Theoretical investigation of an intermediate in the STM tip-induced atomic process on H/Si(100) surfaces

Q. H. Yuan,[1,*] Q. S. Li,[1] K. D. Wang,[2] and Z. F. Liu[3]

[1]*Center for Computational Quantum Chemistry, South China Normal University, Guangzhou, 510631 Guangdong, People's Republic of China*

[2]*Department of Physics, Chinese University of Hong Kong, Shatin, Hong Kong, China*

[3]*Department of Chemistry, Chinese University of Hong Kong, Shatin, Hong Kong, China*

(Received 5 February 2010; published 3 May 2010)

STM tip-induced atomic process on hydrogenated Si(100) surfaces [H/Si(100)] has been explored for decades of years. The surface atomic processes at low sample bias voltages where direct electronic excitation from $\sigma \rightarrow \sigma^*$ is inaccessible had been attributed to multiple-vibrational excitation induced by inelastic tunneling electrons from STM tip. However, some experimental observations cannot be fully explained by the multiple-vibrational excitation theory. In this paper, we proposed reaction mechanisms to explain the surface atomic processes occurred on different H/Si(100) surfaces, based on our theoretical calculations. The proposed reaction mechanisms revealed a common hydrogen bridged intermediate on different H/Si(100) surfaces and such intermediate could explain the experimental observation of single dangling bonds which had been previously ascribed to Si-H bond broken induced by multiple-vibrational excitation. Moreover, some experimental observations, such as site selectivity, temperature, and isotope effect can be well explained by the mechanisms.

DOI: 10.1103/PhysRevB.81.205301 PACS number(s): 73.20.−r, 68.43.Nr, 68.37.Ef, 71.15.Mb

I. INTRODUCTION

In recent years, surface atomic processes induced by electrons from a tip of scanning tunneling microscope (STM) have received a lot of attention due to its application not only in fundamental science for understanding the processes from a microscopic view point but also in applied research for using as lithographic tool to manipulate matter at atomic scale. The inelastic electrons induced by STM tip interact with surface atoms (and molecules), leading to the electronic and vibrational excitation, induces variety of atomic motions, like diffusion, bond breaking, desorption, chemical reactions etc.[1–9]

The hydrogen-covered Si(100) surfaces have been used as model systems to study this kind of tip-induced surface reactions because of the relatively simple bonding configurations and of extensive use in semiconductor device processes.[1,9–20] A case of particular interest involves the desorption of hydrogen from monohydride (M) silicon surface [H/Si(100)-2$\times$1]. Depending on the energy of the tip-emitted electrons, two distinct desorption mechanisms have been identified as: (1) electronic excitation above the threshold of Si-H bond electronic excitation energy ($\sim$6 eV), which was caused by electron transition from the Si-H σ bonding state to the corresponding σ^* antibonding state;[1,9,10,18] and (2) multiple-electron vibrational heating mechanism at lower energies with high current density,[1,9,11,18–20] which has been ascribed to multiple-vibrational excitation of the Si-H species through inelastic tunneling. As the energy of a single electron in this case is not sufficient to break the Si-H bond directly, multiple electrons are required to induce desorption. The relatively long vibrational lifetime and poor coupling to the substrate phonon modes were regarded to allow the Si-H bond to be repeatedly excited and ultimately broken via the vibrational heating mechanism.[1,18]

Except for sample bias and current, STM tip-induced hydrogen desorption process is also influenced by the surface reconstructions. It has been reported that H/Si(100)-2$\times$1 surface has two reconstructed configurations: dihydride (D) silicon surface [H/Si(100)-1$\times$1] in which the surface Si-Si dimer bonds of the H/Si(100)-2$\times$1 surface have been broken and are replaced with SiH_2 groups;[21] and monohydride-dihydride silicon surface [H/Si(100)-3$\times$1] in which rows of monohydride dimers are interplaced with rows of silicon dihydrides.[14,22] STM nanolithography on H/Si(100)-3$\times$1 surface revealed a preference of hydrogen desorption from the monohydride silicon dimers and a reversion to H/Si(100)-2$\times$1 surface construction.[9,10,18,23] The preference of hydrogen desorption from the monohydride silicon dimers has not been fully explained until now. Previous reports attributed the hydrogen desorption to Si-H bond broken through multiple-vibrational heating. However, it is strange that the desorption only took place on monohydride site although the Si-H bond energy on monohydride sites and dihydride sites are similar.[24] Moreover, since thermal desorption of H_2 has a lower desorption temperature from the dihydride sites,[25] it is strange that "H desorption" induced by vibrational excitation has the opposite site-selectivity from that of thermal desorption.

The STM tip-induced hydrogen desorption process is also influenced by sample temperature and isotope effect. The desorption of hydrogen from the H/Si(100)-2$\times$1 surfaces shows different relationship with temperature and isotope effect in different sample bias regime.[10,15,18,23,26,27] In the electronic excitation regime, both desorption yield and isotope effect show no significant dependence on sample temperature. The desorption yield of deuterium at 300 K is about a factor of 50 lower than that of hydrogen, and the same ratio of 50 is also observed at 11 K.[10,18,23] However, a very strong temperature effect was observed in the vibrational heating regime. In this regime, the hydrogen was a factor of $\sim$300

 ©2010 The American Physical Society

easier to desorb at 11K than at 300 K.[23] Furthermore, deuterium could also be observed to desorb at 11 K, which could not be achieved at 300 K. This effect had been attributed to multiple-vibrational excitations of the Si-H bond, and the isotope effect was caused by the different vibrational lifetime of Si-H and Si-D.[1,18,20,28] For this explanation, it was assumed that the adsorbate vibrations was excited by inelastic tunneling electron and these vibrational energies were deposited in the vibration mode of the Si–H(D) bond. The Si-H(D) bond was expected to be broken when the stored energy was enough to desorb H atom, thus the vibrational lifetime plays a critical role in this heating mechanism. However, several studies have reported significantly different results,[1,19,29] leaving the local field effects on the inelastic process unclear.

In this paper, we proposed different reaction mechanisms to explain the surface atomic processes in above mentioned vibrational heating regime ($2\sim4$ V), based on first principle calculations. Our proposed reaction mechanisms can explain not only the phase transition from H/Si(100)-(3×1) surface to H/Si(100)-(2×1) surface and H desorption from the latter surface, but also experimental observations including site-selectivity, temperature effect, and isotope effect. And more importantly, a common intermediate is identified on different H/Si(100) surfaces, demonstrating the uniform mechanism for atomic processes on different H/Si(100) surfaces.

II. COMPUTATIONAL DETAILS

First principle calculations on the total energy and electronic structure were carried out within density functional theory (DFT), using a plane-wave basis set and pseudopotentials for the atomic core regions, as implemented in the Vienna *ab initio* simulation package (VASP). The setup was similar to previous studies in our group on Si(100) reactions,[30–32] with PW91 GGA (general gradient approximation) exchange-correlation functional, Vanderbilt ultrasoft pseudopotentials, and a cutoff energy of 300 eV for the planewave basis set. The H/Si(100)-2×1 and H/Si(100)-1×1 surfaces were modeled by a p(2×2) slab, with a unit cell of the size $7.7\times7.7\times17.50$ Å^3 containing five Si layers and a vacuum region of 10 Å. The H/Si(100)-3×1 surface was modeled by a unit cell of the size $11.56\times11.56\times17.50$ Å^3 which also contained five Si layers and a vacuum region of 10 Å. All the bottom silicon atoms were saturated by H atoms. The sampling for the Brillouin zone included a set of eight special k points.

The minimum energy reaction path was searched by the nudged elastic band method, developed by Jónsson and co-workers.[33–35] Vibrational frequencies were also calculated to verify the transition structures, using the dynamic matrix method. The STM images are obtained for the electron filled states at −2.0 eV bias and calculated within the Tersoff-Hamman approximation.[36]

III. RESULTS AND DISCUSSIONS

A. Mechanism for H_2 desorption from H/Si(100)-2×1 surface and phase transition from H/Si(100)-3×1 to H/Si(100)-2×1 surface

The reaction mechanism for H_2 desorption from the H/Si(100)-2×1 surface has been a subject of debate, addressed in many theoretical studies.[25,37–39] The previously proposed two main mechanisms are: (1) interdimer mechanism, with the desorbing hydrogen molecule formed by two hydrogen atoms from two adjacent silicon dimers; (2) intradimer mechanism, with the hydrogen molecule formed by the two H atoms on a single silicon dimer.[38] Although most recently literatures reported that interdimer desorption mechanism accounted for the hydrogen thermal desorption from H/Si(100)-2×1 surface, our studies only focus on the intradimer mechanism due to the local field effect induced by tunneling electrons from the STM tip (the distance between intradimer Si atoms is much shorter than interdimer Si atoms). Unlike some previous studies which found the intradimer desorption as a concerted reaction,[38,39] our calculations identified the reaction as a stepwise one, as shown in Fig. 1. In the first step, the Si-Si σ bond in HSi-SiH unit was broken and one of the hydrogen atoms moved to a bridge position between two Si atoms, forming an intermediate (IM) structure with a 3-atomic-centers-2-electrons (3c-2e) Si-H-Si bond. The barrier for this step is only 1.48 eV, which is much lower than the measured barrier for H_2 desorption (2.5 eV for experimental value), and the overall energy change is 1.40 eV. This bridge intermediate was unstable and could be readily reversed back to reactant (R) as the reversion barrier was only 0.08 eV. The intermediate could also be converted to product (P) as shown in Fig. 1 by overcoming an energy barrier of 1.09 eV and the final desorption product was 2.0 eV higher in energy than the initial reactant (R). It can be obviously seen that the barrier for reversing back to reactant is much lower than the barrier for dissociating into products. However, it is also possible that latter dissociation pathway plays role if the density of excitation electrons is high. When the excitation electrons are in high density and the short-lived intermediate may have chance to adsorb another excited electron to produce products. On the other hand, the continuous and high density electrons from the STM tip can ensure the presence of the intermediate. Such stepwise intradimer desorption pathway has also been mentioned by several previous studies.[11,40]

Phase transition from H/Si(100)-3×1 to H/Si(100)-2×1 surface involves two processes: surface rearrangement from monohydride-dihydride-monohydride (DMD) structure to dihydride-dihydride-monohydride (DDM) structure (shown in Fig. 2); and H_2 desorption from DD structure (shown in Fig. 3). The potential energy surface for rearrangement of DMD to DDM was shown in Fig. 2, together with the geometries for transition, intermediate, and product structures. The rearrangement process was also a stepwise reaction. The first step was the breaking of the Si-Si σ bond on the monohydride dimer coupled with the formation of a Si-H-Si bridge structure, with an activation barrier of 1.34 eV. The bridge intermediate could be further transformed to DDM structure as shown in Fig. 2 by overcoming another barrier of 0.34 eV. The calculated total barrier was in consistent with the experiment measured barrier which is around 1.43 eV.[25] Previous studies have proposed some other mechanisms to explain the phase transition from DMD to DDM structure but the calculated barrier was much higher than the experimental value.[14]

Hydrogen desorption from DD structure is also a stepwise reaction, as shown in Fig. 3. First, one hydrogen atom in the

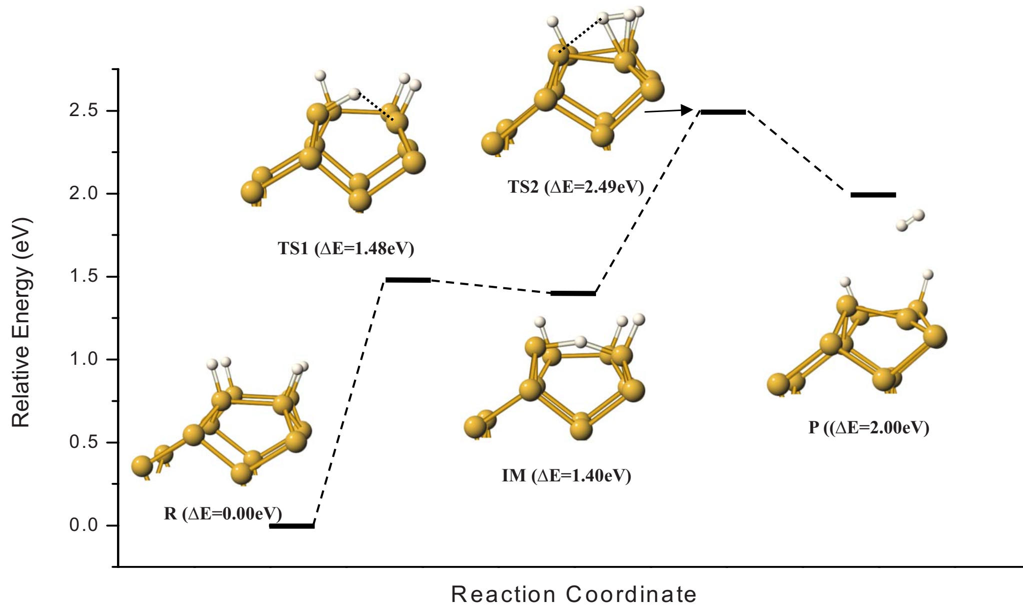

FIG. 1. (Color online) H_2 desorption path for H/Si(100)-2×1 surface. The Si-Si σ bond in HSi-SiH unit was broken and one of the hydrogen atoms moves to the neighbor silicon atom, forming an intermediate structure with 3c-2e bond (Si-H-Si bridge structure) and leave a lone pair electrons on one silicon atom. The formation of intermediate (IM) needs overcome an activation barrier of 1.48 eV with reaction heat about 1.40 eV. This IM can be further converted to desorption product (p) by overcoming 1.09 eV energy barrier.

SiH_2 unit moves to a bridging position between the two neighboring Si atoms, elongating the Si-H bond and pushes the two hydrogen atoms on the neighbor SiH_2 unit away from their original sites. After the two hydrogen atoms were forced to be desorbed as hydrogen molecule, an intermediate labeled as IM was formed. This intermediate could be easily converted to the final product (monohydride) in the second step. The calculated total barrier for this desorption pathway was 1.84 eV, in agreement with the experimental value ~2.0 eV.[41–43] The total reaction is exothermic and the calculated reaction energy is 0.07eV. A similar mechanism has been proposed by previous studies although detailed reaction potential energy surface was not described.[43,44] Another proposed mechanism to explain H_2 thermal desorption from H/Si(100)-1×1 surface is a concerted desorption, in which each dihydride donated one hydrogen atom to recombinatively desorb from the surface concertedly.[44–46] Our calculations demonstrated that the barrier for this concerted desorption pathway was 2.35 eV, which was 0.51 eV higher than the stepwise desorption pathway and kinetically less favorable.

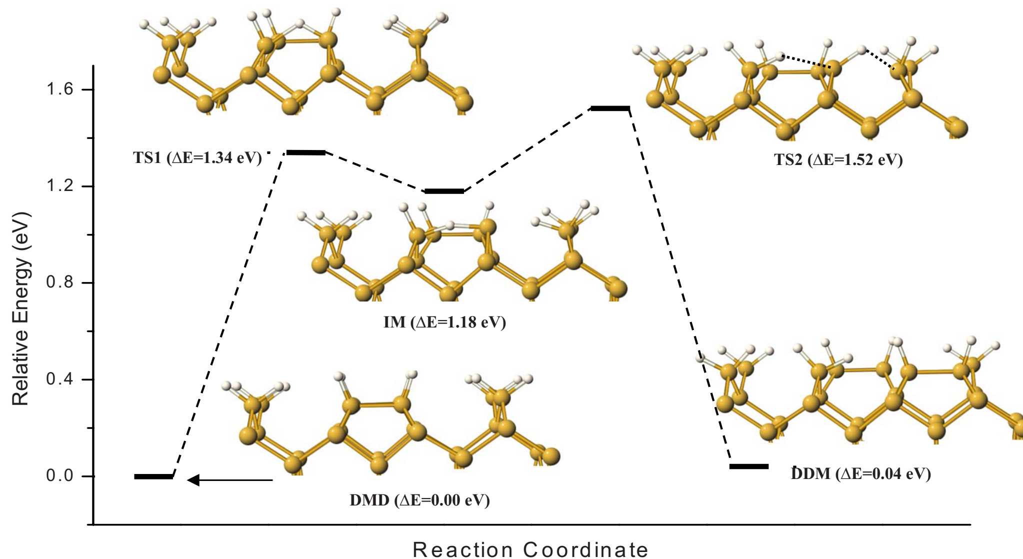

FIG. 2. (Color online) H migration path for H/Si(100)-3×1 surface. One hydrogen atom in the monohydride (m) unit is activated to intermediate (IM) with an activation barrier of 1.34 eV. The dangling bond in the IM can further interact with the neighbor dihydride (d) unit, forming the rearrangement product DDM by overcoming activation barrier of 0.34 eV.

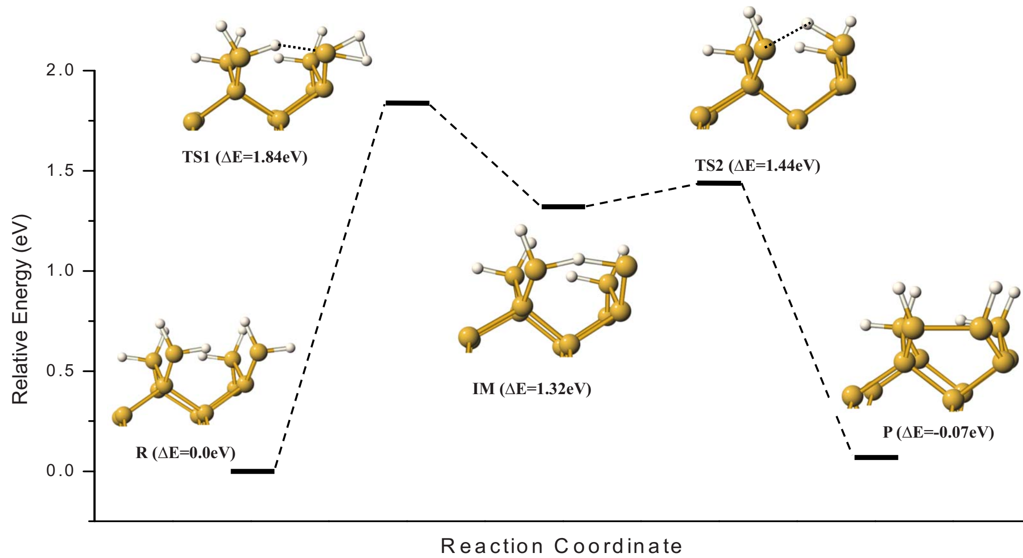

FIG. 3. (Color online) H_2 desorption path for H/Si(100)-1×1 surface. A hydrogen atom in one dihydride (d) unit approaches to the Si atom in neighbor D unit and pushes two hydrogen atoms to leave. An intermediatem (IM) with single dangling bond is formed and this IM is easily transformed to the final product (p) because of the very low activation barrier.

Our calculation results demonstrated that, the H/Si(100)-3×1 can be transformed to H/Si(100)-2×1 surface through STM tip-induced DMD to DDM phase transition and following H_2 desorption from DD surface. The H/Si(100)-2×1 surface can be further converted to bare Si(100)-2×1 surface by desorbing all the H atoms. And what is more, calculations on hydrogen desorption from different H/Si(100) surfaces identified a common intermediate, indicating hydrogen desorption from hydrogenated surfaces has similar reaction mechanism.

B. Bonding analysis for the H-bridged intermediate

The identified intermediate has a bridged H and dangling bond on one of the Si atom [see Fig. 4(c)]. Such a bridge intermediate has been reported before,[47] but its significance in hydrogen desorption has not been fully explored, and neither has its bonding nature been analyzed.

To investigate the bonding characteristics of the intermediate, we did B3LYP/6-311++G(3df,2p) calculation on a Si_9H_{17} cluster which served as a model for the H/Si(100)-2×1 surface dimer in a natural bonding orbital (NBO) analysis.

Since the Si-H bond (bond energy: 3.6–4.5 eV) was stronger than the Si-Si σ bond (bond energy: ~2.4 eV), it was actually easier to break the Si-Si σ bond upon heating. Upon such an event, it was energetically more favorable to put the two electrons in this broken bond to one SiH, producing an ion pair SiH^-...SiH^+ rather than a diradical SiH•⋯SiH•.[47] This process produced a lone pair on SiH^- and an empty p orbital on SiH^+ [see Fig. 4(a)]. Both a Si-H bonding orbital and the electron lone pair on SiH^- (Si1-H1) can serve as donors to the empty p orbital on SiH^+ (Si2-H2) to lower the energy. Previous investigations found that stabilization came from the donor-acceptor interactions of Si-H→p was stronger than that of lone pairs (lp)→p because the lone pair orbital had mainly s-character and hydrogen was more electronegative than Si.[47] The Si-H bonds were better donors than the lone-pair. Therefore, the Si1-H1 donor orbital and the empty p orbital of the Si2H2 fragment were tilted toward each other, and at the same time the H2 atom in Si2H2 moved away from the bridging hydrogen atom, which led to the bridge structure shown in Fig. 4(b).

Our NBO analysis indicated that there was an electron lone-pair on Si1-H1, which had its main contribution from the 3s orbital of Si1. For Si2, two types of bonds were found: a typical covalent bond Si2-H2 and a dative bond Si2-H1 with a Wiberg bond index of 0.6, in agreement with our expectation.

It is therefore not surprising that the bridge structure is often found in the desorption paths identified, both in previous study and in our current report. They could be formed at energy lower than that required to trigger the desorption of hydrogen.

The special electronic structure had already been found in some small hydrogenated silicon clusters. Calculations carried out by Matthias et al. showed that Si_2H_2 gas molecule had several unusual equilibrium geometries,[47] in which the

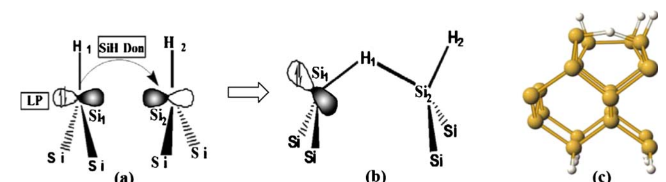

FIG. 4. (Color online) Bonding analysis for the formation of intermediate. (a) Si-Si σ bond is broken and an ion pair SiH^-...SiH^+ is formed; (b) The Si1-H1 donor orbital and the empty p orbital of the Si2H2 fragment were tilted toward each other, and the H2 atom in Si2H2 fragment moved away from the bridging hydrogen atom, resulting into the bridge structure; (c) Si_9H_{17} cluster model which represents the H/Si(100)-2×1 surface dimer.

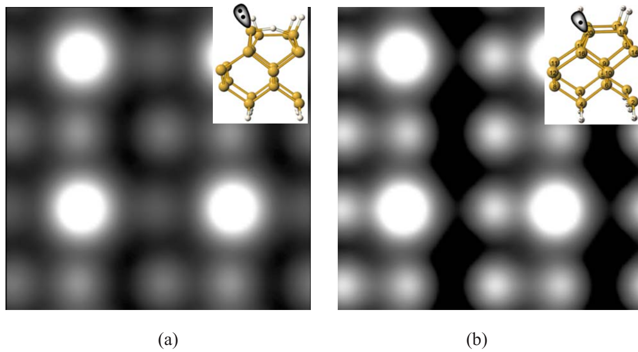

FIG. 5. (Color online) Simulated STM images of electron filled states at 2.0 eV below Fermi surface for (a) H-bridged structure, (b) Si-H bond broken structure. The insets show the corresponding electronic structure.

doubly bridged structure and singly bridged structure were more stable than the linear structure E, demonstrating the possibility of our identified intermediate.

C. Explanation of the experimental results

According to above bonding analysis, the bridge intermediate has a single dangling bond which is similar to what induced by Si-H bond broken. Our simulated STM images for the two electronic structures demonstrated that there was little difference between the two simulated STM images, as shown in Fig. 5. From the STM images, it is hard to tell whether the single dangling bonds were caused by Si-H bond broken or by the bridge intermediate. Previous studies reported that single dangling bonds induced by STM tip can be observed at a sample bias of +2.5 V with the tunneling current of 10 nA and these single dangling bonds were attributed to Si-H bond broken induced by multiple-vibrational excitation.[1,9,10,18,19,26] Here we propose a different explanation that these single dangling bonds are ascribed to the appearance of the bridge intermediate. In another word, the previously observed "H desorption" was actually the observation of bridge intermediate. Since the formation of the bridge intermediate in H/Si(100)-2×1 surface has a barrier of only 1.48 eV (see Fig. 1), the $(SiH)_2$ dimer is expected to be excited to the bridge intermediate rather than Si-H bond broken structure when a low sample bias voltage is applied to a specific monohydride site. Although the intermediate is also easily to revert to its initial state, the continuous and high density electronic excitation from the STM tip can ensure the observation.

This bridge intermediate can explain the experimental observations, for example, the site selectivity detected in the "desorption" of hydrogen from H/Si(100)-(3×1) surface.[18] H/Si(100)-(3×1) surface is composed by interplaced rows of monohydride and dihydrides, individual "H desorption" from it can be observed only in monohydride site at low sample bias voltage. Previous studies did not give a quite reasonable explanation about this site selectivity.[18] However, the formation of H-bridged intermediate can explain this site selectivity very well because the bridge structure can be formed only at monohydride sites in H/Si(100)-(3×1) surface. On the other hand, the site selectivity can be compared more straightforwardly based on the activation barrier. The barrier for H-bridged intermediate, H desorption from monohydride site and dihydride site are 1.48, 3.38, and 3.18 eV, respectively. Hence the reaction rate for the three reaction paths are 3.94×10^{-12}, 6.69×10^{-43}, and 2.08×10^{-40} s^{-1}, respectively, according to Arrhenius formula.[48] It can be obviously seen that the relative reaction rate for H-bridged intermediate is the largest. Here we provided a quite reasonable explanation for this site-selectivity which has not been well explained by previous studies.[18]

The bridge intermediate can also explain the temperature dependence and isotope effect on "H desorption" yield below the threshold energy. Based on above analysis, the observed "H desorption" yield is actually the bridge intermediate yield which is further determined by its lifetime. The lifetime of the intermediate is determined by the balance of the formation and reversion rate. At high temperature (300 K), the reversion rate is fast due to the relatively low reversion barrier (0.08 eV), the calculated rate is 1.94×10^{12} s^{-1} using Arrhenius formula, resulting into short lifetime of the intermediate and low "H desorption" yield. But at low temperature (11 K), the reversion rate becomes much slower and the lifetime of the intermediate becomes longer, resulting into a higher "H desorption" yield. The reversion rate is reduced to 9.22×10^{-24} s^{-1} when the temperature is lowered to 11 K. Thus at low temperature, the increase of desorption yield is attributed to the corresponding increase of lifetime of the bridge intermediate. Substituting deuterium for hydrogen greatly modified the reaction rate since the isotope replacement is in a chemical bond which involves isotopic atom. The formation of deuterium bridged intermediate has the higher thermal activation barrier due to its lower zero-point energy and thus has the lower "desorption yield." This temperature dependence and isotope effect on H desorption yield had been explained by a model that involved multiple-vibrational excitation and took into account the increase of the Si-H vibrational lifetime at low temperature.[9,18,49,50]

In addition, our calculations demonstrated that the bridge intermediate can be further excited to silicon dimer through H_2 desorption. This excitation can be only accessible when the density of electron current is high and coherent multiple-electron excitation is possible. The observation of double dangling bonds on silicon dimer have been reported in some previous studies.[1,9] Avouris *et al.* found that, at high tunneling current, double dangling bonds on Si dimer can be also observed except for the single dangling bonds.[9] These double dangling bonds had been previously attributed to the broken of two Si-H bonds on the same $(SiH)_2$ dimer. However, our calculations demonstrated that it was the intradimer desorption induced by STM tip that accounts for the double dangling bonds. This stepwise intradimer desorption pathway explained why hydrogen desorption from H/Si(100) surface at low sample bias was feasible and why high current density is necessary for desorption.

D. Conclusion

Reaction mechanisms for STM tip-induced phase transition from H/Si(100)-(3×1) to H/Si(100)-(2×1) surface

and H_2 desorption from H/Si(100)-(1×1), H/Si(100)-(2×1) surfaces have been explored by theoretical calculations. A common intermediate was identified in three reaction paths and the intermediate has H-bridged structure with a single dangling bond. The identified intermediate could explain the experimental observation of single dangling bonds, which had been attributed to Si-H bond broken, induced by STM tip at lower sample bias. Moreover, this intermediate can well explain experimental observations which are related with STM tip-induced atomic process at lower sample bias, including site selectivity, temperature, and isotope effect.

ACKNOWLEDGMENTS

The work reported is supported by Earmarked Grants (Project No. CUHK 402202) from the Research Grants Council of Hong Kong SAR Government.

*Corresponding author; qhyuan@liua4.chem.cuhk.edu.hk

[1] T. C. Shen, C. Wang, G. C. Abein, J. R. Tucker, J. W. Lyding, Ph. Avouris, and R. E. Walkup, Science **268**, 1590 (1995).
[2] R. S. Becker, G. S. Higashi, Y. J. Chabal, and A. J. Becker, Phys. Rev. Lett. **65**, 1917 (1990).
[3] M. Schwartzkopff, P. Radojkovic, M. Enachescu, E. Hartmann, and F. Koch, J. Vac. Sci. Technol. B **14**, 1336 (1996).
[4] B. C. Stipe, M. A. Rezaei, and W. Ho, Phys. Rev. Lett. **79**, 4397 (1997).
[5] D. P. Adams, T. M. Mayer, and B. Swarzentruber, J. Vac. Sci. Technol. B **14**, 1642 (1996).
[6] B. C. Stipe, M. A. Rezaei, W. Ho, S. Gao, M. Persson, and B. I. Lundqvist, Phys. Rev. Lett. **78**, 4410 (1997).
[7] Y. Nakamura, Y. Mera, and K. Maeda, Phys. Rev. Lett. **89**, 266805 (2002).
[8] G. Boendgen and P. Saalfrank, J. Phys. Chem. B **102**, 8029 (1998).
[9] Ph. Avouris, R. Walkup, A. Rossi, H. Akapti, P. Nordlander, T.-C. Shen, G. Abeln, and J. W. Lyding, Surf. Sci. **363**, 368 (1996).
[10] T.-C. Shen and P. Avouris, Surf. Sci. **390**, 35 (1997).
[11] X. Tong and R. A. Wolkow, Surf. Sci. **600**, L199 (2006).
[12] K. Stokbro, C. Thirstrup, M. Sakurai, U. Quaade, Ben Yu-Kuang Hu,F. Perez-Murano, and F. Grey, Phys. Rev. Lett. **80**, 2618 (1998).
[13] C. Thirstrup, M. Sakurai, T. Nakayama, and M. Aono, Surf. Sci. **411**, 203 (1998).
[14] T.-C. Shen, J. A. Steckel, and K. D. Jordan, Surf. Sci. **446**, 211 (2000).
[15] J. W. Lyding, K. Hess, G. C. Abeln, D. S. Thompson, J. S. Moore, M. C. Hersam, E. T. Foley, J. Lee, Z. Chen, S. T. Hwang, H. Choi, Ph. Avouris, and I. C. Kizilyalli, Appl. Surf. Sci. **130-132**, 221 (1998).
[16] M. Sakurai, C. Thirstrup, T. Nakayama, and M. Aono, Surf. Sci. **386**, 154 (1997).
[17] A. J. Mayne, D. Riedel, G. Comtet, and G. Dujardin, Prog. Surf. Sci. **81**, 1 (2006).
[18] Ph. Avouris, R. Walkup, A. Rossi, T.-C. Shen, G. Abeln, J. Tucker, and J. W. Lyding, Chem. Phys. Lett. **257**, 148 (1996).
[19] L. Soukiassian, A. J. Mayne, M. Carbone, and G. Dujardin, Phys. Rev. B **68**, 035303 (2003).
[20] B. N. J. Persson and Ph. Avouris, Chem. Phys. Lett. **242**, 483 (1995).
[21] J. J. Boland, Phys. Rev. Lett. **65**, 3325 (1990); C. Cheng and J. T. Yates, Jr., Phys. Rev. B **43**, 4041 (1991).
[22] X. R. Qin and P. R. Norton, Phys. Rev. B **53**, 11100 (1996); J. Y. Maeng, S. Kim, S. K. Jo, W. P. Fitts, and J. M. White, Appl. Phys. Lett. **79**, 36 (2001).
[23] E. T. Foley, A. F. Kam, J. W. Lyding, and P. Avouris, Phys. Rev. Lett. **80**, 1336 (1998).
[24] Y. J. Chabal and K. Ragavachari, Phys. Rev. Lett. **54**, 1055 (1985).
[25] P. Nachtigall and K. D. Jordana, J. Chem. Phys. **101**, 8073 (1994).
[26] B. N. J. Persson and Ph. Avouris, Surf. Sci. **390**, 45 (1997).
[27] C. Thirstrup, M. Sakurai, T. Nakayama, and K. Stokbro, Surf. Sci. **424**, L329 (1999).
[28] Z. Chen, P. Ong, A. K. Mylin, and V. Singh, Appl. Phys. Lett. **81**, 3278 (2002).
[29] K. Stokbro, B. Y.-K. Hu, C. Thirstrup, and X. C. Xie, Phys. Rev. B **58**, 8038 (1998).
[30] X. L. Fan, Y. F. Zhang, W. M. Lau, and Z. F. Liu, Phys. Rev. B **72**, 165305 (2005).
[31] Q. J. Zhang, X. L. Fan, W. M. Lau, and Z. F. Liu, Phys. Rev. B **79**, 195303 (2009).
[32] Q. J. Zhang, J. L. Wang, and Z. F. Liu, J. Phys. Chem. C **111**, 6365 (2007).
[33] H. Jónsson, Annu. Rev. Phys. Chem. **51**, 623 (2000).
[34] G. Henkelman, B. P. Uberuaga, and H. Jónsson, J. Chem. Phys. **113**, 9901 (2000).
[35] G. Henkelman and H. Jónsson, J. Chem. Phys. **113**, 9978 (2000).
[36] J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985).
[37] K. Oura, V. G. Lifshits, A. A. Saranin, A. V. Zotov, and M. Katayama, Surf. Sci. Rep. **35**, 1 (1999).
[38] A. Namiki, Prog. Surf. Sci. **81**, 337 (2006).
[39] W. Brenig and E. Pehlke, Prog. Surf. Sci. **83**, 263 (2008).
[40] J. Shi, H. Chuan Kang, E. S. Tok, and J. Zhang, J. Chem. Phys. **123**, 034701 (2005); E. S. Tok and H. Chuan Kang, *ibid.* **115**, 6550 (2001).
[41] M. C. Flowers, N. B. H. Jonathan, Y. Liu, and A. Morris, J. Chem. Phys. **99**, 7038 (1993).
[42] B. M. H. Ning and J. E. Crowell, Surf. Sci. **295**, 79 (1993).
[43] T. Niida, H. Tsurumaki, and A. Namiki, J. Chem. Phys. **124**, 024715 (2006).
[44] A. Vittadini and A. Selloni, Chem. Phys. Lett. **235**, 334 (1995).
[45] J. E. Northrup, Phys. Rev. B **44**, 1419 (1991).
[46] A. Vittadini, A. Selloni, R. Car, and M. Casarin, Phys. Rev. B **46**, 4348 (1992).
[47] M. Lein, A. Krapp, and G. Frenking, J. Am. Chem. Soc. **127**, 6290 (2005).

[48] Christine J. Wu Irina V. Ionova, and Emily A. Carter, Phys. Rev. B **49**, 13488 (1994).
[49] A. Vittadini, A. Selloni, and M. Casarin, Surf. Sci. Lett. **289**, L625 (1993).
[50] A. Vittadini, A. Selloni, and M. Casarin, in *Proceedings of the 4th International Conference on the Formation of Semiconductor Interfaces*, edited by B. Langer, H. Lueth, W. Moeuch, and J. Pollmann (World Scientific, Singapore, 1994), p. 146.