

**Atomic-scale control of hydrogen bonding on a bare Si(100)-2×1 surface**Hatem Labidi,<sup>1</sup> Lev Kantorovich,<sup>2</sup> and Damien Riedel<sup>1,\*</sup><sup>1</sup>*Institut des Sciences Moléculaires d'Orsay, UMR8214, Université Paris Sud, Orsay Cedex 91405, France*<sup>2</sup>*King's College London, Strand, London WC2R 2LS, United Kingdom*

(Received 7 May 2012; revised manuscript received 17 July 2012; published 25 October 2012)

The control of the dissociative adsorption of individual hydrogen molecules is performed on the silicon surface at the atomic scale. It is achieved using the tip of a low-temperature (9 K) scanning tunneling microscope (STM) exposed to  $10^{-6}$  torr of  $H_2$  and by probing the bare Si(100)-2 × 1 surface at a positive bias. This effect is very localized and is induced by the tunnel electrons. The statistical study of this process reveals an activation energy threshold matching the creation of  $H_2^-$  at the surface of the STM tip. Our results are supported by *ab initio* density functional calculations of a hydrogenated silicon dimer.

DOI: [10.1103/PhysRevB.86.165441](https://doi.org/10.1103/PhysRevB.86.165441)

PACS number(s): 68.43.-h, 34.80.Ht, 68.37.Ef, 82.37.Np

The study of the passivation of the Si(100)-2 × 1 surface with hydrogen has attracted significant interest because of its crucial importance in many technological domains including the fabrication of metal-oxide-semiconductor field-effect transistor (MOSFET) devices,<sup>1,2</sup> the production of solar cells,<sup>3</sup> or for molecular electronics.<sup>4</sup> A detailed analysis of the hydrogen adsorption-desorption cycles on this surface has raised various controversies, in particular, concerning the adsorption barrier of  $H_2$  on Si(100).<sup>5</sup> Today, models describing the initial stage processes responsible for the dissociative adsorption/desorption of  $H_2$  show that the *interdimer* models are at the origin of the dissociation of neutral  $H_2$  on the Si surface.<sup>6-12</sup> In this context, the use of the scanning tunneling microscope (STM) has been of central importance for our understanding of the hydrogenation reactions on the Si(100) on the atomic scale.<sup>13</sup> In particular, the STM has been employed to induce local hydrogen atoms desorption from passivated surfaces via electronically induced processes.<sup>14-16</sup> Yet, the *reverse* process, i.e., the controlled local adsorption of molecular hydrogen on the bare Si(100) surface at the atomic scale has never been reported with such precision.<sup>17</sup>

The hydrogenation process presented in this paper can be essential in various areas of surface science related to molecular electronics,<sup>18,19</sup> hydrogen storage,<sup>20</sup> or photonics.<sup>21</sup> This electronically induced effect is observed when the thermal shields of a low-temperature (9 K) STM is initially filled with pure molecular hydrogen ( $H_2$  5.6 from MESSER) at a pressure of  $1.0 \times 10^{-6}$  torr for 2 min. A cold pipe (77 K) placed before the leak valve prevents other species rather than  $H_2$  to react with the silicon surface. The STM tungsten and copper tips are prepared by chemical etching and are cleaned by electron bombardment heating to remove their oxide layers.<sup>22</sup> The Si(100) samples [*n*-doped (As),  $\rho = 0.005 \Omega \text{ cm}$ ] are cleaned by resistive heating periods as previously described.<sup>23</sup> The cold (12 K) sample with a bare Si(100) surface is introduced in the STM prior to the  $H_2$  gas exposure and is imaged normally.<sup>23</sup> Then,  $H_2$  is introduced and STM topographies of the bare silicon surface can still be observed with a very weak density of defects [Fig. 1(a)].<sup>24</sup> The STM tip is then located at a given position [the red dot in Fig. 1(a)], and the surface voltage is switched from the scanning conditions at a negative bias ( $V_s = -1.4 \text{ V}$ ) to a positive bias  $V_s = +1.4 \text{ V}$ . During this excitation procedure, the feedback loop of the STM is switched

off, and the tunnel current is recorded, whereby, the height of the STM tip is kept constant.<sup>25</sup> A typical tunnel current trace, recorded during the excitation procedure, is reported in Fig. 1(e): The current  $I_{\text{exc}}$  flows during the time  $t_{\text{exc}}$  and drops suddenly before the end of the trace [red arrow in Fig. 1(e)]. A second topography of the same area shows a short dark line centered on the dimer row and located exactly at the excitation position [Fig. 1(b)]. We show that this dark feature corresponds to a fully hydrogenated silicon dimer (HD). Note that the creation of a HD during the excitation process is at the origin of the current drop detected in the current trace in Fig. 1(e). The same procedure can be repeated at various positions to produce similar dark depressions on the Si surface [Figs. 1(c) and 1(d)]. For each excitation, resulting in the appearance of a single HD, the charge  $q_{\text{exc}} = t_{\text{exc}} I_{\text{exc}}$  is calculated, and its distribution over a large number of events presented in Fig. 1(f) allows deducing an average charge ( $Q$ ). The exponential decay of this distribution indicates that the observed processes are independent, i.e., induced by the tunnel electrons.<sup>26</sup> From this distribution, we deduce an average quantum yield ( $Y = e / \langle Q \rangle$ ) required to fabricate the observed HD on the bare surface. For the chosen experimental conditions ( $V_s = +1.4 \text{ V}$ ,  $I_{\text{exc}} = 110 \text{ pA}$ ), the measured quantum yield is  $Y = (2.8 \pm 0.7) \times 10^{-9}$ . We emphasize that the measured voltage threshold to observe this hydrogenation process is found at  $V_s = +1.2 \text{ V}$ , whereas, the local hydrogenation does not occur for negative bias up to  $-3.0 \text{ V}$ .

Our experiments have been performed with four different silicon samples and tips to discard specific tip effects. This allows us to observe hundreds of different successful events. In most cases, the observed feature is the HD shown in Fig. 1, created right below the tip apex location. For the excitation current varying between 50 and 100 pA, our measurements show that, in 87% of the cases, the reaction leads to the creation of a single HD [Figs. 1(a)–1(d)], whereas, in a few cases (13%), two successive HDs can be created [Figs. 2(a)–2(d) where the red dot indicates the excitation location of the tip in each case]. When the excitation current increases to  $\sim 200 \text{ pA}$ , the proportion of double HDs reaches 60% of the fabricated features, leaving the formation of a single HD at 40%. When two HDs are created, the corresponding current trace shows two current plateaus [Fig. 2(e)], indicating that the events occur successively. A statistical study of the process related to the

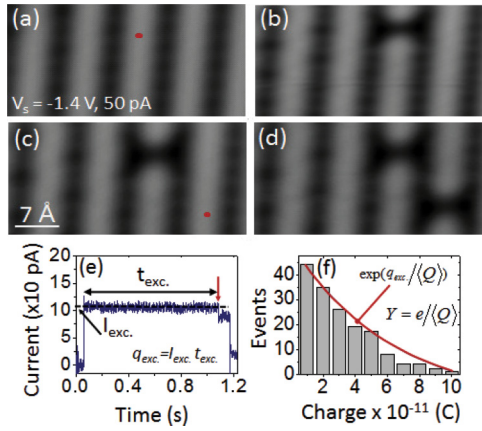


FIG. 1. (Color online) (a)–(d) The ( $3 \times 1.5\text{-nm}^2$ ) STM topographies ( $-1.4\text{ V}$ ,  $50\text{ pA}$ ) of the bare Si(100) surface. (a) and (b) Before and after an electronically induced reaction (see red dot location at  $V_s = +1.4\text{ V}$ ,  $100\text{ pA}$ ) and (c) and (d) before and after a second electronically induced reaction. (e) A typical current trace recorded during the excitation pulse (b) and (d). (f) Distribution of the measured electronic charge ( $I_{\text{exc}} \times t_{\text{exc}}$ ) required to induce the surface reaction observed in (b) and (d).

creation of two consecutive HDs is performed, and the ensuing average quantum yields are  $Y_{\text{HD1}} = (2.7 \pm 0.9) \times 10^{-9}$  and  $Y_{\text{HD2}} = (2.2 \pm 0.7) \times 10^{-9}$  for the creation of the first and the second HDs, respectively. These quantum yields are very similar to the yield needed to create a single HD ( $Y = (2.8 \pm 0.7) \times 10^{-9}$ ), which means that the probability to electronically induce a HD on the silicon surface does not change when the excitation current increases and, hence, arises from a single-electron process.<sup>27</sup> Note that the creation of double HDs is also very local as it is observed around the excitation point either on two adjacent silicon dimer rows

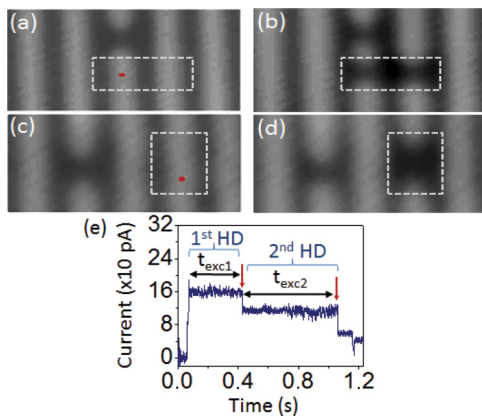


FIG. 2. (Color online) (a)–(d) The ( $3 \times 1.5\text{-nm}^2$ ) STM topographies ( $-1.4\text{ V}$ ,  $50\text{ pA}$ ) of the bare Si(100) surface. (a) and (b) Before and after an electronically induced reaction (at  $V_s = +1.4\text{ V}$ ,  $200\text{ pA}$ ) on two successive horizontal dimers and (c) and (d) before and after an electronically induced reaction (at  $V_s = +1.4\text{ V}$ ,  $200\text{ pA}$ ) on two successive vertical dimers. The red dot indicates where the tip is placed during the excitation, and the white dashed rectangles are landmarks that locate the apparition of the HDs. (e) A typical current trace recorded during the electronically induced reaction in (b) or (d).

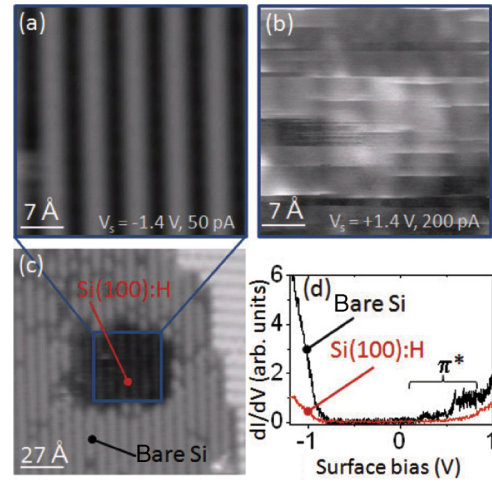


FIG. 3. (Color online) (a) and (b) The ( $4.6 \times 4.6\text{-nm}^2$ ) STM topographies of the same area of the bare Si(100)- $2 \times 1$  surface at  $-1.4\text{ V}$ ,  $50\text{ pA}$  and  $+1.4\text{ V}$ ,  $200\text{ pA}$ , respectively (scan speed of  $\sim 1000\text{ \AA/s}$ ). (c) The ( $14.6 \times 14.6\text{-nm}^2$ ) STM topography ( $-1.4\text{ V}$ ,  $50\text{ pA}$ ) of the bare Si(100) surface centered at the same location as in (b). (d) An averaged  $dI/dV$  spectroscopy acquired on the bare Si(100) (dark curve) and the reacted area (red curve).

[Figs. 2(a) and 2(b)] or on two adjacent silicon dimers of the same row [Figs. 2(c) and 2(d)].

To validate the proposition of a local hydrogenation via the dissociative adsorption of  $\text{H}_2$  molecules,<sup>28</sup> we have performed STM topographies of the same scanning area of a bare silicon surface initially at a surface voltage ( $V_s = -1.4\text{ V}$ ) that does not activate the surface reaction [Fig. 3(a)] and, subsequently, at a positive surface voltage ( $V_s = +1.4\text{ V}$ ,  $I = 200\text{ pA}$ ) to induce the fabrication of the HD's features [Fig. 3(b)]. Then, a third STM topography on a larger scale is performed ( $V_s = -1.4\text{ V}$ ) in which a dark square of about the size of the previous STM topographies appears [Fig. 3(c)]. The comparison of  $dI/dV$  measurements performed on the bare surface and the dark area shows that the unoccupied  $\pi^*$  surface states disappear on the created dark zone and show a surface gap of  $\sim 2\text{ eV}$  [Fig. 3(d)]. These differences are characteristics of the electronic properties of silicon-hydrogenated surfaces.<sup>29</sup> To control the nature of these hydrogenated areas, we have shown that it is possible to desorb a single H atom from them by applying positive voltage pulses ( $+2.5\text{ V}$ ) to the surface as reported previously.<sup>15</sup> However, this process implies evacuating the hydrogen from the STM chamber prior to applying the pulse.<sup>22</sup>

To further highlight that the observed HD's features are local hydrogenated silicon dimers [Figs. 4(a) and 4(b)], we have simulated STM images of the Si(100) surface with one HD [Figs. 4(c) and 4(d)], both for occupied ( $V_s = -1.0\text{ V}$ ) and unoccupied ( $V_s = +1.0\text{ V}$ ) states, respectively. The calculations are performed using the Tersoff-Hamman approximation and the plane-wave Vienna *ab initio* simulation package (VASP) code,<sup>30</sup> which implements periodic boundary conditions, generalized gradient approximation for the exchange and correlation,<sup>31</sup> and the projector augmented-wave method of pseudopotentials.<sup>32</sup> To ease the comparison with the experiment, the symmetric ( $2 \times 1$ ) surface reconstruction

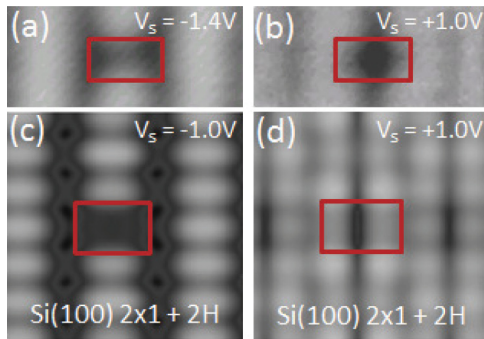


FIG. 4. (Color online) (a) and (b) The  $(2.3 \times 1.3\text{-nm}^2)$  experimental STM topographies of the occupied ( $-1.4\text{-V}$ ,  $50\text{-pA}$ ) and unoccupied ( $+1.0\text{-V}$ ,  $50\text{-pA}$ ) states of the bare Si(100) surface, respectively, with one hydrogenated dimer located by a red rectangle. (c) and (d) Calculated LDOS of the bare Si(100) surface with one hydrogenated dimer for the occupied ( $-1.0\text{-V}$ ) and unoccupied ( $+1.0\text{-V}$ ) states, respectively.

was modeled, although the  $c(4 \times 2)$  phase is known to be the ground-state structure of the bare silicon surface<sup>33–35</sup> [the calculation of the  $c(4 \times 2)$  phase is detailed in the Supplemental Material].<sup>22</sup> As observed in Fig. 4, the local density of states (LDOS) shows a depression at the hydrogenated site for the occupied states, which clearly reproduces the observed HD [Figs. 4(a) and 4(c)]. Similarly, excellent agreement with the experiment is also observed for the unoccupied states images as seen in Figs. 4(b) and 4(d) confirming that the fabricated HDs are fully hydrogenated silicon dimers.

Our experimental results show that the hydrogenation occurs only on silicon dimers via an *intradimer* hydrogenation process involving the dissociation of  $\text{H}_2$  molecules whose origin must be precisely investigated. During the gas introduction in the thermal shields of the microscope, the cold STM ( $\sim 9\text{ K}$ ) is exposed to  $\text{H}_2$  ( $1.0 \times 10^{-6}$  torr for 120 s). At these conditions,  $\text{H}_2$  molecules are, *a priori*, rapidly condensed on each part of the STM.<sup>36</sup> However, we find that the STM topographies of the silicon surface are similar before and after the introduction of molecular hydrogen, indicating that the silicon surface is not covered with multiple layers of molecular hydrogen,<sup>37,38</sup> in particular, in the region of the STM junction where weakly adsorbed  $\text{H}_2$  molecules on Si(100) can easily be brushed off by the STM tip. This is consistent with the fact that, at 9 K,  $\text{H}_2$  molecules stick differently on the tungsten tip compared to the silicon surface on which weakly adsorbed  $\text{H}_2$  can easily diffuse.<sup>39–41</sup> Indeed,  $\text{H}_2$  molecules initially dissociate on crystalline tungsten at 9 K with a saturating coverage of  $\sim 0.8$  monolayer forming patches of H-passivated tungsten on the surface.<sup>42,43</sup> The additional adsorbed  $\text{H}_2$  molecules will physisorb on the passivated areas of the W tip to form structured adlayers of molecular  $\text{H}_2$  similar to what is observed on noble-metal surfaces.<sup>44,45</sup> Hence, the trend of these observations indicates that, in our experiments, the tungsten tip is covered with molecular hydrogen that acts as a source of  $\text{H}_2$  for the hydrogenation reaction, whereas the few  $\text{H}_2$  molecules that diffuse on the silicon surface can hardly participate in the observed *local* hydrogenation due to their higher mobility.

This implies that, in order to induce the local hydrogenation process,  $\text{H}_2$  molecules desorb from the STM tip and then re-adsorb on the silicon surface. The desorption energy of the  $\text{H}_2$  molecules from an amorphous tungsten tip is rather difficult to estimate precisely, but it was reported to be lower than  $\sim 100\text{ meV}$ .<sup>40,46,47</sup> Once the  $\text{H}_2$  molecule has left the STM tip, the dissociative *intradimer* adsorption of  $\text{H}_2$  on Si(100) requires overcoming an energy barrier of  $\sim 0.6\text{ eV}$ .<sup>5,28</sup> The initial transfer of this amount of energy to the  $\text{H}_2$  molecule would imply strong inelastic multielectron processes, which are in contradiction with our experimental observations showing that the local hydrogenation is a one-electron process. Additionally, the energy threshold observed experimentally to produce the local hydrogenation of the silicon dimer with W tips is much higher ( $\sim 1.2\text{ eV}$ ) than the energy required to desorb  $\text{H}_2$  from the STM tip and re-adsorbs it on the surface.

Thus, our experimental data rather indicate that an electron attachment on the  $\text{H}_2$  molecule triggers the observed hydrogenation process similarly to what has been reported for molecular  $\text{H}_2$  desorption on metal surfaces.<sup>48,49</sup> Therefore, the measured electronic quantum yield represents the probability per electron to create  $\text{H}_2^-$  on the tungsten tip. The energy barrier  $U$  required to create  $\text{H}_2^-$  from molecular  $\text{H}_2$  in the gas phase is  $\sim 2\text{ eV}$ .<sup>50</sup> On a metallic surface, this value is reduced ( $U_{\text{corr}}$ ) due to the presence of the image charge potential of the anion.<sup>51</sup> Considering the anion as a point charge, the image charge potential for a  $\text{H}_2^-$  anion located at  $z_1$  above the surface is  $V_{\text{inter}} = -q^2/4(z_1 - z_0)$ , where  $z_0$  is the effective position of the metal surface.<sup>51</sup> For physisorbed molecules, an average value of  $z_1 \sim 4$  to  $5\text{ \AA}$ <sup>4</sup> leads to an estimate of  $V_{\text{inter}}$  in the range of  $\sim 0.9 - 1.1\text{ eV}$ . Thus, the energy barrier  $U_{\text{corr}}$  to create  $\text{H}_2^-$  on the tungsten tip is in the range of  $\sim 0.9 - 1.1\text{ eV}$ , matching well our measured threshold required to induce the local hydrogenation of a silicon dimer ( $\sim 1.2\text{ V}$ ).<sup>22</sup> This result strongly indicates that the ensuing local hydrogenation process is, indeed, related to the initial creation of a  $\text{H}_2^-$  anion on the STM tip. To further validate this model, we have performed similar experiments with copper tips that offer a slightly higher image charge potential than tungsten due to its higher electron density ( $E_F \sim 7\text{ eV}$ ).<sup>49</sup> Our measurements show a threshold energy to induce local hydrogenation with Cu tips at  $\sim 1.0\text{ eV}$ . This difference in threshold energy compared to the one measured with the tungsten tips ( $1.2\text{ eV}$ ) fits with the image charge potential model<sup>22</sup> and clearly demonstrates that our proposed mechanism correctly describes the observed local hydrogenation process in which  $\text{H}_2$  molecules are initially desorbed in their anionic form from the STM tip.

When  $\text{H}_2^-$  is formed on the STM tip, it is rapidly attracted by the positively charged silicon surface ( $V_s = +1.4\text{ V}$ ) initiating desorption of the  $\text{H}_2^-$  molecule from the STM tip and, subsequently, its transport towards the silicon surface by the electrostatic field applied in the STM junction. The time of flight of the  $\text{H}_2^-$  anion in an electrostatic field of  $1.4\text{ V}$  over a distance of  $1\text{ nm}$  before impacting on the silicon surface can be estimated to be  $\sim 300\text{ ps}$ . This relatively short time warrants the  $\text{H}_2^-$  anion to rapidly interact with a silicon dimer prior to its dissociation or neutralization because its lifetime exceeds microseconds.<sup>52</sup> The charging process of a  $\text{H}_2$  molecule from the STM tip combined with the attraction of the produced  $\text{H}_2^-$  anion towards the surface completely

explains our experimental findings and, in particular, the strong localization of the hydrogenation process. It also clarifies why this local hydrogenation reaction cannot be observed for negative biases at which the creation of  $\text{H}_2^-$  anions on the STM tip might also be possible. This is mainly due to the repulsion of the created  $\text{H}_2^-$  anions away from the negatively charged silicon surface at  $V_s < 0$  combined with an increased probability for the  $\text{H}_2^-$  anions to lose their extra electrons in the positively charged tungsten tip. We wish to emphasize that the probable presence of silicon microtips at the apex of the STM tip will not change the above-described local hydrogenation process drastically as they will lead to the formation of metallic silicide structures with similar properties.<sup>53,54</sup>

Conversely, for previous studies establishing a predominantly *interdimer* model with neutral  $\text{H}_2$  to explain the hydrogenation, our observations show that the *intradimer* process is clearly privileged with the  $\text{H}_2^-$  anion.<sup>55</sup> The *intradimer* process might also be favored by the reduced dissociation energy of  $\text{H}_2^-$  (1.5 eV) compared to the neutral  $\text{H}_2$  (4.5 eV).<sup>50</sup> Additionally, the silicon surface is known to present a  $c(4 \times 2)$  reconstruction at 9 K where tilted dimers have small dipole moments.<sup>56</sup> This suggests that, when  $\text{H}_2^-$  interacts with the Si surface, the anion may slightly orientate itself along the dimer, prior to its dissociation, to favor the *intradimer* hydrogenation mechanism.

In conclusion, we show that it is possible to create single hydrogenated dimers on the bare Si(100) surface. This can be performed when the shield of a low temperature STM

is beforehand exposed to molecular hydrogen. The local hydrogenation process of the silicon surface occurs when a positive surface bias pulse is applied to the surface. A statistical analysis of these pulses shows that the tunnel electrons activate the local hydrogenation via a one-electron process at an energy threshold of 1.2 eV and 1.0 eV for W and Cu tips, respectively. The ensuing electronic process is shown to be responsible of the formation of  $\text{H}_2^-$  anions via an electron attachment to the  $\text{H}_2$  molecules adsorbed on the STM tip that triggers  $\text{H}_2$  desorption from its surface followed by a subsequent local re-adsorption on the silicon dimer beneath the STM tip apex. The theoretical calculations of a single hydrogenated dimer on the Si(100) surface using the density functional theory show similar features to those observed in STM topographies and hence support our conclusion about the hydrogenation process based on the *intradimer* dissociative adsorption of  $\text{H}_2$  on Si(100). Finally, the atomic scale control of this hydrogenation process has been used to fabricate large hydrogenated areas, demonstrating its potential impact in nanotechnology including, for instance, chemical reactions with  $\text{H}_2^-$  anions. Looking to the future, this process might be extended to the use of molecules other than  $\text{H}_2$  and may be exploited to induce chemical reactions on nanodevices, such as the graphene sheets via, for example, Diels-Alder-type reactions.<sup>57,58</sup>

The authors wish to thanks Prof. E. Charon from the Institut des Sciences Moléculaires d'Orsay for valuable discussions.

\*damien.riedel@u-psud.fr

<sup>1</sup>M. Budde, G. Lüpke, E. Chen, X. Zhang, N. H. Tolk, L. C. Feldman, E. Tarhan, A. K. Ramdas, and M. Stavola, *Phys. Rev. Lett.* **87**, 145501 (2001).

<sup>2</sup>J. W. Lyding, K. Hess, and I. C. Kizilyalli, *Appl. Phys. Lett.* **68**, 2526 (1996).

<sup>3</sup>R. Lüdemann, *Mater. Sci. Eng. B* **58**, 86 (1999).

<sup>4</sup>A. Bellec, F. Ample, D. Riedel, G. Dujardin, and C. Joachim, *Nano Lett.* **9**, 144 (2009).

<sup>5</sup>K. W. Kolasinski, W. Nessler, A. de Meijere, and E. Hasselbrink, *Phys. Rev. Lett.* **72**, 1356 (1994).

<sup>6</sup>J. H. Choi, K. S. Kim, and J. H. Cho, *J. Chem. Phys.* **131**, 244704 (2009).

<sup>7</sup>M. Dürr, M. B. Raschke, and U. Höfer, *J. Chem. Phys.* **111**, 10411 (1999).

<sup>8</sup>M. Dürr, Z. Hu, A. Biedermann, U. Höfer, and T. F. Heinz, *Phys. Rev. Lett.* **88**, 046104 (2002).

<sup>9</sup>M. Dürr, A. Biedermann, Z. Hu, U. Höfer, and T. F. Heinz, *Science* **296**, 1838 (2002).

<sup>10</sup>P. Bratu and U. Höfer, *Phys. Rev. Lett.* **74**, 1625 (1995).

<sup>11</sup>T. Matsuno, T. Niida, H. Tsurumaki, and A. Namiki, *J. Chem. Phys.* **122**, 024702 (2005).

<sup>12</sup>A. Namiki, *Prog. Surf. Sci.* **81**, 337 (2006).

<sup>13</sup>A. Bellec, D. Riedel, G. Dujardin, N. Rompotis, and L. N. Kantorovich, *Phys. Rev. B* **78**, 165302 (2008).

<sup>14</sup>E. T. Foley, A. F. Kam, J. W. Lyding, and P. Avouris, *Phys. Rev. Lett.* **80**, 1336 (1998).

<sup>15</sup>A. Bellec, D. Riedel, G. Dujardin, O. Boudrioua, L. Chaput, L. Stauffer, and P. Sonnet, *Phys. Rev. Lett.* **105**, 048302 (2010).

<sup>16</sup>K. Stokbro, C. Thirstrup, M. Sakurai, U. Quaade, B. Yu-Kuang Hu, F. Perez-Murano, and F. Grey, *Phys. Rev. Lett.* **80**, 2618 (1998).

<sup>17</sup>H. Kuramochi, H. Uchida, and M. Aono, *Phys. Rev. Lett.* **72**, 932 (1994).

<sup>18</sup>G. P. Lopinski, D. D. M. Wayner, and R. A. Wolkow, *Nature (London)* **406**, 48 (2000).

<sup>19</sup>S. Katano, Y. Kim, M. Hori, M. Trenary, and M. Kawai, *Science* **316**, 1883 (2007).

<sup>20</sup>M. Blanco-Rey, M. Alducin, J. I. Juaristi, and P. L. de Andres, *Phys. Rev. Lett.* **108**, 115902 (2012).

<sup>21</sup>D. Riedel, R. Delattre, A. G. Borisov, and T. V. Teperik, *Nano Lett.* **10**, 3857 (2010).

<sup>22</sup>See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.86.165441> containing simulations of STM images of the bare Si(100) surface with one hydrogenated dimer in a  $c(4 \times 2)$  asymmetric configuration as well as an example of the local dehydrogenation of a single H atom from a fabricated hydrogenated zone. The procedure used to prepare the copper tips and the local hydrogenation induced with these tips is detailed. The method to calculate the energy barrier  $U$  required to create  $\text{H}_2^-$  on the STM tips is described.

<sup>23</sup>D. Riedel, M. Lastapis, M. G. Martin, and G. Dujardin, *Phys. Rev. B* **69**, 121301 (2004).

<sup>24</sup>F. Chiaravalloti, G. Dujardin, D. Riedel, H. P. Pinto, and A. S. Foster, *Phys. Rev. B* **84**, 155433 (2011).

- <sup>25</sup>G. Comtet, G. Dujardin, L. Hellner, D. Riedel *et al.*, *Philos. Trans. R. Soc. London, Ser. A* **362**, 1217 (2004); See also D. Riedel, M. Cranney, M. Martin *et al.*, *J. Am. Chem. Soc.* **131**, 5414 (2009).
- <sup>26</sup>D. Riedel, M.-L. Bocquet, H. Lesnard *et al.*, *J. Am. Chem. Soc.* **131**, 7344 (2009).
- <sup>27</sup>D. Riedel, *J. Phys.: Condens. Matter* **22**, 264009 (2010).
- <sup>28</sup>M. Dürr and U. Höfer, *Surf. Sci. Rep.* **61**, 465 (2006).
- <sup>29</sup>A. Bellec, D. Riedel, G. Dujardin, O. Boudrioua, L. Chaput, L. Stauffer, and P. Sonnet, *Phys. Rev. B* **80**, 245434 (2009).
- <sup>30</sup>G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996); See also *Phys. Rev. B* **54**, 11169 (1996).
- <sup>31</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- <sup>32</sup>G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- <sup>33</sup>Y. J. Li, H. Nomura, N. Ozaki, Y. Naitoh, M. Kageshima, Y. Sugawara, C. Hobbs, and L. Kantorovich, *Phys. Rev. Lett.* **96**, 106104 (2006).
- <sup>34</sup>C. Manzano, W.-H. Soe, H. Kawai, M. Saeys, and C. Joachim, *Phys. Rev. B* **83**, 201302 (2011).
- <sup>35</sup>K. Sagisaka, M. Kitahara, D. Fujita, G. Kido, and N. Koguchi, *Nanotechnology* **15**, S371 (2004).
- <sup>36</sup>J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
- <sup>37</sup>J. Järvinen, V. V. Khmelenko, D. M. Lee, J. Ahokas, and S. Vasiliev, *J. Low Temp. Phys.* **162**, 96 (2011).
- <sup>38</sup>M. Sohaili, J. Klier, and P. Leiderer, *J. Phys.: Condens. Matter* **17**, S415 (2005).
- <sup>39</sup>B. A. Chuikov, V. V. Dvurechenskikh, V. D. Osovskii, Y. G. Ptushinskii, and V. G. Sukretnyi, *Surf. Sci.* **285**, 75 (1993).
- <sup>40</sup>P. Bratu, W. Brenig, A. Groß, M. Hartmann, U. Höfer, P. Kratzer, and R. Russ, *Phys. Rev. B* **54**, 5978 (1996); See also M. Watamori, M. Naitoh, H. Morioka, Y. Maeda, and K. Oura, *Appl. Surf. Sci.* **82**, 417 (1994).
- <sup>41</sup>K. Kolasinski, *Int. J. Mod. Phys. B* **9**, 2753 (1995).
- <sup>42</sup>J. Järvinen, V. V. Khmelenko, D. M. Lee, J. Ahokas, and S. Vasiliev, *J. Low Temp. Phys.* **162**, 96 (2011).
- <sup>43</sup>R. Romer, R. Wortman, and R. Lundy, *J. Chem. Phys.* **26**, 1147 (1957).
- <sup>44</sup>P. Norlander, C. Holmberg, and J. Harris, *Surf. Sci.* **152**, 702 (1985).
- <sup>45</sup>Y. G. Ptushinskii, *Low Temp. Phys.* **30**, 1 (2004).
- <sup>46</sup>Henriksson *et al.*, *Surf. Sci.* **600**, 3167 (2006).
- <sup>47</sup>T. U. Nahm and R. Gomer, *Surf. Sci.* **380**, 434 (1997).
- <sup>48</sup>S. Andersson and K. Svensson, *Phys. Rev. Lett.* **102**, 156104 (2009).
- <sup>49</sup>W. Eberhardt, R. Cantor, F. Greuter, and E. W. Plummer, *Solid State Commun.* **42**, 799 (1982).
- <sup>50</sup>T. E. Sharp, *At. Data* **2**, 119 (1971).
- <sup>51</sup>N. D. Lang and W. Kohn, *Phys. Rev. B* **7**, 3541 (1973).
- <sup>52</sup>R. Golser, H. Gnaser, W. Kutschera, A. Priller, P. Steier, A. Wallner, M. Čížek, J. Horáček, and W. Domcke, *Phys. Rev. Lett.* **94**, 223003 (2005).
- <sup>53</sup>T. Shimizu, J. T. Kim, and H. Toumoto, *Ultramicroscopy* **73**, 157 (1998).
- <sup>54</sup>A. G. Sault and D. W. Goodman, *J. Catal.* **126**, 57 (1990).
- <sup>55</sup>A. Biedermann, E. Knoesel, Z. Hu, and T. F. Heinz, *Phys. Rev. Lett.* **83**, 1810 (1999).
- <sup>56</sup>Y. Pennec, M. Horn von Hoegen, X. Zhu, D. C. Fortin, and M. R. Freeman, *Phys. Rev. Lett.* **96**, 026102 (2006).
- <sup>57</sup>M. Zakir Hossain, M. A. Walsh, and M. C. Hersam, *J. Am. Chem. Soc.* **132**, 15399 (2010).
- <sup>58</sup>S. Sarkar, E. Bekyarova, and R. C. Haddon, *Acc. Chem. Res.* **45**, 673 (2012).