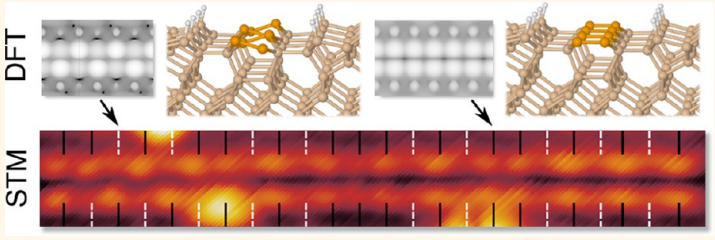
Scalable Patterning of One-Dimensional Dangling Bond Rows on Hydrogenated Si(001)

François Bianco,[†] David R. Bowler,[‡,§] James H. G. Owen,[†,⊥] Sigrun A. Köster,[†,∥] Maria Longobardi,[†] and Christoph Renner[†,*]

[†]Department of Condensed Matter Physics, University of Geneva, NCCR MaNEP, 24 Quai Ernest-Ansermet, 1211 Geneva 4, Switzerland, [‡]Department of Physics & Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom, and [§]London Centre for Nanotechnology, 17-19 Gordon Street, London WC1H 0AH, United Kingdom. [⊥]Present address: Zyvex Laboratories, 1301 North Plano Road, Richardson, Texas 75081. [∥]Present address: IBM Research, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland.

ABSTRACT



Silicon dangling bonds exposed on the monohydride silicon (001) (Si(001):H) surface are highly reactive, thus enabling site-selective absorption of atoms and single molecules into custom patterns designed through the controlled removal of hydrogen atoms. Current implementations of high-resolution hydrogen lithography on the Si(001):H surface rely on sequential removal of hydrogen atoms using the tip of a scanning probe microscope. Here, we present a scalable thermal process that yields very long rows of single dimer wide silicon dangling bonds suitable for self-assembly of atoms and molecules into one-dimensional structures of unprecedented length on Si(001):H. The row consists of the standard buckled Si dimer and an unexpected flat dimer configuration.

KEYWORDS: scanning tunneling microscopy · scanning probe lithography · self-assembly · one-dimensional · dangling bond · silicon · dimer

Development of novel functional materials and devices is motivating increasingly sophisticated processes, where the synthesis is controlled at the atomic or molecular level. Functional structures and devices have been assembled one atom[1] or one molecule[2] at a time using the tip of a scanning probe microscope. Although extremely versatile, such building procedures are not scalable and far too slow for any practical purpose. An alternative route to assemble functional structures with atomic scale precision is self-assembly. Given an appropriate choice of materials and thermodynamic parameters, large structures of ordered atoms and molecules can be obtained in massively parallel ways.[3]

Self-assembly is particularly appealing to build one-dimensional (1D) chains of atoms and molecules on surfaces[4] but comes with its own challenges, such as how to control the position, dimension, and layout of the 1D chains. One possible approach is to control the location of the chain nucleation sites, as has been demonstrated recently, for In chains on Si(001):H.[5] The layout and dimensions of self-assembled surface structures can be mastered by locally modifying the surface reactivity using lithographic techniques.[6] The ultimate atomic scale resolution has been achieved through scanning probe lithography (SPL), where the tip of a local probe is used to design the desired pattern on the Si(001):H surface.[7,8]

Si(001):H is a particularly appealing surface for SPL. Individual hydrogen atoms can be removed to expose Si dangling bonds (DBs) which are significantly more reactive than the surrounding hydrogen-terminated surface. SPL has been used to design a

* Address correspondence to christoph.renner@unige.ch.

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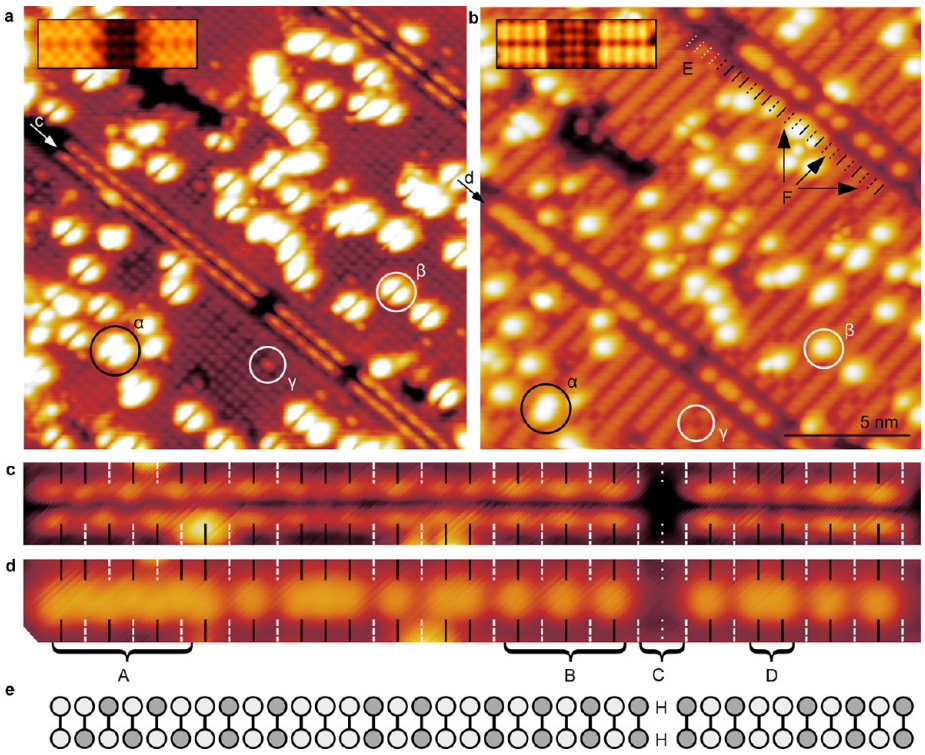

Figure 1. High-resolution STM micrographs of two Haiku dangling bond rows on Si(001):H measured in constant current mode at 100 pA (a) +1.8 V (empty state) and (b) −1.8 V (filled state). Insets show a fully hydrogenated Haiku stripe at (a) +2.5 V, 80 pA, and (b) −2.5 V, 150 pA. Site α has two neighboring dehydrogenated Si dimers; β corresponds to a single completely dehydrogenated Si dimer and γ to a split dimer. (c,d) Zooms on the HDB. Region A shows buckled Si dimers; B has five flat dimers with alternating contrast; the darker regions C and E correspond to the standard Haiku stripe; D and F indicate two flat adjacent Si dimers with the same contrast. The continuous (dashed) markers correspond to the position of bright (dark) dehydrogenated Si atoms, and dotted markers indicate hydrogenated Si atoms. (e) Schematic orientation of the dimers where the white (gray) circles represent up (down) Si atoms. H stands for hydrogenated silicon atoms.

range of patterns[9−15] into the Si(001):H surface down to subnanometer wide wires of silicon dangling bonds, where a single H atom per dimer is removed.[16−19] The reverse process where individual DBs are passivated by controlled dissociative adsorption of individual hydrogen molecules from a scanning tunneling microscope (STM) tip has recently been demonstrated,[20] completing this H-based SPL lithography toolkit.

A number of applications exploiting SPL-designed DB patterns have been demonstrated. They take advantage of atoms and molecules that do not stick on the H-terminated dimers but adsorb strongly at DBs. Precise control of dopant positioning in silicon has been achieved using SPL templates prior to phosphine exposure.[21−23] Adsorption of organic molecules on semiconductors is well-suited to functionalize surfaces.[24−26] Many molecules are known to bind easily to dehydrogenated Si(001) such as phenol,[27] biphenyl,[8,28] acetylene,[29] CuPc and C_{60},[8] $Fe(CO_5)$,[30] norbornadiene,[31] polyaromatic hydrocarbons,[32] acetylacetone,[33] and phenylacetylene.[34] In addition to templating molecules, silicon DB rows also hold promise to form self-assembled wires of selected atoms.[4,35] Gallium[12,13] and silver[4] atoms diffuse fast on the hydrogenated surface but stick to DBs. Arsenic,[36] gold,[11] and sodium[37] atoms might follow the same path.

These numerous examples of DB templating on Si(001):H demonstrate the broad interest to create such structures. However, SPL is a sequential process, not optimal to produce long DB rows. Here, we propose an alternative path to self-assemble very long and perfect one dimer wide dangling bond rows on Si(001):H. It is based on the Haiku stripe, an endotaxial 1D nanoline self-assembled on Si(001):H terraces.[38,39] Their length and density can be tuned through the growth parameters. The Haiku structure is known in great detail,[39,40] enabling very accurate density functional theory (DFT) modeling of the STM micrographs. This precise knowledge of the template structure is an essential ingredient to model and understand the structure and properties of the Haiku dangling bond row template and the adsorbed atom and molecule chains.

RESULTS

The hydrogenation of the precursor Bi nanolines[4] exposes the underlying Haiku structure by removing completely the Bi dimers from the Si(001) surface. Depending on the substrate temperature, either fully passivated monohydride Si surface with Haiku stripes are formed[38,39] or, at higher temperature, Si dangling bonds (DB) are left unsaturated, predominantly above

the Haiku core. Two such self-assembled Haiku dangling bond (HDB) rows, just one Si dimer wide, are shown in an empty state (Figure 1a) and a filled state (Figure 1b) high-resolution STM micrograph. The HDB rows run perpendicular to the well-resolved monohydride Si dimer rows and extend along the two central Si atom sites of the Haiku stripes. Fully hydrogenated Haiku stripes appear as four atom wide dark trenches, both in empty and filled state micrographs (see insets Figure 1a,b).[38,39] The modified appearance of the Haiku stripe in Figure 1 is consistent with dehydrogenating the two central Si atom rows. The bright defects on the terraces between the HDB rows correspond to known features formed by missing hydrogen atoms on Si(001):H surfaces: site α corresponds to two adjacent dehydrogenated Si dimers;[41] site β corresponds to a single dehydrogenated Si dimer;[42,43] and site γ corresponds to a split dimer.[44,45]

To first approximation, the bright feature along the dehydrogenated center of the Haiku stripe is consistent with an alignment of the missing hydrogen defects α or β, rotated 90° in the surface plane. DBs located on the Haiku stripe appear darker than those located on the Si(001) terrace because the Haiku stripe is lower than the surrounding Si(001) terrace.[38] Comparing an amplitude profile through a DB along a standard Si(001) dimer row with an amplitude profile through a DB along the Haiku stripe actually reveals that the contrast is largest along the Haiku stripe (see Supporting Information). The similar shape of the two profiles supports the assumption of a dehydrogenated Haiku central dimer row. Upon closer inspection, the STM micrographs reveal different regions along the dehydrogenated Haiku stripe (Figure 1). We can identify them as buckled dimers (A), flat dimers (B,D,F), and the original hydrogenated Haiku stripe (C,E). Meanwhile, the two outer Si sites appear dark for both imaging polarities. This contrast is similar to the fully hydrogenated Haiku stripe, indicating that they retain their hydrogen atom.

Region A is reminiscent of the buckled dimer rows observed on clean 2 × 2 reconstructed Si(001) terraces. The buckling is clearly resolved in the two out-of-phase traces cutting along the two central Si atom rows of the Haiku stripe (Figure 2). This result is consistent with the observation that the top two Si layers of the Haiku stripe are locally equivalent to the top two Si layers of a dimer row in the standard Si(001) surface but rotated 90° in-plane. Regions B, D, and F exhibit a strikingly different atomic contrast, with in-phase traces along the two central Haiku Si atom rows (Figure 2). DFT enables us to assign this signature to flat dangling bond dimers, a totally unexpected configuration of bare Si dimers on the Si(001) surface. Finally, the trenches interrupting the HDB, especially dark at positive sample bias (region C), correspond to sections of fully hydrogenated Haiku stripes, where all four

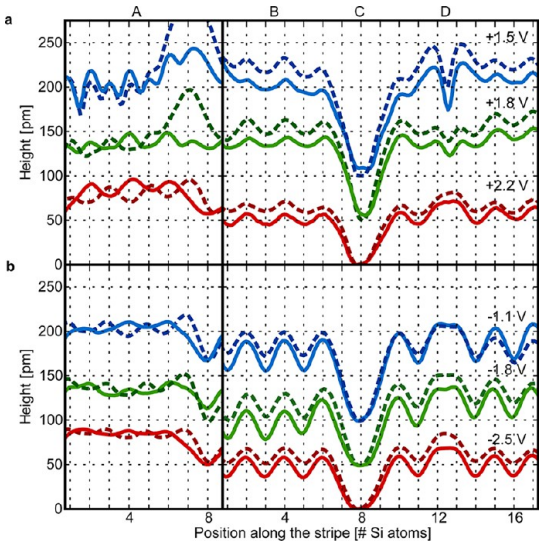

Figure 2. Height profiles along the Haiku dangling bond row extracted from (a) empty and (b) filled states STM micrographs at different voltages. The profiles are averaged over 4 Å, corresponding to the width of the DB in empty state. Profiles across region A (see text) clearly reveal the buckling of the dimers. Profiles across regions B, D, and F are in-phase, characteristic of flat dimers. C corresponds to a single hydrogenated dimer.

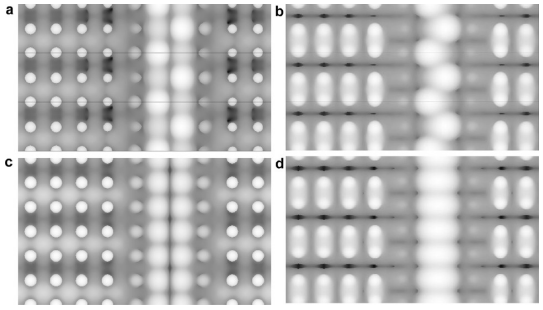

Figure 3. DFT-based STM simulations of dehydrogenated Haiku stripes at different energies: (a) +1.0 eV and (b) −1.0 eV model buckled dimers corresponding to region A (see text); (c) +1.0 eV and (d) −1.0 eV model flat dimers at the same height matching regions D and F.

Si dangling bonds spanning the Haiku structure are H-terminated.[39]

The above features are all perfectly reproduced in our DFT simulations (Figure 3). The buckled and flat dangling bond dimers (Figure 4) correspond to two stable structures for the central Haiku Si dimer with very similar energies. The bond strengths calculated for the different H positions listed in Table 1 confirm the assumption of a dehydrogenated central dimer row and hydrogenated side atoms. The HDB row is thus physically isolated from the nearest background dimer by 8 Å. Rehydrogenating the HDB row restores the standard Haiku STM contrast (Figure 5), in agreement with the above assumption of missing H to explain the modified contrast. This reversibility excludes any contamination or spurious tip effect to explain the bright structures running along the middle of the Haiku stripe

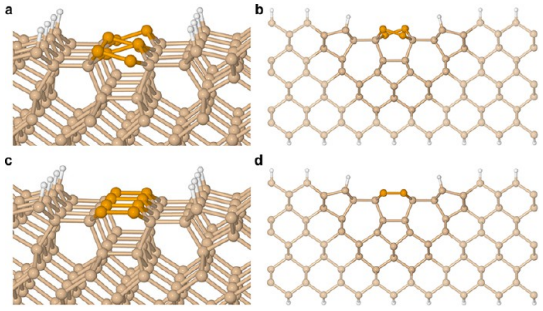

Figure 4. Ball-and-stick models relaxed by DFT. The two edge Si atoms of the Haiku stripe are covered with H (white), whereas the central Si atoms are dehydrogenated (orange): (a,b) buckled central Si dimers, (c,d) flat dimers at the same height. In (b) and (d), the distorted Si cage of the Haiku structure (highlighted) is visible underneath the surface.

TABLE 1. Hydrogen Binding Energy Per Atom Relative to the H Bond on a Clean Si(001) Dimer (4.37 eV)[a]

H position on the Haiku stripe	dimer configuration	relative binding energy (eV)
side	flat	+0.16
side	buckled	+0.13
center	flat	−0.10
center	buckled	−0.15
center one dimer only	flat	−0.13
center one side of dimers	as DB wire	+0.13

[a] A positive energy implies stronger binding and more stable H atoms than on the clean dimer.

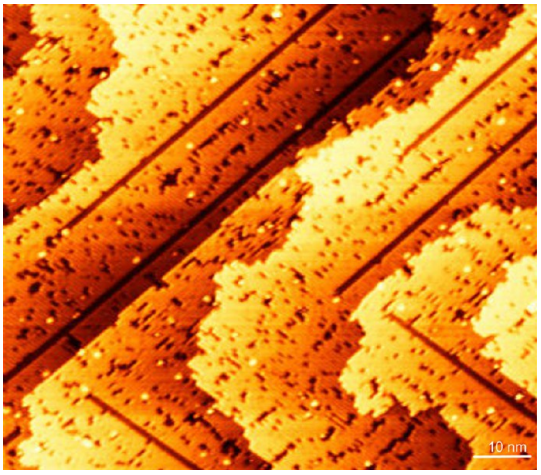

Figure 5. STM micrograph (−2.20 V, 100 pA) after rehydrogenation of the HDB rows, restoring the standard dark appearance of the Haiku stripes on Si(001):H. The dimer vacancies seen in this micrograph are due to the large number of thermal cycles this sample went through.

in Figure 1. The HDB rows share the structural properties of the precursor Haiku stripes which self-assemble on Si(001) flat terraces: they are independent of any step edges, grow perfectly straight up to several micrometers long, and form isolated stripes or densely packed arrays depending on growth parameters.[39] These characteristics make them a very appealing template to self-assemble long 1D atomic or molecular chains.

DISCUSSION

STM micrographs are a complex convolution of crystalline and electronic structures. Therefore, theoretical modeling is required to assert the nature of the HDB rows observed here. DFT modeling (Figure 3a,b) reproduces precisely the STM imaging contrast of region A in Figure 1, assuming that the Si dimers along the center of the Haiku stripe are dehydrogenated (Figure 4). The model captures all of the experimental features in remarkable detail, both in empty and filled state micrographs: the DBs are in registry with the surrounding Si lattice; they change from two narrow parallel ridges at positive bias to a single broad chain at negative bias; they become brighter upon reducing the bias voltage at both polarities (see Supporting Information).

The STM imaging contrast in regions D and F, quite different from region A (Figure 1), is also reproduced in great detail by DFT modeling (Figure 3c,d). However, in order to achieve this detailed reproduction, we need to assume the presence of flat dehydrogenated Si dimers (Figure 4b) rather than buckled dimers. Such flat DB dimers correspond to a new configuration of neighboring Si DBs which has not been reported so far. While a flat dimer configuration is not stable on the ideal Si(001) surface, on the Haiku center, our DFT calculations find it very close in energy to the buckled DB configuration, being only 0.11 eV/dimer less stable. We propose that the local strain induced by the Haiku reconstruction contributes to stabilize this unexpected flat dimer configuration. DFT simulations found that flat dimers in the Haiku stripe are stable (Figure 4b) but relax to essentially the same height, with the same appearance in simulated STM images (Figure 3c,d). This result matches well the STM contrast in regions D and F of Figure 1, where neighboring flat dimers have indeed the same contrast. However, the contrast of neighboring flat dimers in the experimental data is predominantly alternating between bright and dark (Figure 1, region B), suggesting that some ingredient is missing in our model. This discrepancy could be explained in terms of alternating high and low lying flat dimers, but it could also reflect charge transfer between neighboring flat dimers or another electronic degree of freedom.

The alternating bright and dark dimers observed in region B of Figure 1 closely resemble the STM contrast of single DB wires obtained on Si(001):H after the controlled removal of the hydrogen atoms from the same side of five adjacent Si dimers using an STM tip.[16] Hitosugi *et al.* ascribed this alternating contrast to a Peierls distortion induced through charge transfer in the clean Si atom chain[17,46] similar to the buckling of the clean Si(001) surface.[47] Changing the bias polarity

was found to invert the STM contrast of these single DB wires, which the authors took as evidence for the charge transfer scenario.[16,47] In our case, we do not see such contrast inversion between positive and negative sample bias when imaging the flat DB dimer rows. This suggests a different scenario for the alternating amplitude we observe for the flat DB dimers. We are currently exploring possible mechanisms that might lead to alternating high and low flat dimers along the Haiku core.

DFT modeling leads to the interesting conclusion that the irregular appearance of the dehydrogenated Haiku core (Figure 1) can be explained with two basic building blocks: hydrogenated and dehydrogenated Haiku core dimers. This conclusion implies that the weakest Si−H bond is on the central Haiku Si atom, and that desorption of both H from a single dimer is favored. Indeed, DFT (Table 1) finds that the Si−H bond is 0.10−0.15 eV/atom weaker on the central Haiku Si atoms compared to Si(001):H terraces, and that once one H has left a central dimer, the desorption of its neighboring H is favored compared to the formation of a DB wire on one side of the central row. The outer Si atoms of the Haiku stripe separate domains where Si dimer rows run perpendicular to each other, similar to atoms at B steps. The Si−H bond at a B step is significantly enhanced by 0.16 eV/dimer compared to dimer on the clean terrace.[41] We find the binding energy of H to the side Si atoms of the Haiku stripe to be 0.13−0.16 eV/H stronger than the Si(001):H surface and 0.23−0.31 eV/H stronger than the binding to the central Haiku dimer (Table 1). Moreover, the diffusion across dimer rows over B-type step edges is prevented by a very high barrier of 2.4 eV.[41] These striking results are consistent with preferential desorption of hydrogen from the central dimer of the Haiku stripe while preserving the dark appearance of the side sites with strongly adsorbed H.

Finally, counting all of the Si sites on a Si(001):H terrace, excluding Haiku stripes, we find approximately 6% of bare Si dimers. We note that half of these missing H are linked to defects on the surface. The strain caused by the defects is probably lowering the H binding energy and favoring H desorption in similar way as on the strained central dimer of the Haiku stripe. Along the Haiku stripe, the number of missing H reaches 85%, confirming the highly preferential thermal desorption from the two central Haiku H sites.

An interesting possibility to use the weaker bond above the Haiku stripe is to perform SPL at voltage and electron dose conditions which favor depassivation from the central Si dimers in the Haiku stripe. Given the lower binding energy, and the relative physical isolation of the H atoms on the central dimer row, the tip could write a clean line without generating DB on the rest of the surface. This would enable the possibility to depassivate only one Haiku stripe and leave the rest of the surface-passivated, producing a very precise and long Si DB row template without the need for exact tip positioning.

CONCLUSIONS

The results reported here present a novel route to self-assemble very long Si dangling bond (DB) dimer rows on Si(001):H. These highly reactive and perfectly straight single dimer wide Si DB rows offer a unique template to self-assemble one-dimensional (1D) single atom or molecular structures of unprecedented length. The thermal process involved is fully scalable, enabling the growth of micrometers long 1D structures in large numbers difficult to achieve by means of scanning probe lithography. Although we cannot yet control the positioning of these rows, we can control their density which added to their length and perfection may well turn them into an attractive interface to other methods of forming nanostructures on silicon. The DB rows reported here further reveal a novel and unexpected Si DB configuration. Besides the buckled dimers well-known for clean Si(001) terraces, we find that our DB rows consist of chains of flat DB dimers, a configuration not seen before. This striking result is supported by the outstanding correspondence we find between STM micrographs of the DB rows and DFT simulations. This particular configuration may be an interesting one-dimensional electronic system in its own right.

METHODS

The self-assembled silicon dangling bond rows were grown in ultrahigh vacuum (UHV) on p-type Si(001) [boron doped, 0.1 Ωcm resistivity from Siltronix]. The base pressure in the preparation chamber is in the range of 5×10^{-11} mbar. The starting material is a Si(001) surface with Bi nanolines whose fabrication is described in detail elsewhere.[4] The Haiku dangling bond rows are formed by exposing the Bi nanolines to a hot atomic hydrogen flux (H_2 dose = 5×10^{-7} mbar for 5 min, 120 L) while keeping the substrate temperature close to the hydrogen desorption temperature for the Si(001):H surface (T = 420 °C).[43] The STM data were obtained at 77 K with a PtIr tip using an Omicron LT-STM directly attached to the preparation chamber. Data analysis was performed with Gwyddion, a dedicated free software for scanning probe microscopy.[48]

DFT calculations have been performed with the Vienna ab initio simulation package (VASP) using a plane-wave implementation within the generalized gradient approximation (GGA).[49,50] Ultrasoft pseudopotentials[51] are used for all of the elements considered. Convergence of forces and energy differences is achieved by selecting a Monkhorst-Pack[52] mesh of $4 \times 2 \times 1$ to sample the Brillouin zone and an energy cutoff of 200 eV. Energy differences are converged to within 0.01 eV and forces to 0.02 eV/Å. We used a unit cell which was one dimer row wide, 10 dimers long, and 10 layers deep, with the bottom two layers fixed and the bottom layer terminated with hydrogen.[53,54] The commonly used scheme to simulate STM images

is based on the Tersoff-Hamann approximation which asserts that the LDOS is proportional to the tunneling current. STM simulations correspond to the integral of all the partial charge densities for the bands between the bias voltage and the Fermi level, assuming that the tip has a flat density of states.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Additional figures as described in the text: DB height profiles on Si(001):H and on a Haiku stripe, bias-dependent STM micrographs and DFT simulations. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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