SUPPLEMENTARY INFORMATION

Effect of Doping Density on the Charge Rearrangement and Interface Dipole at the Molecule-Silicon Interface

Omer Yaffe, 1 Sidharam Pujari, 3 Ofer Sinai, 1 Ayelet Vilan, 1 Han Zuilhof, 3
Antoine Kahn, 4 Leeor Kronik,*, 1 Hagai Cohen,*, 2 and David Cahen*, 1

1 Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel
2 Department of Chemical Research Support, Weizmann Institute of Science, Rehovoth 76100, Israel
3 Laboratory of Organic Chemistry, Wageningen University, Dreijenplein 8, 6703 HB Wageningen, the Netherlands
4 Department of Electrical Engineering, Princeton University, Princeton, New Jersey, 08544 USA

1 – Sample preparation

The surface orientation of all wafers, used in this study, was <111>.

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Dopant (cm⁻³)</th>
<th>Resistivity (ohm-cm)</th>
<th>Average Doping density (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDn</td>
<td>Siltronix (France)</td>
<td>As</td>
<td>&lt;0.006</td>
</tr>
<tr>
<td>MDn</td>
<td>Virginia semiconductors (USA)</td>
<td>P</td>
<td>1-20</td>
</tr>
<tr>
<td>MDp</td>
<td>Virginia semiconductors (USA)</td>
<td>B</td>
<td>1-20</td>
</tr>
<tr>
<td>HDp</td>
<td>Virginia semiconductors (USA)</td>
<td>B</td>
<td>&lt;0.006</td>
</tr>
</tbody>
</table>

Alkyl and alkenyl monolayer preparation: Sample preparation and characterization followed literature descriptions. 1,2 Briefly, pieces of Si wafer were cleaned by sonication in acetone and oxidized in an oxygen plasma (Harrick PDC-002 setup) for 3 min. Subsequently, the Si(111) substrates were etched in an Ar-saturated 40% NH₄F solution for 15 min. After etching the samples were rinsed with water, blown dry with nitrogen, and immersed in Ar-saturated neat 1-alkyne or 1-alkene (GC purity > 99.9%) at 120 °C.
alkenyl) or 200°C (alkyl) and ∼10 mbar. After 16 h (alkenyl) or 4h (alkyl), the reaction was stopped and the monolayers were rinsed extensively with EtOH and CH₂Cl₂ and sonicated for 5 min in CH₂Cl₂ to remove physisorbed molecules.

2 – XPS results of alkenyl monolayers

**Figure S1** – Alkenyl equivalent of Fig. 1 (alkyl) in main text. (a) Si 2p photoelectron peaks of Si-C₁₀H₂₁ samples with different Si doping density and type. The reason for the large broadening of the Si 2p peak of the HD p-Si samples (top curve) is discussed below. (b) Si 2p peak position as a function $E_F$, relative to the Si conduction band edge, the position of which was extracted from the nominal doping type and density of each Si sample. Dashed line is a guide to the eye that represents the ideal case if charge rearrangement were unaffected by the doping density of the Si substrate. (c) C 1s photoemission peak of Si-C₁₀H₂₁ samples with different Si doping density and type. The reason for the large broadening of the HDp Si 2p peak (top curve) is discussed below. Arrows mark the signal of the C atom attached to the Si (see text). (d) Difference between the C 1s and Si 2p peak positions as a function $E_F$, relative to the Si CB edge. The error bars for the binding energies represent the measurement accuracy and those of the $E_F$ position reflect the uncertainty in doping density according to the Si wafer manufacturer.

3 - Characterization of the alkyl monolayer on HDp-Si
The surface of freshly etched H-terminated HD p-Si has unusual chemical and structural properties, compared to all n-Si and lower doped p-Si ones. (Ramonda, Dumas, & Salvan, 1998; Roche et al., 1994; Allongue, 2000) This strongly affects the chemical and structural properties of the alkyl monolayer that is formed on the surface.

To stress this point we first compare between the F 1s XPS signals of freshly etched HDn- and HDp-Si (Fig. S3). It is clear that the F1s signal is significantly higher for the HDp than for the HDn sample.

![Figure S2](image)

**Figure S2** — F1s XPS signal from a freshly etched (10 min NH₄F) HDn- (bottom) and HDp- (top) Si.

Next we present and compare AFM images of an alkyl monolayer on both types of Si substrates. In the case of HDn (Fig S3 (b)), the typical <111>Si “steps” are observed. In the case of HDp (Fig S3 (a)) the surface seems to have no long range order, as is also observed for freshly etched HDp-Si (without alkenyl monolayer). The RMS roughness of the p- and n-type Si-C₁₈H₃₇ samples is 3.6 Å and 1.1 Å, respectively.

Finally, we present and compare the FTIR spectra of the alkyl monolayer on both Si substrates. The position of νₐ(CH₂) is commonly used as an indicator of the intermolecular environment of the organic chains. Values of 2919-2920 cm⁻¹ are typical for crystalline, solid alkanes and 2926-2928 cm⁻¹ values characterize liquid, isotropic alkanes. For the alkyl monolayers on HD p- and n Si(111) the νₐ(CH₂) and νₕ(CH₂) peaks were detected at 2925 cm⁻¹ and 2854 cm⁻¹ and, 2919 cm⁻¹ and 2851 cm⁻¹ respectively. Thus the monolayer on p-type seems to be less dense and more “liquid-like” than the monolayer on n-type. This is probably due to the less ordered Si-H surface on which the film grows.
Figure S3 - AFM scans of p- (a) and n- (b) type Si-C18H37. The image was obtained in ac mode and the scale of both images is 400 x 400 nm². The RMS roughness of the p- and n-type Si-C\textsubscript{18}H\textsubscript{37} samples is 3.6 Å and 1.1 Å, respectively.

Figure S4 – IR-RA Spectra of the octadecyl (C18) monolayers on HD p- (a) and n- (b) Si(111). For the octadecyl monolayers on HD p- and n-Si(111) the \( \nu_6(\text{CH}_2) \) and \( \nu_5(\text{CH}_2) \) peaks were detected at 2925 cm\(^{-1}\) and 2854 cm\(^{-1}\) and at 2919 cm\(^{-1}\) and 2851 cm\(^{-1}\), respectively.

In conclusion, the results presented above clearly indicate that the alkyl monolayer on HD p-Si is less dense than alkyl monolayers on the other Si substrates, used in this study. In addition there are significant Fluorine residues on the HDp-Si surface, compared to what we find to be the case on HDn-Si. Both the high roughness and the F presence can strongly affect the electronic properties of the Si-monolayer sample.
References


