

Electron Transport Suppression from Tip– π State Interaction on Si(100)- 2×1 Surfaces

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 Supporting Information

ABSTRACT: We investigate the electron transport between a scanning tunneling microscope tip and Si(100)- 2×1 surfaces with four distinct configurations by performing calculations using density functional theory and the nonequilibrium Green's function method. Interestingly, we find that the conducting mechanism is altered when the tip–surface distance varies from large to small. At a distance larger than the critical value of 4.06 Å, the conductance is increased with a reduction in distance owing to the π state arising from the silicon dimers immediately under the tip; this in turn plays a key role in facilitating a large transmission probability. In contrast, when the tip is closer to the substrate, the conductance is substantially decreased because the π state is suppressed by the interaction with the tip, and its contribution in the tunneling channels is considerably reduced.

INTRODUCTION

Surface states originating from dangling bonds (DBs) play a pivotal role in providing active reaction sites^{1–5} with covalent attachments and assisting conductance^{6–11} in electron transport. For instance, the π/π^* states induced from silicon surface dimerization are of great importance for understanding the conducting mechanisms.^{9,10} Moreover, such π -like states are important in organic molecular electronics and have been intimately associated with the formation of some particular phenomena such as negative differential resistance (NDR) in recent studies.^{12,13} In the theoretical research of Fan et al.,¹² the mismatch of the energy alignment between the nonlocal π^* state of the conducting molecule and the metallic lead states results in NDR, while the NDR mechanism in the theoretical investigation by Bevan et al.¹³ of a styrene adsorbed on a silicon substrate is attributed to the bias-induced pulling of the π state of the molecule out of the resonance window and into the band gap of the silicon substrate.

The DBs of an unpassivated silicon surface can serve as localized charge trap sites, and their corresponding energy levels often appear within the band gap close to the Fermi level and hence determine much of the electronic behavior of the surface. Intense research has been devoted to exploring the functionality of the DB in forming or characterizing reconstructed surfaces both experimentally^{6–8} and theoretically.^{9–11} One area of heavy interest is electron transport through crystallized surfaces with DBs. Hata et al.⁶ presented a refined interpretation of images of Si(100) produced by a scanning tunneling microscope (STM) and attributed the typical high surface bias used to observe the

π/π^* state to the influence of the adsorbed defects. Brown et al.⁷ found that the π/π^* state shows different signatures in band bending in the presence of positively charged defects when imaging both filled and empty states. Recently, D'angelo et al.⁸ experimentally determined the metallic DB state of Si(111)- 7×7 through a metal-to-insulator transition process induced by Na adsorption.

In general, theoretical transport studies of DBs are performed in two directions: along⁹ and perpendicular^{10,11} to the surface. Much work has been done in these regards. Doumergue et al.⁹ reported theoretical results on the conductance along a DB line stabilized on a Si(001)- 2×1 :H surface in two different configurations. They found that the DB line with a Peierls distortion creates a small energy gap straddling the Fermi level compared with that without the Peierls distortion. Theoretical investigations on vertical transport through silicon surface states refer mainly to the simulations of an STM tip–sample interaction image. Ono et al.¹⁰ found that the surface π states of the bare silicon dimer dramatically influence the STM image on a hydrogen-terminated Si(001) surface. Jelínek et al.¹¹ observed a substantial decrease of conductance during approach of the tip to the Si(111)- 7×7 surface and revealed that this unusual feature results from the formation of the strong covalent bond between the tip apex atom and the adatom on the surface. We conjectured that such an abnormal conductance drop could also be observed on a Si(001)- 2×1 surface on which DB states π/π^* were

Received: September 1, 2010

Published: January 10, 2011

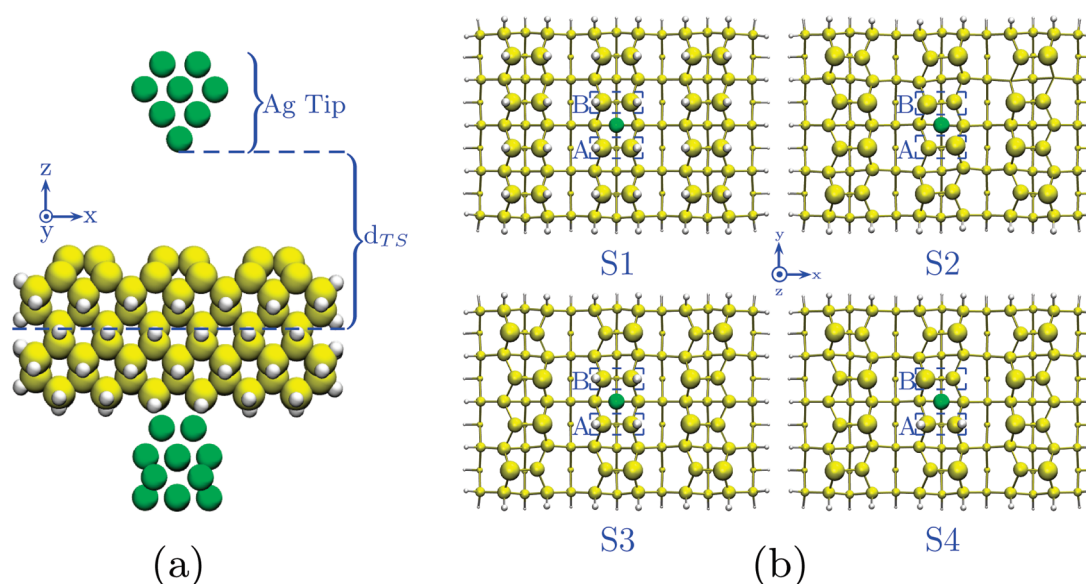


Figure 1. (a) Schematic diagram of the tip–substrate model. The slab consists of nine silicon layers. (b) Top view of upper four layers of different silicon slabs under the tip after relaxation: the fully hydrogen-terminated surface containing three monohydride chains (S1), the clean surface with buckled dimers (S2), the two central silicon dimers, A and B, are hydrogen terminated (S3), and only dimer A is hydrogen terminated (S4). The yellow and white balls are silicon and hydrogen atoms, respectively. The green ball represents the hollow site where the tip locates above. The upper layer atoms are bigger balls, while lower layer atoms are smaller ones.

considered to be localized mainly on the silicon dimer atoms.^{6,14,15} To explore such a possibility, in the present work, we investigated the electron transport between an STM tip and Si(100)- 2×1 surfaces with four distinct configurations by performing calculations using density functional theory and the nonequilibrium Green's function (NEGF) method.

MODELS AND METHOD

To model the silicon surface, we adopted a slab structure with the top layer containing three adjacent silicon dimer rows. Each row, consisting of four silicon dimers together with eight underlying silicon layers, represented the reconstructed Si(100)- 2×1 surface. We considered four models for the Si(100)- 2×1 surface, which Figure 1b depicts: a fully hydrogen-terminated surface containing three monohydride chains (S1), a purely clean surface with buckled dimers (S2), both central silicon dimers A and B, which are hydrogen terminated (S3), and a hydrogen-terminated dimer A only (S4).

To reduce computational cost, we adopted two ultrathin semi-infinite Ag nanowires as the source and drain electrodes, which we connected to the STM tip and the silicon substrate, respectively. The tip was modeled by a 14 silver-atom cone-shaped structure, which was obtained by sharpening the terminal unit cell of the source electrode neighboring the silicon substrate. The lateral and bottom sides of the slab were terminated with hydrogen atoms except for the four center silicon atoms on the bottom side, which were coupled to the drain electrode. These terminating hydrogen atoms were used to eliminate the unnecessary DBs of the silicon slab so as to create a chemical environment similar to that of an actual Si(100)- 2×1 surface. Although partial surface oxidation cannot be ruled out under experimental conditions, this surface model allows for the study of the transport characteristics of dimer states in a well-defined environment.¹¹ We have used our models to successfully mimic the flipping dynamics of bare dimers next to the H-passivated

dimers revealed by DFT calculation²² and experimentation.²³ The details are shown in the Supporting Information. The tip–substrate model is schematically shown in Figure 1a. We performed a structural optimization with the first unit cell of the drain electrode and the bottom four silicon layers of the slab, with the other five layers of atoms of the slab fixed (in the absence of the tip). We then located the tip always above the hollow site of the two central silicon surface dimers (refer to A and B in Figure 1b) in all four models and gradually moved it toward the substrate. At each instant state after moving a distance, the topmost four layers of the substrate were fully relaxed from their presetting symmetrically reconstructed 2×1 structure, with the other parts fixed. From Figure 1b, we can see that for the S2, S3, and S4 models, the initial presetting symmetrical silicon dimers relaxed to favorable buckling structures owing to the approach of the tip. During the geometry relaxations, the fifth layer of the silicon slab was always kept fixed in its bulk configuration, which acted as a reference to define the distance between the tip and the substrate.

Our theoretical study of the Si(100) surface was performed with the gDFTB¹⁶ code, which is an extension of the NEGF method of electron transport via density-functional-based tight binding (DFTB).¹⁷ This method allows an efficient treatment of systems composed of a large number of atoms to high precision. During the nonequilibrium process, the chemical potential of the tip, μ_T , was kept at the equilibrium Fermi level of the source electrode, while the chemical potential of the substrate was shifted following the applied bias by $\mu_s = \mu_T + eV_b$. We performed transport calculations by sampling only the Γ point of the surface Brillouin zone. We included one unit layer of the drain electrode neighboring the silicon substrate, as well as the 14 silver-atom tip and the nine atomic layers of the Si(100) surface as the scattering region. The tunneling current of the system was calculated on the basis of Landauer theory.¹⁸ Details on the gDFTB implementation are available in a recent review.¹⁹

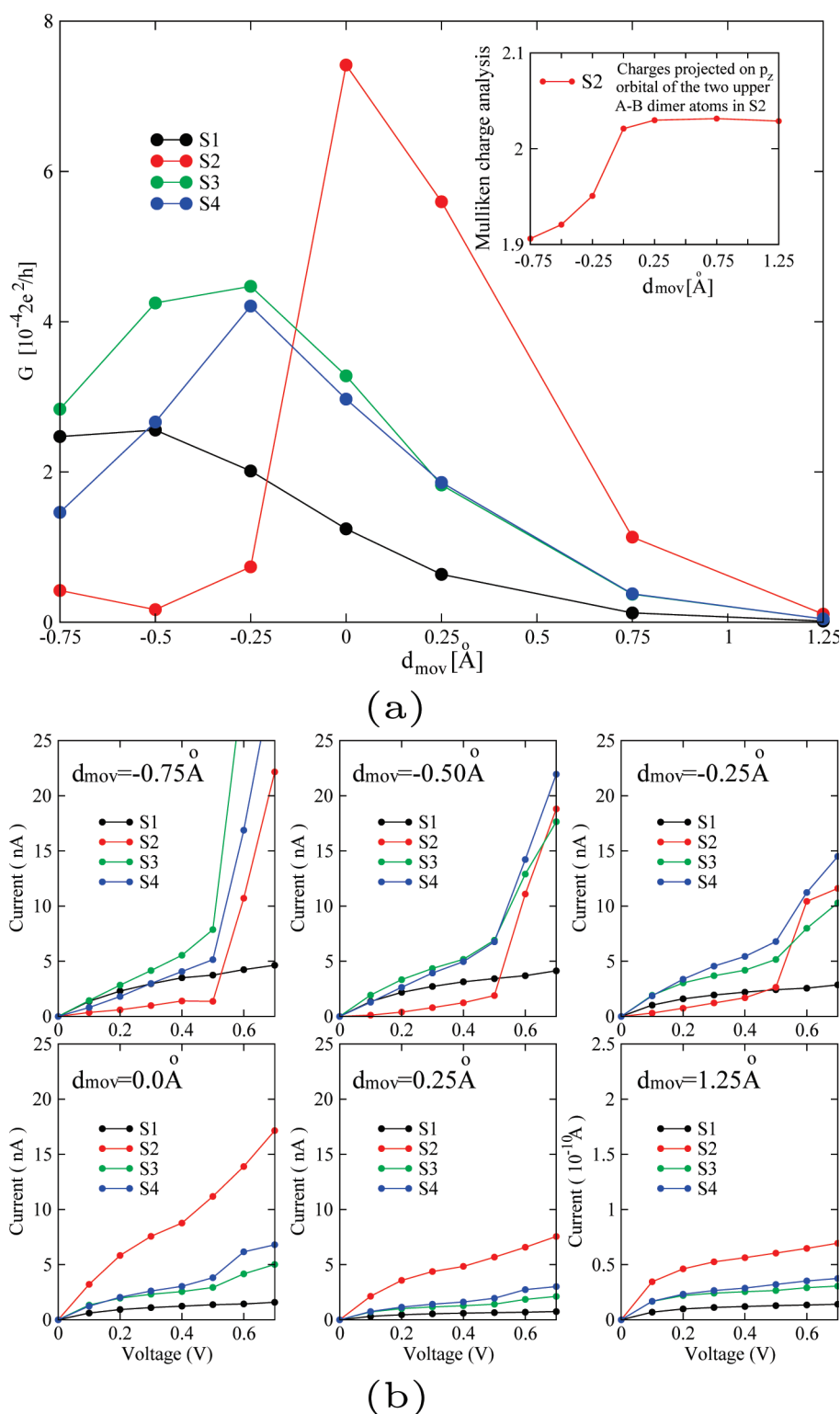


Figure 2. (a) Equilibrium conductance of four models shown in Figure 1b as a function of the tip movement at $V_b = 0.0$ V. The inset plots the Mulliken charges projected on the p_z orbital of the two upper silicon dimer atoms on A and B also as a function of the tip movement at $V_b = 0.0$ V in S2. (b) I - V curves of four silicon slabs shown in Figure 1b at different tunneling distances. The case at $d_{\text{mov}} = 0$ Å is considered to be the switch point for alternative tunneling mechanisms dominating the electron transport.

RESULTS AND DISCUSSION

During the geometric optimization, the upper layers of the substrate were relaxed and reconstructed, which caused the distance from the tip to the upper layers to be ill-defined. We

therefore fixed the middle layer of the slab during the relaxation and defined a distance, d_{TS} , between this layer and the tip as the tip-substrate distance variable for the following presentation. As shown in Figure 1a, the so-defined tip-substrate distance

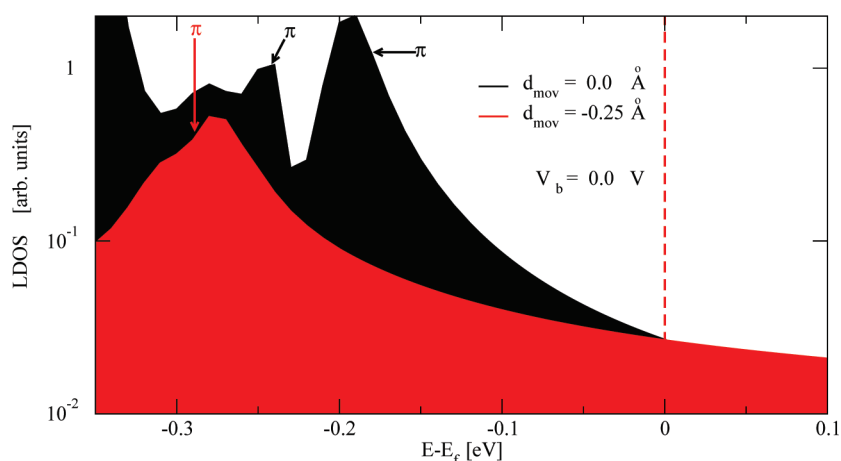


Figure 3. LDOS of silicon atoms on two central dimers A and B in S2 at $d_{\text{mov}} = 0 \text{ Å}$ and $d_{\text{mov}} = -0.25 \text{ Å}$ for zero bias. The red dashed line located at 0 indicates the Fermi level of the source electrode.

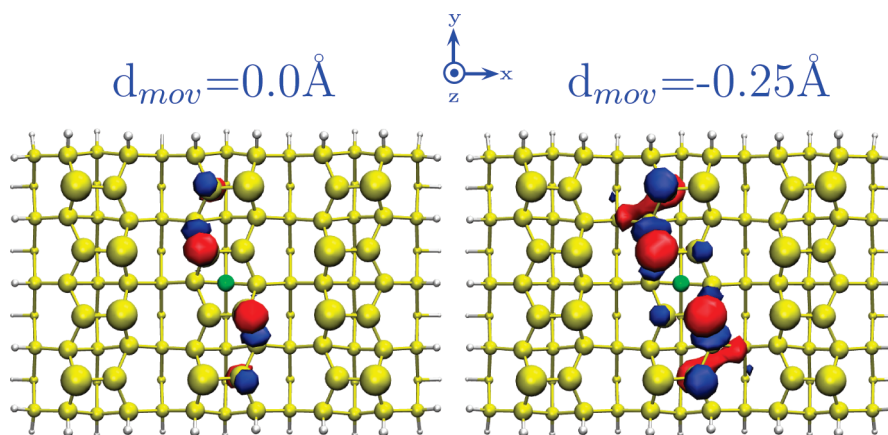


Figure 4. Evolution of the HOMO state on the silicon surface in S2 at two typical tip movement representatives $d_{\text{mov}} = 0 \text{ Å}$ and $d_{\text{mov}} = -0.25 \text{ Å}$ under zero bias.

transformed the ill-defined quantity into one that was well-defined. With the d_{TS} , we could perform tunneling calculations with varied tip–substrate distances. So that the tip-moving process is well explained, we defined the $d_{\text{TS}} = 9.04 \text{ Å}$ model as the static location $d_{\text{mov}} = 0 \text{ Å}$. At this location, the average distance between the tip apex atom and the upper dimer atoms on A and B is 4.06 Å in the clean surface model S2. With this reference position, a positive d_{mov} indicated that the tip was lifted up, whereas a negative one meant it was dipping down. In this paper, we consider five movements of the tip starting from its original position ($d_{\text{mov}} = 0 \text{ Å}$).

Figure 2a represents a characteristic set of equilibrium conductances as a function of the tip movement. It shows that at a large tip–substrate distance, the conductance increases quickly with the decrease of the tip–substrate distance and then undergoes a sudden drop after $d_{\text{mov}} = 0 \text{ Å}$ in the clean surface model S2. It appears that the closer tip–substrate distance does not increase the capability of tunneling for carriers but instead strengthens the suppression of electron transport, although the interatomic coupling should be enhanced between the tip apex atom and the silicon surface atoms, especially the atoms of the two central dimers A and B.

In the following, we uncover the origin of the electron transport suppression by virtue of the local density of states

(LDOS) on the silicon atoms of dimers A and B in S2 at two typical tip movement representatives, $d_{\text{mov}} = 0 \text{ Å}$ and -0.25 Å , as shown in Figure 3. Note that in both cases there are dimer-derived surface states in the band gap known as π states.^{20,21} It is clearly seen that the π state located at the atoms of the two central silicon dimers A and B in S2 is greatly suppressed and is pushed away from the Fermi level for the d_{mov} varying from 0 Å to -0.25 Å . The change of the localized DB π state on the dimer atoms is induced by the tip proximity. To obtain an intuitive image of such changes resulting from the tip– π interaction, it is necessary to investigate the evolution of the frontier orbitals of the silicon surface in the scattering region at different d_{mov} values. In our transport calculations, the Fermi level of the source electrode is close to the occupied surface π states rather than being in the middle of the gap. So the highest occupied molecular orbitals (HOMOs) are the key states in determining the transport behavior of the model at equilibrium and at low biases. As presented in Figure 4, at the large tip–substrate separation $d_{\text{mov}} = 0$, the HOMO is localized mainly on the atoms of the two central dimers A and B, showing a localized DB π character at equilibrium in S2. When the tip further approaches the substrate, the HOMO becomes delocalized, and this delocalization carries further along the silicon surface and down to the lower layers of the substrate rather than upward to the tip. Consequently, the

projection of the charge on the DB π state to the transport direction is reduced. It is known that the DB π -like state on such a dimerized surface originates mainly from the p_z bond orbital of the silicon dimer atoms pointing normally to the surface plane.¹⁵ We also analyzed the variation of the Mulliken charges projected on the p_z orbitals of the two upper silicon dimer atoms on A and B, which were closest to the tip apex atom in S2. As shown in the inset of Figure 2a, there exists a sudden drop after $d_{\text{mov}} = 0$ Å and a monotonic loss tendency on the p_z orbitals of the two upper silicon atoms immediately under the tip with the approach of the tip, hence limiting the tunneling through them.

Similar conductance behavior also appeared for models S3 and S4 but not at all for S1. This is because the DBs were terminated by hydrogen atoms with different coverage in the three models, and the orbital hybridization around the hydrogen atoms and the Si–H bonds was stronger and less delocalized than in the DB π state. Thus, the transport suppression in S3 and S4 was not as remarkable as that in S2. In S1, on the other hand, all of the DB states were eliminated by hydrogen chemisorption, and there was no longer a tip– π interaction. Consequently, the tip proximity did not suppress transport.

For better clarity on how the DB π state suppression induced transport discrepancies in the four models, we further performed calculations under bias to obtain the current–voltage (I – V) characteristics of all models. The I – V curves are presented in Figure 2b. The plots are divided into two rows, which show quite different characteristics. In the lower row of Figure 2b, the current of the S2 model is always larger than that of the other models. The order of the current magnitude is always $I(\text{S2}) > I(\text{S4}) > I(\text{S3}) > I(\text{S1})$. At a positive d_{mov} , the tip– π interaction is still not strong enough to suppress the transport; meanwhile, the DB π state is more widely expanded than the states around the hydrogen-adsorbed dimer.¹⁰ As a result, the current of S2 is larger than that of the other three models. In the first row at the negative d_{mov} , the current of S2 is obviously suppressed as a result of the tip– π interaction increase, as mentioned in the equilibrium discussion.

On the basis of the above discussion, when $d_{\text{mov}} \geq 0$, the dominant tunneling should be from the widely expanded π state of the surface dimers, whereas when $d_{\text{mov}} < 0$, the strong hybridization of the atomic orbitals around the Si–H bonds should be the main contribution in the conducting channels.

SUMMARY

We have studied vertical electron transport through an STM tip to a Si(100)- 2×1 reconstructed substrate. The π states from the silicon dimers immediately below the tip assist tunneling primarily at large tip–substrate distances. However, the π state is delocalized when the tip approaches the substrate and leads to transport suppression. Such suppression can be reduced or even eliminated by hydrogen chemisorptions.

ASSOCIATED CONTENT

S Supporting Information. Simulation for the flipping dynamics of bare dimers next to the H-passivated dimers on silicon surface by using our models. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT

The work described in this paper was supported by grants from National Basic Research Program of China (Grant No. 2006CB933000) and the Research Grants Council of the Hong Kong Special Administrative Region, China (CityU5/CRF/08, CityU 103609).

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■ NOTE ADDED AFTER ASAP PUBLICATION

This article was published ASAP on January 10, 2011. The spelling of the third author's name has been corrected. The correct version was published on February 9, 2011.