Nonlocal Activation of a Bistable Atom through a Surface State Charge-Transfer Process on Si(100)-(2 × 1):H

A. Bellec, D. Riedel,* and G. Dujardin

Institut des Sciences Moléculaires d'Orsay, CNRS, Bâtiment 210, Université Paris Sud, 91405 Orsay, France

O. Boudrioua, L. Chaput, L. Stauffer, and Ph. Sonnet

Institut de Sciences des Matériaux de Mulhouse (IS2M–LRC 7228), Université de Haute-Alsace, 4 rue des frères Lumière, 68093 Mulhouse, France

(Received 9 December 2009; published 19 July 2010)

The reversible hopping of a bistable atom on the Si(100)-(2 × 1):H surface is activated nonlocally by hole injection into Si-Si bond surface states with a low temperature (5 K) scanning tunneling microscope. In the contact region, at short distances (<1.5 nm) between the hole injection site and the bistable atom, the hopping yield of the bistable atom exhibits remarkable variations as a function of the hole injection site. It is explained by the density of state distribution along the silicon bond network that shows charge-transfer pathways between the injection sites and the bistable atom.

DOI: 10.1103/PhysRevLett.105.048302 PACS numbers: 82.37.Gk, 73.21.Cd

Nonlocal activation of atomic and molecular reactions on surfaces refers to the propagation of energetic charge carriers (electrons or holes) through surface states and the subsequent activation of reactions at a distance from the initial excitation site [1–10]. Such "chemistry at a distance" is of ubiquitous importance not only in solid interfacial architectures [11] but also for charge transport properties inside large molecular systems such as DNA [12,13]. On surfaces, it has been shown that charge carriers, primarily injected with a scanning tunneling microscope (STM) tip, can be transferred toward the reaction site through surface states over long distances (a few tens of nm) [2–7,13]. Hence, charge-transfer processes through surface states are expected to play a crucial role in charge transport properties of the studied materials. This is of particular interest in molecular electronics where charge transfer between adsorbed molecules and the substrate surface determines the efficiency of molecular devices such as solar cells [14] or organic light-emitting diodes [15].

So far, nonlocal activation processes through surface state charge transfer have been mainly studied by considering that the band structure of the surface states is not perturbed by the adsorbed atom or molecule [2–7]. In this Letter, we chose to explore the contact region, at short distances (<1.5 nm), which is crucial to understand the atomic-scale electronic coupling between an adsorbed atom or molecule and the surface states. We show that, in this contact region, the charge transfer is strongly affected by the atomic-scale modifications of the density of surface states around the adsorbate. We study the nonlocal activation of a bistable atom (BA) on the hydrogenated Si(100)-(2 × 1) surface using a low temperature (5 K) STM [16]. The BA is fabricated, *in situ*, by desorbing a single hydrogen atom with the STM tip [17]. Hence, the ensuing silicon dangling bond (DB) let the neighbor hydrogen atom behave as a BA by reversibly hopping from one silicon atom to the other of the Si dimer. We show that BA hopping can be reversibly activated nonlocally by injecting holes into surface states with the STM tip. Measurements of the BA activation efficiency show strong variations when the hole injection sites are located within the contact region of the BA. Calculation of the charge density distribution along the silicon bond network allows us to clarify the anisotropic variation of the measured hopping yield in the contact region of the BA.

Experiments are performed using a low temperature (5 K) ultrahigh vacuum (UHV) STM. A clean Si(100) sample (n-type, As-doped, resistivity $0.005\ \Omega \cdot \mathrm{cm}$) is prepared in a UHV chamber, as well as its hydrogenation, as described elsewhere [16,18]. The occupied state STM topography of the hydrogenated Si(100):H surface in Fig. 1(a) shows the rows of the hydrogenated silicon dimers of the 2×1 reconstruction. A single hydrogen atom can be desorbed at a desired position on the surface by positioning the STM tip on top of a hydrogen atom [blue dot in Fig. 1(b)], switching off the feedback loop of the STM, and applying a surface voltage pulse ($V_s = +2.5$ V, $I = 100$ pA) during ~1 s. Such hydrogen desorption processes with the STM have been studied in detail [Fig. 1(c)] [17,19].

The electronic activation of the BA is first tested by positioning the STM tip on top of the BA [red dot in Fig. 1(d)]. The reversible hopping of the hydrogen atom from position B to A within the same silicon dimer [Fig. 1(a)] has been previously studied at room temperature by continuously scanning the STM tip over the surface [20,21]. However, with this scanning method, the measured hopping yield is averaged over many STM tip positions. Here, the STM tip is fixed and precisely located on top of the initial position

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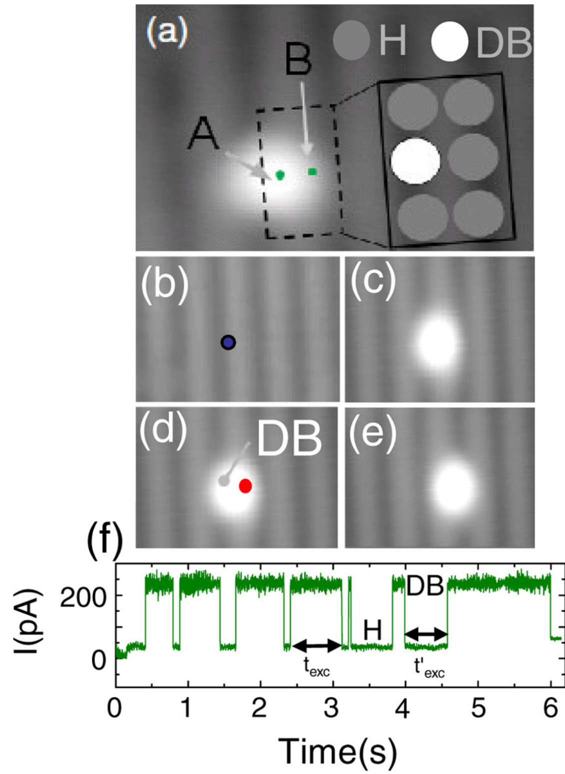

FIG. 1 (color online). (a) 40×26 Å^2 STM topography of the Si(100):H surface ($V_s = -1.7$ V, $I = 69$ pA). The silicon DB and the H atom are in position A and B, respectively (green dots). (b),(c) 40×28.5 Å^2 STM topographies of the Si(100):H surface ($V_s = -1.7$ V, $I = 70$ pA) before and after a surface voltage pulse at $+2.5$ V (blue dot), respectively. The created silicon DB is seen in (c). (d),(e) 40×28.5 Å^2 STM topographies of the Si(100):H surface ($V_s = -1.7$ V, $I = 69$ pA) before and after the hopping of the H atom, respectively. The hopping is activated by applying a -2.5 V voltage pulse while the STM tip is on top of the H atom (red dot). (f) Tunnel current trace recorded during a voltage pulse ($V_s = -2.5$ V) while the STM tip is fixed at the red dot position in (d).

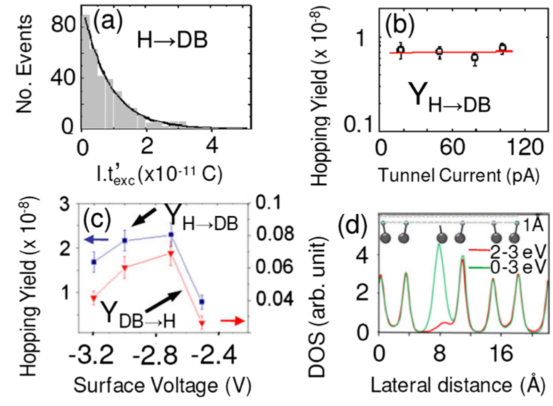

FIG. 2 (color online). (a) Variation of the number of events (H hopping) as a function of the quantity of charges (It'_{exc}) when the STM tip is on top of the H atom (H → DB movement). (b) Variation of the H hopping yield $Y_{H\rightarrow DB}$ as a function of the tunnel current ($V_s = -2.5$ V) when the STM tip is on top of the H atom. (c) Variations of the hopping yields $Y_{H\rightarrow DB}$ and $Y_{DB\rightarrow H}$ of the BA as a function of the surface voltage. (d) Variation of the DOS integrated over the 0–3 eV (green line) and the 2–3 eV (red line) energy ranges (below the Fermi level) as a function of the lateral distance across the dimer rows, calculated 1 Å above the H atoms.

of the hydrogen atom. A negative voltage is then applied to the surface ($V_s = -2.5$ V) while the tip is kept at a constant height (feedback off). The recorded tunnel current shows stepped oscillations of duration t_{exc} or t'_{exc} [Fig. 1(f)], varying between $I = 250$ pA and $I = 50$ pA, respectively, due to the reversible movement of the H atom from position B to position A [Fig. 1(a)]. The hopping yield, i.e., the probability per electron for the hydrogen atom to hop, is then deduced by the method described in Ref. [22], when the STM tip is on top of the hydrogen atom [low current in the curve in Fig. 1(f), hopping yield $Y_{H\rightarrow DB}$] or on top of the dangling bond [high current in the curve in Fig. 1(f), hopping yield $Y_{DB\rightarrow H}$]. The exponential distribution of It'_{exc} values [Fig. 2(a)] and the constant values of $Y_{H\rightarrow DB}$ as a function of the tunnel current I [Fig. 2(b)] clearly indicate that the activation of the H hopping is a one electron process [22]. Both hopping yields ($Y_{DB\rightarrow H}$ and $Y_{H\rightarrow DB}$) have an extrapolated threshold surface voltage of -2.4 ± 0.2 V [Fig. 2(c)]. The corresponding threshold energy is assigned to occupied Si-Si bond surface states [23]. This means that the excitation mechanism for H hopping consists of a resonant hole injection into Si-Si bond surface states, thus creating a local positive charge. The H hopping dynamics following the creation of the positive charge has been discussed in [20,21]. Our results rule out the vibrational ladder climbing model [24] since we show that the H hopping is a one electron process. Note that the hydrogen hopping yield decreases by a factor of ~40 when the STM tip is moved parallel to the surface by only 0.3 nm from the H atom to the silicon DB position. This indicates that the electrostatic field under the STM tip, which is expected to extend over several nanometers, has a negligible effect. This extremely local variation of the hydrogen hopping yield is explained by the sharp decrease of density of states (DOS) of the Si-Si dimer bond surface state, in the -2 to -3 eV energy range, involved in the hopping excitation process when the STM tip is on top of the silicon DB [Fig. 2(d)]. The calculations are carried out by means of the density functional theory within the generalized gradient approximation using the VASP code as described in [25]. To simulate the n-doped silicon surface, one substituted As atom is introduced in the 3rd silicon atom layer.

The nonlocal activation of the BA is studied at 12 different STM tip positions on the surface whose distances from the BA lie between 8 and 23 Å. The STM tip positions, shown in Fig. 3(a), are labeled $2H_\parallel$, $4H_\parallel$, $6H_\parallel$ and $2H_\perp$, $4H_\perp$, $6H_\perp$ when located parallel and perpendicular to the Si dimer row, respectively. They are chosen such that the

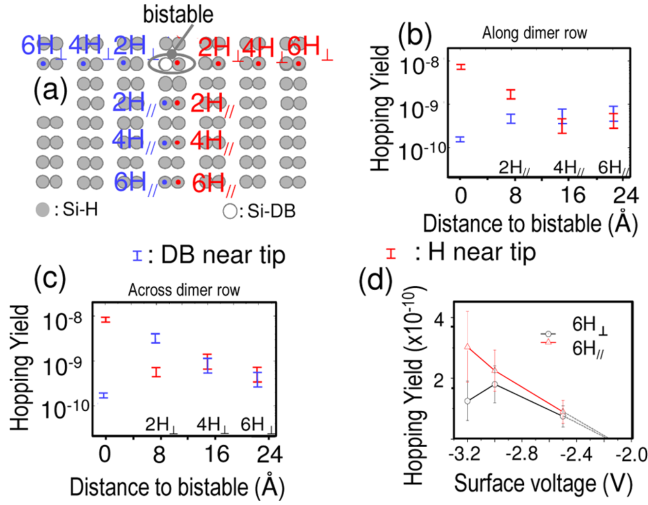

FIG. 3 (color online). (a) Top view of the first layer of silicon dimers of the Si(100):H surface indicating the 12 positions of hole injection to activate the BA remotely when the tip is either on the H side (red dots, left) or on the DB side (blue dots, right) of the BA. The light gray circles correspond to H atoms and the white circle is the DB. (b),(c) Measured hopping yields for hole injection sites distributed along ($2H_{\parallel}$, $4H_{\parallel}$, $6H_{\parallel}$) or across ($2H_{\perp}$, $4H_{\perp}$, $6H_{\perp}$) the silicon dimer row, respectively. The surface pulse voltage is -2.5 V. The red bars and the blue bars correspond to measurements realized when the tip is placed near the H atom or near the DB of the BA, respectively. (d) Variations of the hopping yields of the BA as a function of the surface voltage at the $6H_{\perp}$ and $6H_{\parallel}$ hole injection sites.

same distances from the BA to the hole injection sites can be compared. For each of these 6 positions, the STM tip can be on the side of either the silicon DB [blue dots in Fig. 3(a), i.e., left side of the bistable] or the H atom (red dots, i.e., right side). Measuring the hydrogen hopping yield remotely is more difficult than when the STM tip is directly on top of the BA since the tunnel current does not show any step variation as in Fig. 1(f). Here, the surface is first imaged such that the BA cannot be activated ($V_S = -1.7$ V). Then, a surface voltage pulse ($V_S = -2.5$ V) is applied during a time T, with a chosen tunnel current while the STM tip is on top of one of the 12 positions of Fig. 3(a). Afterwards, the same surface area is imaged to check whether the H atom hopping has occurred. If T is smaller than the mean excitation time τ to activate the hopping, then the hopping probability per voltage pulse is $p_{\mathrm{hop}} = 1 - e^{-T/\tau}$. To measure the probability p_{hop} at each of the 12 positions, a large number of voltage pulses ($\sim$2500) are repeated by varying randomly the successive excitation positions to avoid any systematic influence of STM tip changes. We choose $T = 0.8$ s, and the tunnel current I is adjusted to have $T < \tau$. Thus, for each of the 12 positions, p_{hop} is measured, from which τ is deduced and the yield Y per electron for hopping the BA is obtained as $Y = e/I\tau$, where e is the electron charge. Results are shown in Figs. 3(b) and 3(c). In order to rule out any influence of the STM tip shape, additional measurements are performed for the same STM tip on two perpendicular terraces of the Si(100):H surface and are repeated with 3 separate samples and STM tips. All these measurements give similar results. The nonlocal H hopping yields measured at $6H_{\parallel}$ and $6H_{\perp}$ [Fig. 3(d)] show a surface voltage dependence similar to the one in Fig. 2(c); i.e., the hopping yield strongly decreases when V_s varies from -3 to -2.5 V. This suggests that the electronic excitation processes are similar whether the STM tip is on top or at a distance from the BA. Similar results are observed at $2H_{\parallel}$, $2H_{\perp}$, $4H_{\parallel}$, and $4H_{\perp}$.

The nonlocal activation of the BA is thus related to the hole propagation through Si-Si bond surface states from the STM tip position up to the BA site. As seen in Figs. 3(b) and 3(c), at long distances ($4H_{\parallel}$, $6H_{\parallel}$, $4H_{\perp}$, and $6H_{\perp}$), the BA hopping yield is only weakly influenced by the STM tip position and the relative location of the H atom. On the contrary, at short distances ($2H_{\parallel}$ and $2H_{\perp}$), the hopping yield strongly depends on the STM tip site ($2H_{\parallel}$ versus $2H_{\perp}$) and the relative position of the H atom (H near the tip versus DB near the tip). Note, in particular, the $2H_{\perp}$ positions for which the hopping yield is higher when the STM tip is near the dangling bond than the hopping yield when the STM tip is near the H atom. This is the opposite case when the STM tip is placed on top of the BA: the hopping yield is higher when the H atom is under the STM tip. Surprisingly, the calculated DOS projected onto the Si-Si dimer bonds are similar for all the $2H_{\parallel}$ and $2H_{\perp}$ sites (see Ref. [25]) indicating that the observed variations of the hopping yield as a function of the hole injection site ($2H_{\parallel}$ and $2H_{\perp}$) cannot be ascribed to any difference of local electronic DOS at the various injections positions, contrary to what is observed in Refs. [3,4].

To explain the specific variations of the hopping yield in the contact region ($2H_{\parallel}$ and $2H_{\perp}$ sites), we calculate the spatial distribution of the local DOS (LDOS) in the -2.3 to -3.0 eV energy range of the Si-Si bond surface states, for two sectional drawings parallel [Fig. 4(a)] and perpendicular [Fig. 4(b)] to the silicon surface. From these LDOS distributions, the higher experimental hopping yields are shown to be related to the continuous path of high LDOS along the Si-Si bonds (i.e., above 0.1 $e^-/\text{Å}^3$) connecting the hole injection site to the BA. Indeed, in the direction parallel to the silicon dimer rows, the hopping yield is higher when the H atom is near the STM tip [$2H_{\parallel}^{H}$ in Fig. 4(a)], whereas the distribution of LDOS has a lower continuity on the DB side [$2H_{\parallel}^{DB}$ in Fig. 4(a)]. Similarly, in the direction perpendicular to the silicon dimer rows [Fig. 4(b)] the hopping yield is higher when the silicon DB is near the STM tip ($2H_{\perp}^{DB}$). This can be also related to the continuous distribution of high LDOS on the DB side along the interdimer row Si-Si backbond surface states [Fig. 4(b)].

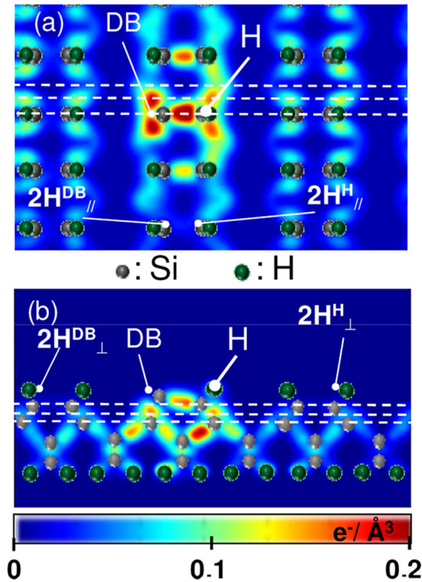

FIG. 4 (color online). (a),(b) Calculated sectional drawings of the LDOS spatial distribution integrated over the −2.3 to −3 eV energy range. In (a), the calculated LDOS is the superposition of three planes indicated by the dotted lines in (b). In (b), the LDOS is the superposition of three planes indicated by the dotted lines in (a).

In conclusion, the reversible hopping of a BA can be activated nonlocally on the hydrogenated Si(100) surface by injecting holes into occupied Si-Si bond surface states with the STM tip. In the contact region, at short distances (<1.5 nm, $2H_{\parallel}$ and $2H_{\perp}$ sites), the hopping yield of the BA strongly depends on the hole injection site and the relative position of the H atom. The charged silicon DB and the ensuing tilted silicon dimer of the BA anisotropically modify the LDOS along the Si-Si bond network in the contact region. From these results, the nonlocal activation of the BA is assigned to the hole transfer from the injection site to the BA site through Si-Si surface states. The hole transfer efficiency is shown to depend on the distribution of LDOS along the Si-Si bond network between the injection site and the BA. This effect is enhanced in the contact region because of the anisotropic modifications of the LDOS around the BA and the high spatial resolution measurements of the hopping yield. At larger distances between the hole injection site and the BA, the hopping yield does not show any anisotropic variation. This is most probably arising from the hole transfer mechanism that occurs at long distances through isotropic delocalized surface states, whereas in the contact region hole transfer occurs along more localized surface states that show anisotropic variations around the BA.

These results provide a new insight into atomic-scale charge-transfer processes in the vicinity of a surface defect, an adsorbed molecule, or a surface step edge. They are shown to play a central role in molecular nanoelectronics and surface chemistry.

This work was supported by the European Integrated project PicoInside (Contract No. FGP-015847). Theoretical work was performed using HPC resources from GENCI-IDRIS (Grant 2010-096459).

*Corresponding author.
damien.riedel@u-psud.fr

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