Static and dynamic electronic characterization of organic monolayers grafted on a silicon surface†

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Organic layers chemically grafted on silicon offer excellent interfaces that may open up the way for new organic–inorganic hybrid nanoelectronic devices. However, technological achievements rely on the precise electronic characterization of such organic layers. We have prepared ordered grafted organic monolayers (GOMs) on Si(111), sometimes termed self-assembled monolayers (SAMs), by a hydrosilylation reaction with either a 7-carbon or an 11-carbon alkyl chain, with further modification to obtain amine-terminated surfaces. X-ray photoelectron spectroscopy (XPS) is used to determine the band bending (∼0.3 eV), and ultraviolet photoelectron spectroscopy (UPS) to measure the work function (∼3.4 eV) and the HOMO edge. Scanning tunneling microscopy (STM) confirms that the GOM surface is clean and smooth. Finally, conductive AFM is used to measure electron transport through the monolayer and to identify transition between the tunneling and the field emission regimes. These organic monolayers offer a promising alternative to silicon dioxide thin films for fabricating metal–insulator–semiconductor (MIS) junctions. We show that gold nanoparticles can be covalently attached to mimic metallic nano-electrodes and that the electrical quality of the GOMs is completely preserved in the process.

Introduction

Molecular electronics offers new strategies for downscaling integrated circuit devices. On the one hand, single-molecule experiments strive to investigate the fundamental phenomena when electrons are driven through a single molecule. On the other hand, a layer of organic molecules can provide a unique connection to the existing silicon-based electronics, and be used to perform specific functions such as diodes, resonant tunnel diodes, memory devices or transistors. Unfortunately, the interface of silicon (Si) is often affected by oxidation and it is extremely challenging to prepare a silicon–molecule interface with tailored and defect-free electronic characteristics. Even more challenging is to fabricate metal–insulator–semiconductor (MIS) junctions with an organic monolayer as the insulating layer. In the past fifteen years, several chemical methods have been proposed for functionalizing silicon surfaces with highly ordered organic monolayers. Hydrosilylation involves the reaction of oxide-free, H-terminated Si surfaces with alkene functionality. This enables the grafting of alkyl chain molecules to form a stable Si–C bond using several different activation processes: thermal, catalytic, photochemical or radical. The mechanisms at play for this reaction are now well established, and the properties offered by such grafted organic monolayers (GOMs) are harvested for a number of applications. An alternative method, based on supercritical carbon dioxide, has also been used to prepare organic layers on oxide-free Si. A few devices have already been proposed, based on GOM/Si heterostructures, such as organic memory devices, ideal Schottky diodes, organic photovoltaic solar cells, biological sensors, and double-tunnel junctions for Coulomb blockade.

GOMs are highly ordered organic layers, in which structural homogeneity leads to spatially homogeneous electronic properties and well-defined band structures. For these sensitive applications, these ultrathin molecular layers have to meet several requirements: (1) chemical: to protect the silicon substrate from oxidation and minimize the formation of interface states especially...
during post-processing steps, (2) dielectric: to function well as a rectifier, a Schottky barrier, a tunnel junction, and (3) linker: to connect another electrode (thin film or nanoscale electrode). In this context, it is crucial to precisely evaluate the work function, the amount of surface defects, band bending throughout the processing steps and ensure that they meet the expected electronic requirements.

Different molecules have been investigated in the last ten years, and the band diagram of the corresponding monolayers was established with X-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS),28–33 and Kelvin probe force microscopy (KPFM).34,35

In the present work we focus on two types of GOMs with different thicknesses that can each act as a tunnel junction. We also chemically post-modify the layer with an amine moiety, making it possible to attach gold nanoparticles, i.e. nanoscale electrodes, acting as a non-planar MIS junction. We have already shown that this structure exhibits Coulomb blockade under the tip of a scanning tunneling microscope (STM).27,36 In the present study, we monitor the dependence of the main electric parameters of the interface (band bending, work function, LUMO edge) on each processing step of their chemical preparation. We also measure and describe the transport regime through these tunnel junctions by using conductive atomic force microscopy (c-AFM).

Experimental section

Materials and methods

The samples are obtained from Si(111) monocrystals, n+ doped with a resistivity of 0.01 Ohm cm (a dopant concentration of \(2 \times 10^{18} \text{ cm}^{-3}\)) and with a miscut of 0.5° in the \(\langle 112\rangle\) direction. They are cut into 10 × 8 mm² pieces and prepared using wet chemical methods in a N₂-purged glovebox (amount of water and oxygen below 1 ppm) following a well-established protocol described in our previous studies (see also ESI† for additional details).27,36,37 Briefly, the Si substrates are cleaned with a Piranha solution, then with an NH₄F solution to produce atomically flat, H-terminated Si(111) surfaces.28 Next, two different alkene molecules (with different alkyl chain lengths) are used to synthesise grafted organic monolayers (GOMs) by hydrosilylation, denoted SiC₁₁-COEth and SiC₇-COEth (Fig. 1a and d). The long GOM, ethyl-undecylenate, is reacted with H-Si(111) by thermal hydrosilylation (details in the ESI†). Two alkyl chains were grafted (C7 and C11) and two terminations were prepared. Gold nanoparticles were deposited on the amine terminated surfaces.

Gold nanoparticles (AuNPs) are prepared as a colloidal solution from the reduction of HAuCl₄ by ascorbic acid27,36,39,40 (details in the ESI†). The amine terminated surfaces are dipped into the colloidal solution for about 10 min after the solution was acidified at pH ~ 5. The amine is protonated, which enables the attachment of AuNPs. The surface density is measured with AFM and found to be \(7 \times 10^9\) AuNP per cm².27,36 TEM measurements have shown that the AuNPs are spherical and with an average diameter of 8.2 nm and a size dispersion of 4.0 nm, which allows Coulomb blockade experiments.27,36 We estimate that 0.3% of the surface is covered with gold (average distance between AuNPs is 120 nm). The two AuNP-functionalized surfaces depicted in Fig. 1c and f are labeled C₁₁NH₂-AuNP and C₇NH₂-AuNP.

Instrumentation

STM was used to check the quality of the GOMs, performed in an UHV chamber (a base pressure of \(3 \times 10^{-11}\) mbar) after the surface was annealed in a vacuum at 150 °C for 30 min. This procedure removes the physisorbed molecules (mostly water) and stabilizes the STM imaging conditions. Importantly it does not alter the organic layer as revealed by infrared absorption measurements.27,37

X-Ray Photoelectron Spectroscopy (XPS) was carried out under UHV conditions and the core-level spectra were measured with a non-monochromatized Al K\(\alpha\) source (\(h\nu = 1486.61\) eV for the main Al K\(\alpha_1\) line). The takeoff angle of the photoelectrons was normal to the surface. The overall energy resolution was 0.85 eV (source and analyzer). For UV photoemission spectroscopy (UPS) measurements, the UV source was the He I line (\(h\nu = 21.21\) eV) and a spectral resolution of 50 meV was achieved. Binding energies (BEs) and kinetic energies (KEs) are referenced with respect to the Fermi level. The Fermi edge is determined via UV photoemission spectroscopy of a freshly sputtered (unannealed)
polycrystalline gold foil. Work functions are determined by measuring the cutoff of the secondary electron edge (see below). Conductive AFM measurements were performed in an UHV chamber (a base pressure of $5 \times 10^{-9}$ torr) to measure the transport properties of the GOMs. The AFM measurements were carried out with a Cr/Pt tip on samples previously annealed for 30 min at 120 °C in a vacuum. Finally, AFM was also used in contact mode to record the topography of the samples and to record $I-V$ data for selected points.

**Results**

**Morphology of the GOM surface (STM)**

Fig. 2 shows STM images of the C$_7$-NH$_2$ surface. This 100 × 100 nm$^2$ image remains stable, as expected for a compact and homogeneous GOM monolayer. The surface exhibits circular spots (the inset of Fig. 2) of typically 4 nm diameter due to small domains of molecules in which the C$_7$ alkyl chains are tilted in the same direction with respect to the surface, as schematically shown in Fig. 1c and f.

GOMs with long chain molecules, C$_{11}$-NH$_2$, also yield stable STM images similar to those in Fig. 2 (see ESI†), consistent with good molecular organization. The thickness of the amine-terminated monolayers, measured by ellipsometry, is 1.3 nm for C$_7$-NH$_2$ and 1.6 nm for C$_{11}$-NH$_2$.27,37

**Estimation of the surface oxidation (XPS)**

The XPS chemical analysis of C$_7$-NH$_2$ and C$_{11}$-NH$_2$ surfaces was essential for confirming the bonding of the organic layer as depicted in Fig. 1 and published earlier.27,36 We focus now on analyzing the traces of oxide at the interface since they are responsible for most of the electronic surface defects. The Si 2p core-level spectra of three C$_{11}$ GOMs are presented in Fig. 3. Under the present experimental conditions, photoelectrons probe ca. 3 nm below the surface (details of the calculation given in the ESI†). Deconvolution of the main spectral feature therefore includes the bulk contribution denoted B, and weaker surface components shifted +0.3 eV upwards and representing Si–C bonds.42 The Si–H component, expected at +0.14 eV from B, is incorporated into the main peak.43 Four Si oxidation states (+0.9 eV per O ligand) need to be considered as the samples were shortly exposed to air.44 The intensity of these oxidation states is used to measure the impact of the successive treatments on the silicon wafer. For the C$_{11}$-COEt sample, the bulk line is at 99.50 eV and the sum of the four oxidation states $\Sigma_{ox}$ corresponds to 9% of the spectral weight. It can be roughly interpreted as 9% of the silicon atoms being in an oxidized state. The 4th oxidation state 4+ (SiO$_2$) has a weight of only 1%. For the C$_{11}$-CNH$_2$ sample, the bulk line is at 99.57 eV, and $\Sigma_{ox} =$ 8%, similar to the C$_{11}$-COEt case, but the 4th oxidation state is now more visible (2%). Finally, after attaching the Au NPs (C$_{11}$-CNH$_2$-AuNP), the bulk line is at 99.63 eV and $\Sigma_{ox}$ is equal to 9% (the 4th state weighs now 3%). While oxidation progresses slightly with each subsequent treatment, the attack is believed to be local (closer to “pitting”, occurring at ill-protected spots) rather than homogeneous, and remains at an acceptably low level, even after overseas shipping. The Si 2p$_{3/2}$ positions for the two types of GOMs are collected in Table 1. The Si 2p$_{3/2}$ values found for the C$_7$ GOMs are very close to that found for the C$_{11}$ one.

![Fig. 2](image-url) STM image (100 × 100 nm) of the C$_7$-NH$_2$ molecular layer grafted on Si(111) recorded at room temperature under a sample bias of −2 V. The surface was annealed at 150 °C for 30 min before scanning. Molecules are organized in bundles of ~4 nm diameter (inset).

![Fig. 3](image-url) Si 2p$_{3/2}$ core-level peaks from XPS experiments (red dots) of the (a) C$_{11}$-COEt, (b) C$_{11}$-NH$_2$ and (c) C$_{11}$-NH$_2$-AuNP grafted organic monolayers. Fits are made with sums of pseudo-Voigt curves (see text) and several contributions are highlighted. The main peak from the bulk is denoted B. The four oxidation states of silicon are indicated from 1+ to 4+. The position of peak B is used for measuring the surface band bending in our samples using the fact that the energy distance between the valence band maximum and the Si 2p$_{3/2}$ binding energy is 98.74 eV.41

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Surface band bending measurements (XPS)

Band bending is observed because electrically active defects are present at the surface.44 Indeed, if the functionalization process could saturate every dangling bond, the surface would be electrically neutral, and the semiconductor would be under flat-band conditions. The presence of defects leads to the localization of charges at the surface (negative for n-type silicon or positive for p-type), and the formation of a space charge of opposite sign in Si. An electric field appears and the bands bend upward (n-type) or downward (p-type). The absolute position of Si 2p3/2 (peak B) is determined by the measurement of the space charge at the surface atom nS.

The index B and S designates the bulk and surface, respectively, EF is the Fermi level and EVBM is the silicon valence band maximum (see Scheme 1). (£EF – EVBM)B is calculated from the dopant concentration ND and in the present case (£EF – EVBM)B = 1.05 eV. At the surface (£EF – EVBM)S is determined by the measurement of the BE of the Si 2p3/2 core level, BE(Si 2p3/2)meas and the knowledge of the energy difference (EVBM – BE(Si 2p3/2)), which is constant and equal to 98.74 eV.45 Then £Vbb can be written as:

£Vbb = (£EF – EVBM)S – (£EF – EVBM)B  
(1)

Equation (1) can be rearranged into:

£Vbb = (£EF – EVBM)S – (£EF – EVBM)B

The index B and S designates the bulk and surface, respectively, £EF is the Fermi level and EVBM is the silicon valence band maximum (see Scheme 1). (£EF – EVBM)B is calculated from the dopant concentration ND and in the present case (£EF – EVBM)B = 1.05 eV. At the surface (£EF – EVBM)S is determined by the measurement of the BE of the Si 2p3/2 core level, BE(Si 2p3/2)meas and the knowledge of the energy difference (EVBM – BE(Si 2p3/2)), which is constant and equal to 98.74 eV.45 Then £Vbb can be written as:

£Vbb = (£EF – EVBM)S – (£EF – EVBM)B

For example, for the C11-COEth sample, the Si 2p3/2 BE is measured to be 99.49 eV and the Si bands were bent upwards by an amount £Vbb = +0.30 eV. Once the band bending is known, the surface charge density σ can be derived following the method shown by Sze:45 £σ = £VbbNσ£D, where ε0 is the relative permittivity of Si, £Vbb is the band bending energy (in J) and ND is the donor concentration in the semiconductor. Knowing that the Si atom surface density is 7.85 × 1014 atom per cm2,45 we can express σ in terms of the number of unit charges per Si surface atom nS.

The £Vbb and nS values obtained for our different samples are collected in Table 1. All band bending values are circa +0.3 eV and for all terminations, nS is in the range ~3 × 10−12 unit charges per Si atom, which corresponds to an amount of unit charge per surface area of 2.4 × 1012 e− cm−2. For comparison, transport measurements were carried out with the mercury probe method on a similar Si/GOM interface prepared in our group with the same method. An interface state density as low as 1.6 × 1011 V−1 cm−2 was obtained, which corresponds to an interface density of ~1 × 1011 e− cm−2 at an applied bias of 0.5 V.46,47 We observed 25 times more interface states in our case, possibly due to extra handling needed for these measurements.

Table 1  Electronic properties measured for our six samples. BE(Si 2p3/2) (referenced to £F) is used to compute (£F – EVBM)S, the (positive) band bending £Vbb, and the surface charge density expressed in unit charge per Si atom (per monolayer). (*) These values are averaged over the photoemission probing depth, the "true" £Vbb values being slightly greater as explained in the ESI. The work function WF is obtained from the secondary electron edge cutoff (He I source). Values for the electronic affinity are taken from (a) Akremi et al.57 (b) Hunger et al.58 (c) Hunger et al.59 (d) Michaelson et al.60 (e) Hollinger et al.61

<table>
<thead>
<tr>
<th>Sample</th>
<th>BE(Si 2p3/2) (eV)</th>
<th>(£EF – EVBM)S</th>
<th>£Vbb (eV)</th>
<th>nS e−/Si atom</th>
<th>WF (eV)</th>
<th>£ (eV)</th>
<th>HOMO edge (eV)</th>
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<tr>
<td>C11-COEth</td>
<td>99.48</td>
<td>0.74</td>
<td>0.31</td>
<td>3.5 × 10−3</td>
<td>3.58</td>
<td>0.37</td>
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<td>99.49</td>
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<td>3.39</td>
<td>0.35</td>
<td>5.11</td>
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<tr>
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<td>99.57</td>
<td>0.83</td>
<td>0.22</td>
<td>3.0 × 10−3</td>
<td>3.03</td>
<td>0.30</td>
<td>4.76</td>
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<td>C11-NH2-AuNP</td>
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<td>0.85</td>
<td>0.20</td>
<td>2.8 × 10−3</td>
<td>3.32</td>
<td>0.30</td>
<td>5.22</td>
</tr>
<tr>
<td>C11-NH2-AuNP</td>
<td>99.63</td>
<td>0.89</td>
<td>0.16</td>
<td>2.5 × 10−3</td>
<td>3.05</td>
<td>0.28</td>
<td>5.22</td>
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<td>Si(111)-7 × 7</td>
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<tr>
<td>CH3-Si(111)</td>
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<tr>
<td>Sputtered Au</td>
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<td></td>
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<tr>
<td>Au(111)</td>
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</table>

Scheme 1  Band diagram of an n-doped silicon surface. In the ideal case (a), when there are no interface states the conduction and valence bands (cb and vb respectively) are flat near the surface. WF is the work function (WF = 4.12 eV in our case), £ is the electronic affinity of the surface and the vacuum level is denoted vac. In the presence of electrically active surface states (b), the defects below the Fermi-level £F are charged and the interface acquires a net negative charge. This charge transfer is compensated by an electric field. The surface band bending can be measured by comparing the measured value of £F – EVBM to the bulk value.
To obtain a flat band situation, the areal density of defects should be at least one order of magnitude below this value. The electrical defect is likely a triply coordinated silicon $P_x$-like defect with a double occupancy ($Si^-$) given the present high n-doping. As the $\sigma$ Si-C bond does not introduce (bonding and antibonding) states in the gap, the origin of electrical defects is very likely related to the unintentional oxidation of the surface, which is hard to fully avoid during air exposure during the required transfer steps. We see no difference in $qV_{bb}$ between the C$_{11}$-COEth and the C$_{11}$-COEth, which confirms that the two molecular layers have very similar structures despite the slightly different hydrosilylation processes (UV or thermal activation). Rather we observe a slight decrease in $qV_{bb}$ (towards a flat band configuration) after NH$_2$ termination. Interestingly, gold nanoparticle deposition does not create new defects.

**GOM electronic structure (UPS)**

The UV photoelectron spectra of C$_{11}$-COEth and C$_{7}$-COEth GOMs are presented in Fig. 4. Note that He I emission is composed of a main line I$_z$ at 21.21 eV and of a satellite I$_B$, shifted to higher energy by 1.854 eV and representing 3% of the I$_z$ intensity; therefore, the corresponding photoemission contribution is subtracted from the raw data for all the spectra in Fig. 4. Because the 2$p$/Si 3$p$ cross-section ratio is ~18.5 at $h\nu = 21.21$ eV, the UPS spectra are dominated by the contribution of the organic layer. The Highest Occupied Molecular Orbital (HOMO) of the organic layer appears in the steep decrease of the UPS signal on the right side of the spectra in Fig. 4. It is accompanied by a tail on its low binding energy side, which has previously been assigned to filled induced density of interface states (IDISs). Typically, the tail extends up to 3.6–3.2 eV in the GOM gap. Nevertheless, the overall barrier height for electrons between the Si conduction band and the alkyl electronic levels is determined by the edges of the LUMO levels because these states extend throughout the alkyl chain, unlike the tails. As shown in Fig. 4, we determine the HOMO edges graphically at the intersection of two lines, one for the HOMO edge and one for the gap state tail. The HOMO edge is ~4.9 eV below the Fermi level for C$_{11}$-COEth and for C$_{7}$-COEth (see also Table 1 for more data). This value is consistent with data obtained by Salomon on a very similar Si-C$_{12}$H$_{25}$ GOM on n-Si(111). For the Si-C$_{11}$ GOM, the addition of the NH$_2$ moiety only slightly shifts the HOMO edge to 5.1–5.2 eV.

**Work function of the GOMs**

The work function (WF) is by definition the energy difference between the vacuum level and $E_F$. It is obtained from the secondary electron edge (SE) curve measured with the He source, as follows:

$$WF = h\nu + KE_{cutoff} - KE_{Fermi}$$

where $KE_{Fermi}$ is the kinetic energy of the Fermi level (measured on a clean gold surface) when no bias is applied to the sample (see ESI for more details). The electron affinity $\chi$ is the energy difference between the vacuum level and the minimum of the conduction band $E_{cbm}$. It is an intrinsic property of the modified Si surface. The expression for $\chi$ is:

$$\chi = WF - (E_{cbm} - E_F) = WF - (E_g - (E_F - E_{VBM}))$$

where $E_g$ is the band gap (1.12 eV).

The secondary electron edges (the excitation source is the He lamp) are shown for all the samples in Fig. 4 and in Fig. S4 of the ESI. As the KE scale is referenced to $E_F$, the position of the cutoff gives directly the WF. WF and electron affinity $\chi$ are given in Table 1. Note that the SE edges are very sensitive to the homogeneity of the surface. Indeed on a patchy surface the lower cutoff is the averaged cutoff of the different areas and the edge of the higher WF region can emerge as a distinct onset. The steepness of the cutoffs in Fig. 4 points to a good surface homogeneity. It should also be noted that C$_{11}$-COEth and C$_{7}$-COEth have the same WF and $\chi$, indicating that there is no effect of the alkyl chain length on the work function in this case. This is in line with previous theoretical studies as well as experiments with alkanethiols on gold, showing that the WF is practically the same for molecules ranging from CH$_3$(CH$_2$)$_7$SH to CH$_3$(CH$_2$)$_3$SH. The value of $\chi$ (~3.2 eV) is about 1 eV smaller than that of the H-terminated Si(111)-1×1 surface (~4.2 eV). On H-terminated Si(001) surfaces, the attachment of an
octadecene GOM leads to a decrease in WF in the range 0.6–0.9 eV. A DFT calculation on a (CH₃(CH₂)₄) GOM on Si(001) shows that the WF decrease is due to the substitution of Si–H by Si–C bonds and to the dipole of the polar groups (CH₃) within the molecule. Note that χ is still 0.5 eV lower than that of Si(111) surfaces directly terminated by CH₃ (3.7 eV), possibly due to the dipole (with a normal projection oriented outward) borne by the ethanoate.

Finally, the addition of the terminal amine moiety produces layers with WF (Fig. 4) and χ (Table 1) smaller than that of the original ethanoate GOM. This means that the projection of the dipole of the amine terminal (oriented outward) is larger, in absolute value, than that of the ethanoate. However in stark contrast with the ethanoate GOMs, the WF decrease is much smaller for the “short” C₇NH₂ (−0.15 eV) than for the “long” C₁₁NH₂ (−0.48 eV) GOM. This strongly suggests that the amine termination process is much more efficient on the C₁₁-COEth than on the C₇-COEth GOM. A plausible explanation is that C₇ is less ordered than the C₁₁ GOM, with ethanoate functionalities less available for reaction. It is consistent with the higher resistance of C₇-COEth against oxidation in air, compared to that of C₁₁-COEth.

GOM conductivity (conductive-AFM)

The electron transport through the GOM was measured using conductive-AFM in contact mode. A typical AFM image is shown in Fig. 5 for an area of 300 × 300 nm² taken on a C₇-NH₂ surface. A series of images was recorded with different values of sample bias (tip grounded) and the topography was found to be closely similar to that of Fig. 5a. It displays parallel structures that are 30 nm wide corresponding to atomic terraces of the Si(111) surfaces and consistent with the sample miscut (xo = 0.5°) in the (112) direction yielding ~35 nm wide terraces. At 0 V bias, the RMS roughness of this functionalized surface is 1.3 nm (see ESI for another AFM image). The surface morphology remains unchanged even after scans with 8 V sample bias. Spectroscopic data were also recorded at various points of the surface and two of them are displayed in Fig. 5b (taken at spots indicated on the image).

Discusson

Surface dipole

The surface dipole is used to describe the energetic profile that a test charge undergoes when it crosses the interface. It is intrinsically linked to the electronic affinity and the work function of a surface. The formation of an ordered molecular layer creates a surface dipole layer that can either enhance or reduce the ability of extracting electrons from the surface. An electron coming from the bulk material will need more energy for crossing the interface if an inward oriented dipole is formed. The surface dipole energy −eδ is obtained as the difference between the actual electron affinity χ and the intrinsic silicon affinity χₚ:

$$-e\delta = \chi - \chi_p$$

where e is the absolute value of the elementary charge.

In eqn (6) a value of 4.05 eV is taken for χₚ, as it is commonly used in evaluating Schottky barriers.

The measured values for the molecular dipole energies presented in Table 2 lead to several conclusions. First, molecular grafting leads to negative dipole energies (all χ are smaller than χₚ), corresponding to a dipole oriented outward. For all the GOMs studied here, the dipole energy has the same sign (negative) as those found for comparable organic layers. A comparison between SiC₇-COEth and SiC₁₁-COEth shows that the dipole energies are identical (δ = −0.85 eV). Actually it was shown that the potential drop occurs mostly because of the strong polarization of the Si–C bond. The alkyl chain length has a more subtle effect on the WF that was discussed in detail by Fagas et al. whose conclusion supports our results of a limited difference in dipolar contribution between 7 and 11 carbon chain lengths. However, further modification of SiC₇-COEth into SiC₇-NH₂ increases the absolute value of the dipole energy (−eδ = −1.0 eV). Calculations further confirm that an amine terminal group greatly contributes to the surface dipole. What might be surprising at first glance is that the effect is still greater for SiC₁₁-NH₂ (−eδ = −1.31 eV) than for SiC₇-NH₂ (−eδ = −1.0 eV), although this is most likely due to the better ordering of the C₁₁ alkyl chain compared to that of the C₇ one, ultimately leading to a denser layer.

Table 2 Comparison of the molecular surface dipole energies for different molecular functionalizations of the n-doped Si(111) surfaces. CH₃ is marked with an asterisk, because it binds to every silicon atom whereas in all the other surfaces the molecule replaces hydrogen for only half of the silicon surface atoms.

<table>
<thead>
<tr>
<th>Termination</th>
<th>C₇OEt</th>
<th>C₇NH₂</th>
<th>C₁₁OEt</th>
<th>C₁₁NH₂</th>
<th>H</th>
<th>CH₃*</th>
<th>C₁₁H₁₁</th>
<th>C₁₈H₃₇</th>
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<td>Ref.</td>
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<td>This work</td>
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<td>Dipole/eV</td>
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<td>−0.85</td>
<td>−1.31</td>
<td>−0.07</td>
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<td>−0.58</td>
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</table>
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probed by spectroscopies that average over millimetric areas. Their surface covered with gold. This is a negligible amount when nanoparticles (C$_7$-NH$_2$-AuNP and C$_{11}$-NH$_2$-AuNP) have 0.3% of their mass, and is the barrier height. Moreover, when the bias is strongly increased (positive bias), the electric field across the GOMs becomes important and the electrons face a triangular barrier. The transport starts being dominated by field emission (Fowler–Nordheim regime), as depicted in Scheme 3c and d, and the current-voltage follows the relationship (positive bias):

\[
I \propto V^2 \exp\left(-\frac{4d\sqrt{2m^*\phi^3}}{3hqV}\right)
\]  

where \(d\) is the barrier thickness, \(m^*\) is the electron effective mass, and \(\phi\) is the barrier height. However, when the bias is strongly increased (positive bias), the electric field across the GOMs becomes important and the electrons face a triangular barrier. The transport starts being dominated by field emission (Fowler–Nordheim regime), as depicted in Scheme 3c and d, and the current-voltage follows the relationship (positive bias):

\[
I \propto V^2 \exp\left(-\frac{4d\sqrt{2m^*\phi^3}}{3hqV}\right)
\]
A Fowler–Nordheim plot is the graph of $\ln(I/V^2)$ against $I/V$ and is given in Fig. 6. From eqn (7), it obvious that $\ln(I/V^2) \propto \frac{1}{V} - \frac{2d}{h} \sqrt{2m^* \phi}$ for a tunneling regime and therefore we expect a linear evolution with a positive slope. This tunneling regime is identified in Fig. 6 for biases comprised between $-2.2$ V and $1.9$ V (large values of $1/V$). On the other hand, eqn (8) shows that a linear evolution is also expected for strong positive biases, but with a negative slope. This trend is confirmed by our experiments for values of $1/V$ smaller than $1/1.9$ Volt. Fig. 6 clearly shows the transition between the tunneling and the field emission regimes, corresponding to the minima at $-2.2$ and $+1.9$ V. Moreover, the intersection with the vertical axis occurs at $-\frac{2d}{h} \sqrt{2m^* \phi}$ for the low bias regime and the barrier height $\phi$ can be evaluated (with $d = 1.3$ nm and $m^* = 0.25m_e$). For positive bias, we calculate $\phi = 0.06$ eV. From the simplified diagram of Scheme 3c, we expect a value of $\sim 2.5$ eV. The discrepancy between the experimental and calculated values points to the complex transport mechanism. It shows that the induced density of interfaces states detected by our UPS spectra provide additional low energy paths for the electron to cross the tunnel barrier. Moreover the simplified diagram of Scheme 3 is calculated for a planar MIS structure, whereas the tip of the AFM cannot be represented with an infinite plane. The curvature will decrease the amount of band bending and therefore also the overall barrier height. The consideration of all these parameters exceeds the scope of the present study.

**Conclusion**

The complete energy diagram was derived for six organic alkyl-chain monolayers directly grafted on oxide-free, atomically flat H-terminated Si(111) surfaces. As shown by XPS, the GOMs clearly provide a barrier to oxidation and other chemical reactions during subsequent chemical processes: replacement of ethanoate by the amine head, AuNP deposition, and inevitable exposure to air. We established and analyzed in detail the band bending diagram of the GOMs on silicon and used it to explain the electronic transport properties of the GOMs. The conclusions derived from this work demonstrate that the surfaces functionalized by hydro-silylation are among the best candidates for building tailored hybrid nano-devices where the organic monolayers provide the electrically active layer. As theoreticians start providing methods for optimizing a priori the band diagram of a grafted organic monolayer and other experimental studies continue to develop new approaches for fabricating MIS structures with organic monolayers, GOMs will likely become essential components for the next generation nano-electronic devices.

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Notes and references

47. The work function of mercury is 4.5 eV, therefore the system studied by Peng et al. is flatband at zero applied bias.
To obtain similar band bending as in our case, and compare the interface state density we use their $D_{it}$ value at 0.3 V which is $1.6 \times 10^{11}$ interface state per volt and per cm$^2$.


62 For a given sample miscut $a$, the width of terraces $a$ is expected to be 35 nm, since $a = h / \tan \alpha$, where $h$ is the height of Si(111) step ($h = 0.313$ nm). This relatively high miscut was not intentional and results from the batch of wafers used for these experiments.


Static and Dynamic Electronic Characterization of Organic Monolayers Grafted on a Silicon Surface

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