was degassed by 4–5 freeze–pump–thaw cycles and dried overnight in high vacuum ($\sim 10^{-1}$ Torr, 30 °C)

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SCHEME 1: Schematic Illustration of the Formation¹⁷ and Partial Modification of Br-Terminated Alkyl-Chain Monolayers on *n*-Si

to remove residuals of gases and water. Br was chosen as the terminal group because it is a good leaving group for nucleophilic reactions. This feature should enable easy modification of the molecules' terminal groups. In addition, the size of the bromide is comparable to that of a methyl group,¹⁸ suggesting that Br-terminated alkyls may form monolayers of a quality, similar to that obtained with pure alkyl chains. This aspect is important because good coverage of the surface is needed for reliable electrical transport measurements.

After monolayer formation, the now molecularly modified Si pieces were removed, rinsed with solvents, further immersed in boiling dichloromethane for a few minutes, and dried under a stream of N₂.

To convert the Br terminal groups into OH (see Scheme 1 for a simplified illustration), the brominated Si substrates were hydrolyzed by immersion in 2.5% NH₄OH solution (pH 10.5 ± 0.5) for 20 min at room temperature, washed afterward with solvents, and dried in a stream of nitrogen.

The brominated monolayers were characterized, before and after hydrolysis, with X-ray photoelectron spectroscopy (XPS), Fourier transform infra-red spectroscopy (FTIR), contact angle measurements, ellipsometry, and atomic force microscopy (AFM).

Contact Angle Measurements. The static contact angle (free-standing drop) on the prepared monolayers was measured with a Ramé-Hart CA goniometer, using a 3 μ L drop of Milli-Q water. The values in the text are the average for 10 different monolayer preparations, before and after hydrolysis.

Ellipsometric Thickness Measurements. The thickness of the monolayers was deduced from ellipsometry measurements, using a Woollam M-2000V multiple wavelength spectrometer with an incidence angle of 70°, using the Cauchy model. An index of refraction between 1.460 and 1.483, as appropriate for the 999–550 nm wavelength range, used for the ellipsometric measurements, was used for the organic monolayers. The values, as mentioned in the text, are the average for 10 different monolayer preparations, before and after hydrolysis.

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS-HS X-ray photoelectron spectrometer at a base pressure of 2×10^{-9} torr, using a monochromatic Al K α source at 75 W and 80 eV detection pass energy. The C 1s peak was also measured at a pass energy of 20 eV. A negatively biased grid (−10 V), located above the sample was used to eliminate surface charging. Spectra were taken at sample–detector angles of 90, 55, and 35°. Data analysis was done by CasaXPS software, using standard fitting procedures and the Kratos database of relative sensitivity factors.

Infrared Spectroscopy. Infrared transmission spectra of brominated monolayers, before and after hydrolysis, were collected with a Bruker spectrometer (model Equinox 55). The spectra were taken at a resolution of 2 cm^{−1} using 1000 scans. The spectra were referenced to an etched silicon sample of the

same type, dopant and dopant density. The spectra were then filtered by an adjacent-averaging filter to reduce noise. Base line subtraction was done with Origin software.

Atomic Force Microscopy Imaging (AFM). Alkyl-Br-modified Si samples were imaged ex situ in air before and after hydrolysis. Topography and friction images were collected simultaneously in the contact mode, using a Nanoscope V Multimode system (Veeco Instruments Inc., U.S.A.). Triangular Si cantilevers with a typical spring constant of 2 N/m (CSC21, Mikromash, U.S.A.) were used. Typical scan rates were around 1 Hz. The images were collected and topography features were measured by using the Research Nanoscope 7.20 software from the same company.

Electrical Characterization. Current–voltage and impedance measurements of the monolayers were performed using the metal–insulator–semiconductor junction structure. The junction was formed by placing a Hg drop (99.9999% purity) on the SAM using a controlled growth hanging Hg drop electrode apparatus (BAS, W. Lafayette, IN). A second contact was made by scratching the back surface of the samples with a diamond knife, followed by applying an In–Ga eutectic. For all measurements, the Si was grounded, acting as the negative contact while the Hg drop was connected to the positive contact of the measuring unit. Measurements were carried out on a vibration-free table in a class 10 000 clean room, held at 20 °C and 40% relative humidity.

The geometric contact area between the Hg drop and the monolayer, typically 0.6 (±0.1) mm in diameter, was determined using an optical microscope. Currents were converted to nominal current densities, using the optically measured geometric contact area.

The electronic properties of the monolayers, given in Table 1, are averages of the values, extracted from *I*–*V* and *C*–*V* curves, for ~5 junctions on each of 5 independent monolayers, before and after hydrolysis. The standard deviations are mentioned as error values in Table 1, as well.

Current–Voltage. Current–voltage characteristics were collected with a Keithley 6430 sub-fA remote source meter through a suitable preamplifier. Typically, bias scans were in the range of −1 to +1 V at a rate of 10 mV/s.

Capacitance–Voltage. Capacitance–voltage measurements were performed using a Hewlett-Packard 4284A precision LCR meter. The DC voltage was swept in the range of −1 to +1 V with a step size of 20 mV. The AC perturbation amplitude was 10 mV at 1 MHz. The impedance model used for the capacitance measurements was a parallel circuit of a resistor and a capacitor. Any influence of external series resistance or capacitance was compensated by the LCR unit during the measurements.

Results

a. Surface Analysis. We followed the Br to OH conversion with XPS and contact angle measurements. Figure 1 shows the

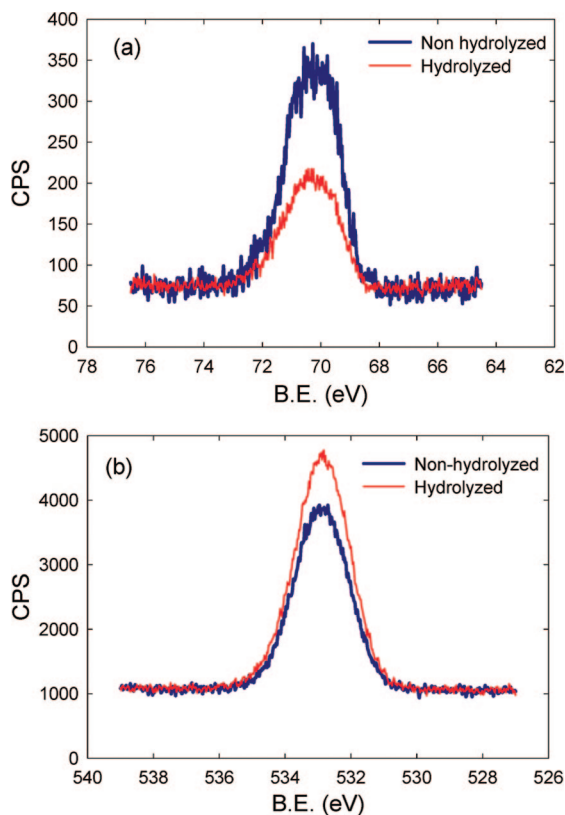


Figure 1. Br 3d (a) and O 1s (b) XPS spectra of the nonhydrolyzed (blue/dark) and hydrolyzed (red/light) brominated monolayers. The Br signal is lower and the O signal is higher after 20 min of hydrolysis. The sample–detector angle of the measurements was 90°. B.E. = binding energy.

XPS peaks of Br and O on top of the brominated monolayers.¹⁹ During hydrolysis the Br intensity decreases (Figure 1a) to half of its original value, while the oxygen peak increases (Figure 1b), implying a partial exchange of Br atoms with OH groups.²⁰ This substitution is possible, because the top part of the molecules in the monolayer is not so dense and the molecules are not tightly packed before hydrolysis (due to the repulsion between the bromine terminations) that they can prevent chemical attack. Additionally, we show further by AFM imaging that the coverage of the silicon by the brominated molecules is not total and that the layer includes islands apparently devoid of molecules (cf. Figure 3 and the relevant discussion). Those islands are expected to enable access for water molecules to the backside of the C–Br bond of molecules in their perimeter. The X-ray intensity used was low enough to avoid damaging the monolayer and evaporation of Br atoms, which may be caused by X-rays, during the measurements. Control measurements of the Br signal during the XPS measurements, given in the Supporting Information, Figure SI-1, show no irradiation effect on the Br signal. The Si 2p data (Supporting Information, Figure SI-2) show a slight shift of the main Si peak toward lower binding energy after hydrolysis, suggesting an increase in band bending. This result implies an increase in the SB. Indeed, a similar increase is deduced from the electrical measurements, as will be discussed later (cf. Table 1). XPS indicates some oxide in the brominated and hydrolyzed monolayer samples (see the Supporting Information, Figure SI-2), in contrast to what is found for the pure alkyl chain monolayer system. The latter is expected to be denser and substantially prevents oxidation for long period of time,¹⁰ which apparently is not the case with the brominated monolayer. We assume that

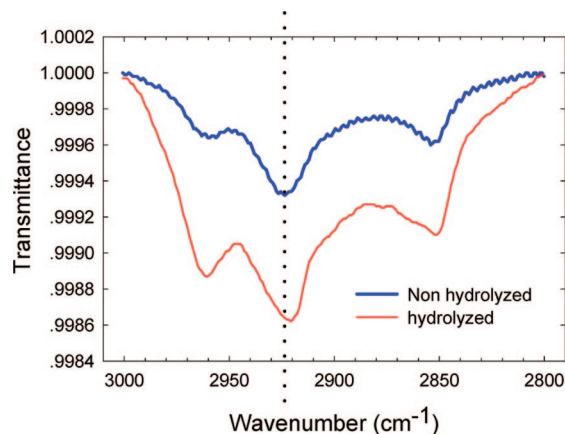


Figure 2. Infrared transmission spectra of the methylene stretching mode region for the nonhydrolyzed (blue/dark) and hydrolyzed (red/light) brominated monolayers. The dotted vertical line helps to see the shift of the CH₂ asymmetric stretch frequency after hydrolysis.

oxidation of the silicon, covered with the brominated monolayers, is also enhanced by the higher hydrophilicity of the system, compared to that of the system with pure alkyl chain monolayers. The data show some difference in this oxide signal between the Br- and OH-terminated systems.^{21,22}

Contact angle (θ) measurements show an average value of 87° (± 1.5) for the Br-terminated monolayers.²³ After hydrolysis, θ decreases to 77° (± 1.5), which agrees with a relative increase in hydrophilicity of the monolayer, due to the partial conversion of the terminal groups from Br to OH.

A 21 (± 1.5) Å thickness of the C₁₁H₂₃–Br monolayers on Si was deduced from ellipsometry measurements. This value is larger than that expected from what we found for saturated alkyl chain monolayers of comparable length, Si–C₁₂H₂₅, which gave a 16 (± 1) Å thickness.¹⁰ The difference may well be the result, in toto or in part,²⁴ of the higher electron density of the Br than that of the methyl groups, which changes the monolayer's refractive index and, thus, its optical thickness.²⁵

After hydrolysis, the thickness of the monolayer decreases to 19 (± 1.7) Å. XPS measurements indicate a reduction in the C density, which may imply partial etching of the monolayer, and subsequent reduction of the average thickness. Therefore, we interpret the change in the optical thickness after hydrolysis as a change in the refractive index of the monolayer, which is affected both by chemical modification and by the removal of some of the monolayer's molecules and the consequent change in the monolayer's optical density.

Remarkably, we deduce from our data that the above-mentioned decrease in density upon hydrolysis is accompanied by an improvement in the molecular layer's packing. This improvement is indicated by FTIR and AFM measurements. Figure 2 shows the infrared transmission spectra of the methylene stretching modes in the brominated monolayers, before and after hydrolysis. A decrease from 2923 to 2920 cm^{−1} in the asymmetric CH₂ stretch frequency is observed.²⁶ It indicates that the monolayer becomes more crystalline-like¹⁸ or, at least, has a higher packing density of the alkyl chains than before hydrolysis.^{11,27,28}

Further on, the peak at 2850 cm^{−1} is assigned to the symmetric CH₂ stretch.²⁶ The 2965 cm^{−1} peak is related to the asymmetric stretch of a methyl group, which may result from the suggested scenario:¹⁷ a Br disconnects from the molecule by the thermally formed Si surface radicals. The abstraction of Br generates a terminal methylene radical, providing an alternate reactive site in the molecule for reaction with the Si surface.

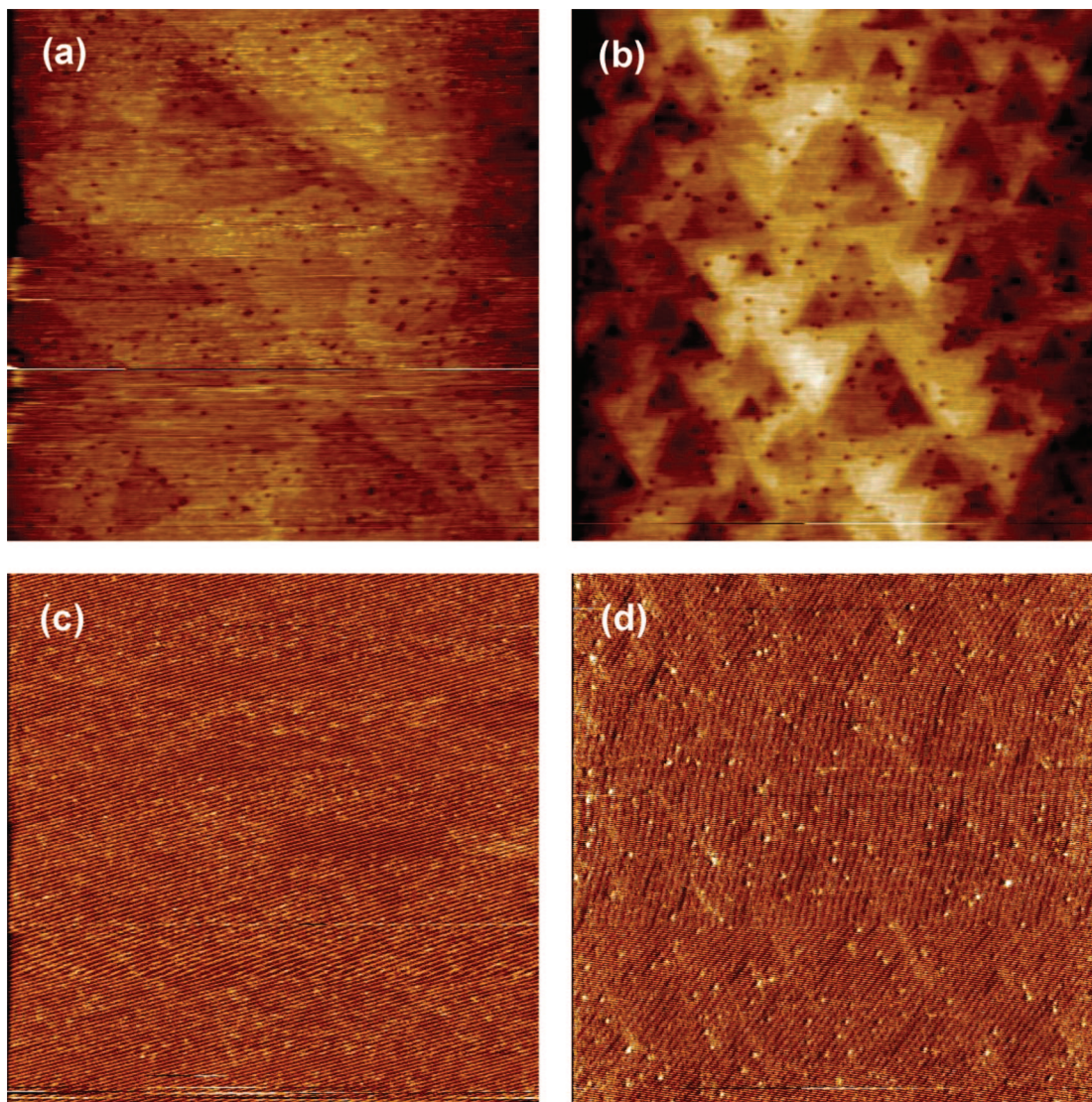


Figure 3. AFM topography (a and b) and friction (c and d) images, acquired simultaneously in the contact mode, of brominated alkyl chain monolayers (a and c) before hydrolysis and (b and d) after 20 min hydrolysis. Scan size: $1.7 \mu\text{m} \times 1.7 \mu\text{m}$. (a and b) $Z = 4 \text{ nm}$, (c and d) $Z = 30 \text{ mV}$. The triangular etch pits, typical for Si(111), below the molecular layer, are better resolved after hydrolysis, both in the topography and in the friction images. Additionally, in the topography images (a and b), dark spots are seen both before and after hydrolysis, while in the friction images white spots appear mostly after hydrolysis (c vs d).

The methylene radical can abstract hydrogen from a neighboring Si–H group, producing a methyl termination to the reacting molecule. Chemisorption of the undecene molecule may proceed via reaction of a Si radical with the terminal olefin, to create a methyl-terminated component in the monolayer. We note that some vinyl terminated molecules may be incorporated in the monolayer, as well, according to the following mechanism:¹⁷ The methylene radical can react directly with another Si surface radical, resulting in a vinyl-terminated surface. The concentration of vinyl-terminated molecules in the layer may increase after the hydrolysis, apparently because of a competition with the substitution of the Br by the OH^- .²⁹ In this route, the hydrogen at C_{10} , next to the Br atom, is eliminated by the OH^- from the NH_4OH solution. The Br is eliminated, as well, to create the double bond at the top of the monolayer.

A similar conclusion, regarding the increase in packing of the monolayer after hydrolysis, is suggested by topography and friction images, as presented in Figure 3. In these images, the features of the etched Si (triangular etch pits, typical for Si(111), below the molecular layer) are better resolved for the (partially) OH-terminated (Figure 3, panels b and d) than for the Br-

terminated monolayers (Figure 3, panels a and c). Furthermore, these triangular features are clearly seen in the friction image of the hydrolyzed layer, while one can hardly notice them, if at all, before hydrolysis (compare Figure 3, panels d and b). Being able to image the Si surface morphology through the adsorbed monolayer indicates a better packing of the monolayer and more uniform coverage of the adsorbed molecules. This result supports the assumption that OH-mediated H bonds along the monolayer's terminal groups increase the attraction between the molecular components of the monolayer and improve monolayer packing.

When comparing the friction images in Figure 3, one notices white spots, which appear clearly after hydrolysis (Figure 3d), while before hydrolysis these spots are hardly seen (Figure 3c). In the topography images, though, similar spots are seen as dark (lower in height) spots both before and after hydrolysis (Figure 3, panel a vs b). The averaged diameter of these spots, before and after hydrolysis, is $28 (\pm 5)$ and $30 (\pm 5) \text{ nm}$, respectively. While the spread is considerable, on the average the spots are slightly larger after hydrolysis. The average depth of these holes in the monolayers, before and after hydrolysis is $8 (\pm 3)$ and 9

(± 2) Å, respectively. We interpret these spots as being indicative of oxide islands in the monolayer.³⁰ Before hydrolysis, the monolayer packing is looser, because of repulsion between the brominated molecules. Consequently, the lower oxide islands are partially shadowed by the molecules from interaction with the tip, which cannot reach the oxidized surface. After hydrolysis, the oxide islands grow laterally, rather than creating new oxide islands in the bulk of the monolayer, causing the surrounding molecules to be less stable and to disconnect from the surface at the perimeter of the oxide islands.³¹ This indication for reduction in the amount of molecules is consistent with the XPS results. While the attractive forces between the hydrolyzed molecules make the molecules form a more rigid monolayer, at the same time this reduces the molecules' ability to shade the oxide islands. This, together with the increase in diameter, facilitates the interaction between the tip and the oxide islands.

b. Electronic Analysis. The effect of the monolayer's terminal groups on the barriers for charge transport through the Si-molecular monolayer junction was studied by current–voltage and capacitance–voltage measurements of a metal–insulator–semiconductor (MIS) structure, which was formed by placing a Hg drop on the molecular monolayer as the metal contact.³² Figure 4a compares the J – V curves of the junctions with Br-terminated monolayers, before and after hydrolysis. In forward bias the J – V curves fall into two voltage regimes.¹³ At low forward bias the current increases logarithmically with bias, which fits with the general diode relations (within the semiconductor). At higher forward bias, the current increase with voltage fits to tunneling (through the monolayer). Interestingly, the currents at high forward bias through the junctions with Br- and OH-terminated monolayers are similar. This result, which agrees with what we found earlier for $-\text{CH}_3-$ vs $-\text{S}-$ terminated alkyl monolayer-based junctions,³³ suggests that the terminal groups do not affect the tunneling barrier significantly. Additionally, the similarity of the high forward bias currents indicates that hydrolysis does not have a detrimental effect on the monolayer quality or on the monolayer thickness, so that both types of monolayers present very similar tunneling barriers.¹⁰

The effect of the terminal groups on the J – V curves is strongest at reverse and low forward bias (Figure 4a). Diode relations are commonly fitted assuming transport by thermionic emission (TE). Such analysis of the data in low forward bias yields values for the effective Schottky barrier height (SBH), ϕ_{eff} , and ideality factor, n , ($=1$ for an ideal diode), by using eq 1^{34,35}

$$\ln\left(\frac{J}{(1 - e^{-qV/kT})}\right) = \ln(AT^2) - \frac{q\phi_{\text{eff}}}{kT} + \frac{qV}{nkT} \quad (1)$$

where J is the current density, q is the electron charge, V is the applied voltage, k is Boltzmann's constant, T is the absolute temperature, and A^* is the effective Richardson constant for Si.

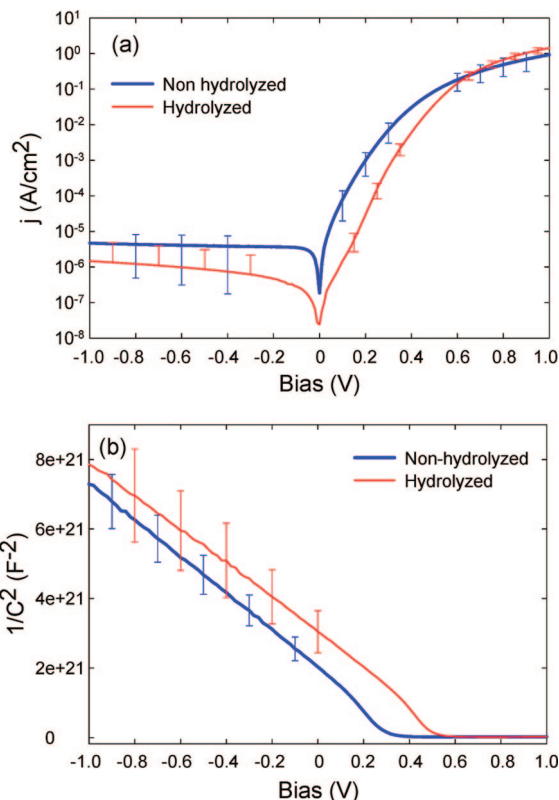


Figure 4. (a) Current density (J) vs voltage (V) and (b) C^{-2} vs V (C : differential capacitance) plots of Si- $\text{C}_{11}\text{H}_{22}\text{Br}$ /Hg junctions, with nonhydrolyzed (blue/dark curves) and 20 min hydrolyzed (red/light curves) monolayers. The C^{-2} – V plots were taken at 1 MHz and with a 10 mV modulation voltage. The data are logarithmically averaged for the J – V , and linearly averaged for the C – V measurements, over >15 curves; error bars are linear standard deviations.

The values that we calculate for the modified monolayers are compared in Table 1 to typical values for junctions made with pure alkyl chain monolayers of comparable length (Si- $\text{C}_{12}\text{H}_{25}$). Similar electronic characteristics for alkyl chain monolayers on silicon were presented, for example, by Faber et al.³⁵ and by Liu and Yu.³⁶ The effective SBH value for the junction with the Br-terminated monolayers is significantly lower than that for junctions with the OH- and CH_3- terminated monolayers. This behavior is similar to what was found for junctions made with alkyl chain monolayers on Si, which had a thiol instead of CH_3 terminal group.³³ The difference in the effective barrier heights of the hydrolyzed and nonhydrolyzed monolayers is also evident in the differences in the reverse bias leakage currents (Figure 4a).

Hydrolysis dramatically improves the ideality factor, n , derived from the $(\log J)$ – V plots in low forward biases using the TE model,³⁵ to a value well below that of the pure alkyl chain monolayer-based junction (Table 1). We note that, among

TABLE 1: Electronic Parameters for the Studied Monolayer-Based Junctions^a

monolayer	n	$q\phi_{\text{eff}}$ (eV)	V_{fb} (V)	N_{D} (10^{15} cm^{-3})	$q\phi_{\text{b}}$ (eV)
$n\text{-Si-C}_{11}\text{-Br}$	1.85 ± 0.23	0.70 ± 0.03	0.36 ± 0.06	0.35 ± 0.25	0.66 ± 0.05
$n\text{-Si-C}_{11}\text{-OH}$	1.30 ± 0.06	0.82 ± 0.02	0.58 ± 0.06	0.40 ± 0.24	0.87 ± 0.06
$n\text{-Si-C}_{12}^b$	1.50 ± 0.09	0.92 ± 0.02	0.69 ± 0.02	1.23 ± 0.54	0.95 ± 0.03

^a Averaged parameters for the monolayer-based junctions studied here, derived from thermionic emission theory (ideality factor, n , and effective barrier height, ϕ_{eff} , from eq 1), and parameters derived from the Mott–Schottky analysis (flat-band voltage, V_{fb} , from eq 2, Si donor doping, N_{D} , and barrier height, $q\phi_{\text{b}}$, from eq 3). Our values for pure alkyl chain monolayer-based junctions are given, as well. Errors are standard deviations of the multiple measurements on multiple samples. ^b These measurements were done on wafers from a different batch than the other two, but with the same nominal specifications.

other possible reasons, a lower ideality factor is consistent with a more homogeneous junction.^{37,38}

Figure 4b shows typical Mott–Schottky (C^{-2} vs V) plots at reverse bias, where the Si is in depletion, for the Br- and the OH- terminated monolayers. The flat band potential (V_{fb}) and donor density (N_D) of the semiconductor, were derived using eq 2³⁵

$$\frac{1}{C_{sc}^2} = \frac{2(V_{fb} - V)}{q\epsilon_0\epsilon_r N_D A^2} \quad (2)$$

where C_{sc} is the measured depletion capacitance, ϵ_0 is the permittivity of vacuum, ϵ_r is the dielectric constant of silicon, and A is the contact area. Values of the barrier height, $q\phi_b$ can be calculated by using the V_{fb} and N_D values, in eq 3, at room temperature³⁵

$$q\phi_b = qV_{fb} + kT \ln\left(\frac{N_c}{N_D}\right) \quad (3)$$

where N_c is the effective density of states in the conduction band ($2.8 \times 10^{19} \text{ cm}^{-3}$ for silicon).³⁴

V_{fb} of the Br-terminated monolayers is lower than that of the CH_3 -terminated ones (see Table 1). Hydrolysis of the molecules then increases V_{fb} by 0.22 V. Such an increase is consistent with the increase in band bending in Si after hydrolysis of the Br-terminated molecules, deduced from the XPS data (see the Supporting Information). V_{fb} for both types of junctions is less than for junctions with the CH_3 -terminated monolayers. The trend between the three types of junctions, regarding the flat band voltages and the barrier heights as deduced from the C – V measurements,³⁵ is similar to that found in the SBH values derived from the I – V data.

Discussion

Can we understand the changes in the interfacial electronic properties as a result of the structural changes of the monolayer? It is clear from the FTIR and AFM data that hydrolysis improves the packing density of the monolayer. The interpretation of this effect on the interfacial electronic properties, though, is more complicated. The reason is that both packing density and monolayer polarity change and both may affect the junctions' electrical behavior, as follows.

a. Monolayer–Dipole Effect. Table 1 shows that the Br to OH conversion increases the effective barrier height of the monolayer, as well as the flat band potential. Simplistically, we can explain the effect of the monolayer terminal groups according to their electron-donating (OH, CH_3) or -withdrawing (Br) character and the resulting effect on the total dipole of the monolayer. An electron-withdrawing (donating) group should increase (decrease) the dipole of the monolayer.³⁹ That will lead, for an n-type semiconductor, to smaller (larger) band bending and, thus, to a smaller (larger) effective barrier for charge transport.

Comparing the CH_3 -terminated monolayers with Br- and OH-terminated ones, we note that, because of the presence of some oxide (see the Supporting Information, Figure SI-2), the changes in SBH, in the case of the brominated monolayers, cannot be immediately assigned to the difference in the monolayer polarity.

Br-terminated monolayers decreased the current considerably, compared to those with either H-Si(111)^{40,41} or SiO_x -Si(111)⁴² substrates. It is reasonable to expect, though, that the further

oxidation of the silicon upon hydrolysis (cf. the Supporting Information, Figure SI-2) and possible removal of some of the molecules by hydrolysis, as indicated by the XPS results and by AFM imaging, would also be expressed in the J – V measurements as an increase of the currents at low forward biases¹⁰ and a decrease in the SBH.^{40,41} Similarly, a decrease in barrier height and V_{fb} would be expected from the C – V measurements. In our case, though, both the SBH and V_{fb} increase and the decrease of currents in the Schottky regime (Table 1 and Figure 4a), in agreement with the effect, expected from the change in dipole going from a Br- to an OH-terminated monolayer-based junction. These results are remarkable in that they indicate that the presence of oxide, at least after 20 min of hydrolysis,⁴² does not appear to dominate the interface electronic characteristics of these junctions.⁴³ We propose the following explanation for these findings:

A relatively small fraction of the silicon surface is covered by oxide, compared to the area covered by the molecules.³⁰ This fraction appears to be primarily present as islands, rather than under the monolayer.

We postulate that the main effects of the oxide are present, already with the Br-terminated monolayer.¹⁰ In such case the system would be sensitive to the Br to OH change, in a similar way to that by which oxide-covered Si is sensitive to changes in molecular dipoles on the Si/Si-oxide substrate.^{44,45}

Furthermore, the oxide islands are lower in height than the monolayer (see Figure 3, panels a and b). Therefore, when the Hg drop lies physically on the monolayer, there is around a 1 nm physical separation of air/vacuum between the metal contact and the oxide. In this situation it is well possible that the charges will go preferably through the molecules and that charge transport through that path dominates, rather than that through the oxide.

Let us now consider the role of the monolayer dipole. Modification of the terminal groups of long molecules, if grafted on semiconductors, was already shown to induce modifications in the semiconductor surface electronic properties.⁴⁶ The dipole effect was used to interpret changes in electronic properties of metal–organic insulator–semiconductor (MOIS) junctions, as well.⁴⁷ Still, one might argue that the direct contact and the consequent chemical interaction between the Hg contact and the terminal groups induces changes in the work function of the metal and that such an effect might affect the band bending in the silicon more than the silicon–monolayer dipole interaction does. This argument is, however, shown to be incorrect by our XPS measurements. In XPS there is no metal contact but the change in band bending is clearly seen after hydrolysis (see the Supporting Information).

b. Monolayer–Packing Effect. The decrease in ideality factor, n , after hydrolysis helps to understand the role that the structural change in the monolayer may play in the change in electronic behavior. Different mechanisms have been discussed for $n > 1$ ideality factors, such as the presence of interface states in the insulating layer.³⁷ The existence and modulation of such states in the gap will affect charge transport through the Schottky barrier (SB), and would be expressed in the effective barrier and the ideality factor.³⁶ Modulation of the interface state density may occur, for instance, by molecule–surface state orbital coupling.⁴⁶

In addition, the ideality factor reflects SBH uniformity over the interface.³⁷ Improving the uniformity of the layer should lead to a more uniform interfacial electronic structure and to a decrease of n . The FTIR, AFM, and XPS results suggest that the brominated monolayer is not so homogeneous, because of

the presence of a small amount of oxide in the layer, the complex surface chemistry on top of the monolayer and because of the low packing density. Therefore, the electrical data can be interpreted in terms of the inhomogeneous SBH model.³⁸ According to this model, the junction current is the sum of the currents, contributed by every part of the interface. The single SBH value, which is extracted from the measurements, represents the average of a distribution of barrier values. The less homogeneous the SBH, the larger the distribution of the SBH and the higher the ideality factor.

We argue that hydrolysis of the brominated monolayer improves the layer's packing and, thus, the junction's homogeneity by introducing H bonds between the terminal groups. This process apparently reduces the number and/or the importance of defects in the junction, which would show up as low SBH segments. Consequently, their contribution to overall charge transport becomes smaller and the distribution of the SBH is reduced. Similarly, the role of dangling bonds on the etched silicon, and the effect of the resulting interface states in lowering the SBH decreases. While the currents of SB diodes are dictated by the low SBH segments in the layer,³⁷ as the layer is more homogeneous and is dominated by higher SBH segments (such as the OH-terminated segments, due to the electron-donating character of the OH group), the mean value of the SB of the monolayer increases, as observed by the C–V measurements.⁴⁸

Summary

Br-terminated alkyl-chain monolayers show an important chemical way to extend semiconductor–insulator and molecular junctions. This type of monolayers allows direct modification of the chemical structure, leading, in the case of Br/OH exchange, to improvement of the packing of the insulating layer, as confirmed by surface analyses. The chemical terminations of the molecules, in conjunction with collective structural changes, affect the interfacial electronic properties of the semiconductor–monolayer junction. The presence of strong leaving groups on top of monolayers is important for nucleophilic substitutions for further chemical modifications. This is interesting for creating molecularly modified semiconductors with desired properties, for example for fine-tuning organic and molecular electronic devices.⁴⁹ In addition, this approach can help us learn about the basics of how electronic carriers are transported through molecules.

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Supporting Information Available: Additional figures as mentioned in the paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- The silicon oxide is 6 (\pm 1) % of the total coverage of the surface, as also agreed by XPS measurements.
- The penetration of water and oxygen through the hydrophobic alkyl chain monolayer is less preferred than through the hydrophilic oxidized islands. Consequently, the oxide preferably grows in a lateral manner onto the silicon at the perimeter of the islands and around the islands, rather than in new locations below the bulk of the monolayer. In this way, the molecules in the periphery of the islands become less stable and can be disconnected under the alkaline conditions of the hydrolysis. The claim that molecules are less stable on oxidized silicon is easily demonstrated when immersing the silicon piece, covered with molecules, in HF solution for few minutes.
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- We define as positive a dipole whose positive pole is the one closest to the semiconductor surface.

(40) Note that n-type H-Si(111)/Hg contacts exhibited a nearly ohmic response at room temperature, with a very low SB. See ref 41.

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(42) After 40 min of hydrolysis, though, the trend is turned over: the currents in reverse bias and in low forward biases increase in comparison to the 20 min hydrolyzed monolayers, which is more typical for charge transport through silicon oxide (see the Supporting Information, Figure SI-3). We assume that at this time scale of hydrolysis, the oxide in the layer becomes dominant in the charge transport.

(43) We have also performed surface photovoltage (SPV) measurements on the Br-terminated monolayers before hydrolysis. Those measurements show only a small amount of band bending, despite the existence of an oxide. Comparing the SPV values of (non- hydrolyzed) Si-C₁₁-Br with that of high quality Si-C₁₂ (with no SiO₂), we get a lower value for the Si-C₁₁-Br than for the Si-C₁₂ (70 vs 100 mV, respectively). This means

that the contribution of oxide to the band bending is negligible and, surely, does not increase the band bending in our case.

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