

Scanning tunneling spectroscopy of methyl- and ethyl-terminated Si(111) surfaces

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(Received 15 December 2005; accepted 30 March 2006; published online 22 June 2006)

Methyl- and ethyl-terminated Si(111) surfaces prepared by a two-step chlorination/alkylation method were characterized by low temperature scanning tunneling spectroscopy (STS). The STS data showed remarkably low levels of midgap states on the CH₃- and C₂H₅-terminated Si surfaces. A large conductance gap relative to the Si band gap was observed for both surfaces as well as for the hydrogen-terminated Si(111) surface. This large gap is ascribed to scanning tunneling microscope tip-induced band bending resulting from a low density of midgap states which avoid pinning of the Fermi levels on these passivated surfaces. © 2006 American Institute of Physics. [DOI: 10.1063/1.2203968]

Alkylation of Si by a two-step chlorination/alkylation process¹ has been shown to produce surfaces that are passivated both chemically and electrically.^{2,3} In common with H-terminated Si surfaces, the alkylated surfaces show extraordinarily low surface recombination velocities.^{2,3} However, unlike H-Si(111) surfaces, alkylated surfaces are not susceptible to rapid oxidation in ambient air and do not suffer concomitant degradation of their surface electrical properties.^{2,3} Alkylation of Si(111) with methyl groups has been shown by low-energy electron diffraction⁴ (LEED) to produce surfaces with long-range order and by scanning tunneling microscopy (STM) to produce surfaces with short-range order.^{5,6} Additionally, photoemission and work function measurements⁴ in ultrahigh vacuum have shown that CH₃-terminated Si samples have relatively little band bending, consistent with a low density of band-gap states and in contrast to the fixed charge that is universally present at Si/SiO₂ interfaces.

We report herein scanning tunneling spectroscopy (STS) data for H-, CH₃-, and C₂H₅-terminated Si(111) surfaces. To date, the only wet chemically prepared Si surface reported to exhibit nearly ideal STS behavior is the H-Si(111) surface.⁷ Interestingly, in ultrahigh vacuum (UHV), this surface exhibits a tunneling gap of >1.6 eV in which little or no midgap conductance is observed,⁸ whereas the band gap of Si is 1.1 eV. The tunneling behavior of CH₃-Si(111) and C₂H₅-Si(111) is thus interesting in this context, given the low midgap density of states expected for such alkylated Si surfaces from macroscopic measurements of such systems.^{2,3}

Silicon surfaces were functionalized using a two-step chlorination/alkylation procedure.¹ Samples were obtained from (111)-oriented, Sb-doped, 0.005–0.02 Ω cm resistivity, *n*-type Si wafers having a miscut error of ±0.5°. The samples were cleaned and oxidized for 5 min at 80 °C in a solution of 1:1:5 (vol) 30% H₂O₂: 30% NH₃: H₂O and were then terminated with Si–H bonds by etching for 15 min in 40% NH₄F(aq). This etching method has been demonstrated to produce large atomically flat terraces.⁵ Chlorination was per-

formed by exposure of the samples to a solution of PCl₅ in chlorobenzene.^{3,9} A small amount of benzoyl peroxide was added to initiate a radical reaction, and the samples were heated at 90–100 °C for 45 min. The surfaces were removed from solution, rinsed with tetrahydrofuran (THF) and CH₃OH, and then dried under a stream of N₂(g). The resulting Cl-terminated surfaces were exposed for 3 h to a solution of 3.0 CH₃MgCl in refluxing THF to form the methylated Si(111) surface, whereas the Cl-terminated surfaces were exposed for 5 h to a solution of C₂H₅MgCl in refluxing THF to form C₂H₅-terminated surfaces.^{3,9} The samples were rinsed with THF and CH₃OH, followed by sonication in CH₃OH and CH₃CN each for 5 min. The samples were dried under a stream of N₂(g), mounted onto a sample stage, and quickly introduced into an Omicron low temperature UHV STM system. STM data of the resulting surfaces were obtained using etched or mechanically cut Pt/Ir STM tips. STS data at 77 K were acquired by fixing the tip-sample distance at a specified bias voltage and set current, and the feedback loop was then opened to record the tunneling current as the bias voltage was swept within the set range.¹⁰ Each reported STS spectrum was an average over 10 000 individual curves.

1(a) displays a STM image of H-Si(111), whereas Fig. 1(b) displays the corresponding STS behavior of this surface. No measurable gap conductance was observed, as expected, and the conductance showed an apparent gap of almost 2 V, with sharp rises in $(dI/dV)/(I/V)$ at further positive or negative bias voltages.

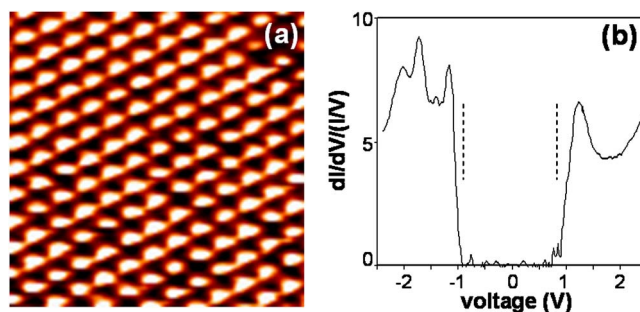


FIG. 1. (Color online) Constant current (0.1 nA) STM image (a), acquired at a sample bias voltage of -2.5 V, and averaged spectroscopy (b) on a H-Si(111) surface, taken at 77 K. Image size: 4×4 nm². The apparent gap in the spectrum is marked by the dashed lines.

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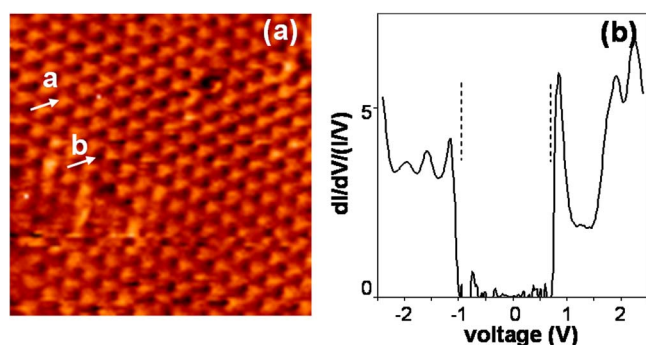


FIG. 2. (Color online) STM image (a) (acquired at -2 V and 0.3 nA) and averaged spectroscopy (b) on a CH_3 -Si(111) surface, taken at 77 K. Image size: 5×5 nm 2 .

tive tip biases. This behavior is in accord with a previous report of the STS of H-terminated Si,⁸ although the conductance increases are sharper than those reported in a very early STS study of H-terminated Si(111) surfaces.⁷

2(a) displays a STM image of a CH_3 -terminated Si(111) surface. As reported previously, the CH_3 -Si(111) surface showed a highly regular 1×1 periodicity ascribable to coverage of every atop terrace site on an unreconstructed Si(111) surface by methyl groups. Figure 2(b) depicts the STS data, reported as the average $(dI/dV)/(I/V)$ behavior from over 100 nominally equivalent locations labeled in Fig. 2(a) as “a,” which is the topographical maximum point on this image. The STS data were remarkably similar to that of H-terminated Si(111), showing no mid-gap conductance and a sharp rise in $(dI/dV)/(I/V)$ for tip biases >1 V or <-1 V versus the sample. STS data obtained at positions that corresponded to topographic minima in the STM image of Fig. 2(a), labeled as position “b” in Fig. 2(a), were essentially identical to those obtained over location “a” [Fig. 2(b)].

Figure 3 reports the STS data for C_2H_5 -terminated Si(111) surfaces. Such surfaces do not show the short- or long-range order of H-terminated Si(111) or CH_3 -terminated Si(111) due to the inability of the ethyl group sterically to terminate every atop site on an unreconstructed Si(111) surface.¹¹ Prior work has shown that alkylation produces Si-C bonds to approximately 80% of the Si atop atoms, with the other sites predominantly terminated by Si-H bonds.¹¹ The STS data for this surface again are remarkably free of midgap conductance and show an abrupt increase in

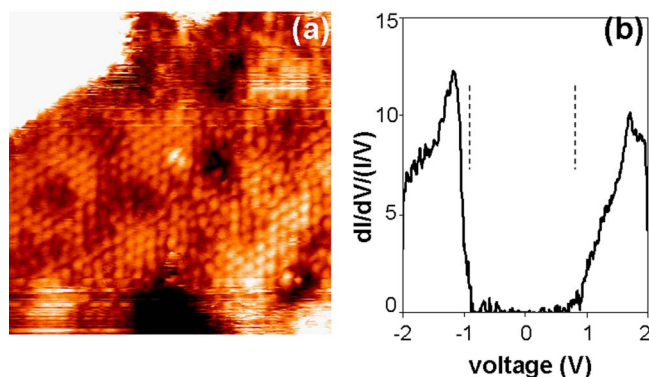


FIG. 3. (Color online) STM image (a) (acquired at -3 V and 0.07 nA) and averaged spectroscopy (b) on a C_2H_5 -Si(111) surface, taken at 77 K. Image size: 10×10 nm 2 .

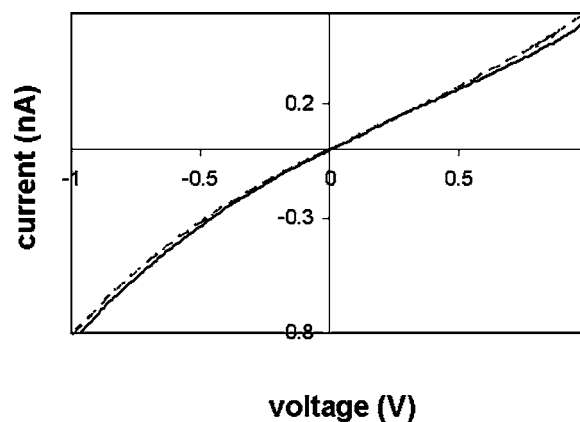


FIG. 4. (Color online) Scanning tunneling spectroscopy of a Au(111) surface acquired before (solid line) and after (dashed line) obtaining spectroscopy data from a CH_3 -Si(111) surface using the same Pt/Ir tip. The two traces, which show the typical I - V characteristics of the Au(111) surface, indicate the relative stability of the STM tip during spectra acquisition.

$(dI/dV)/(I/V)$ at tip biases >1 V or <-1 V versus the sample [Fig. 3(b)].

Figure 4 shows the STS data obtained for a clean Au(111) surface in the same instrument, before and after the STS data were collected on the CH_3 -terminated Si surface, and with the identical tip. The data clearly show the I - V behavior expected for a metallic system, with increased conductance at all nonzero values of the tip bias relative to the sample. The slight increase of the current for voltages below -0.5 V is related to the surface state on the Au(111) surface, as reported previously.¹²

The STS data confirm the remarkably low levels of mid-gap states on alkylated Si surfaces deduced from the prior surface recombination velocity measurements.^{2,3} The atomic-scale STS data are fully consistent with the conclusion that on average such surfaces have less than one electrically active defect per μm^2 , assuming a geometric cross section for carrier capture by the traps. In our images, no measurable midgap states were observed on terraces that contained several hundred atoms on average.

STS data were also obtained on the CH_3 -Si(111) surface in areas that contained edges and steps. These STS spectra were very similar to the ones obtained on flat terraces [Fig. 2(b)], with no significant additional features within the 2 V observed conductance gap. It is likely that the edges and steps are also passivated, possibly by H, if not by $-\text{CH}_3$ groups.¹³

The large conductance gap relative to the Si band gap was observed for both the methyl- and ethyl-terminated Si(111) surfaces prepared by the two-step chlorination/alkylation method. We ascribe this behavior to tip-induced band bending (TIBB), as identified previously by McEllistrem *et al.*¹⁴ TIBB can only occur for surfaces with relatively low levels of midgap states, so that the bias applied between the tip and the sample drops across the sample, and the Fermi level of the sample becomes unpinned at the surface. Surfaces with significant levels of electrical defects will, in contrast, have a pinned surface Fermi level and all of the applied voltage will drop across the tip-sample gap. The most defect-free surfaces will therefore show the largest apparent gap in voltage between tunneling from conduction band states and into valence band states in the biased semiconductor. The data underscore the remarkable ability of the

two-step chlorination/alkylation method to produce electrically passive Si surfaces on both the macroscale and nanoscale, as probed on such systems by surface recombination velocity measurements on wafers and STS measurements on the atomic scale.

The authors acknowledge the National Science Foundation, Grant Nos. CHE-0213589 (NSL) and NSF-CCF-05204490, and the MARCO Materials Structures and Devices Focus Center (JRH) for support of this research. One of the authors (L.J.W.) thanks the NSF for a graduate fellowship. The authors thank Peigen Cao for helpful discussions and technical assistance.

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