PHYSICAL REVIEW B **83**, 033406 (2011)

First-principles calculations of the structure and growth mechanism of allyl mercaptan lines on the H/Si(100)-2 × 1 surface

Jin-Ho Choi and Jun-Hyung Cho[*]
Department of Physics and Research Institute for Natural Sciences, Hanyang University, 17 Haengdang-Dong, Seongdong-Ku, Seoul 133-791, Korea

(Received 11 August 2010; revised manuscript received 17 December 2010; published 31 January 2011)

Using first-principles density-functional calculations, we investigate the structure and growth mechanism of allyl mercaptan lines on the H-terminated Si(100)-2×1 surface. The earlier structural model (termed the linear structure), where the terminal C atom of the C=C bond initially reacts with a single Si dangling bond, has been competing with a new structural model (termed the branched structure) where the medial C atom of the C=C bond initially reacts with a single Si dangling bond. We find that formation of the branched structure is kinetically unfavored over that of the linear structure. Moreover, the simulated scanning tunneling microscopy (STM) image of the branched structure cannot reproduce the features observed in the STM experiment, such as the position and origin of the bright protrusion. Thus, the present results do not support the branched structure in many respects.

DOI: 10.1103/PhysRevB.83.033406 PACS number(s): 68.43.Bc, 68.43.Fg, 68.43.Mn

Fabrication of organic nanostructures on a silicon surface has received much attention because of its potential application for molecular electronic devices.[1–5] Particularly, the fabrication of one-dimensional (1D) molecular lines is necessary for elemental building blocks in nanocircuits. In their pioneering work, Wolkow and co-workers[6] proposed a self-assembly approach for fabricating 1D molecular lines on the H-terminated Si(100)-2×1 surface. This self-assembly approach has been employed to fabricate a variety of 1D molecular lines either along the dimer rows or across the dimer rows on the H/Si(100)-2×1 surface.[6–17] Many alkene molecules with a C=C double bond such as styrene CH_2=CH–C_6H_5,[6] vinylferrocene CH_2=CH–$C_5H_4FeC_5H_5$,[7] and 2,4-dimethylstyrene CH_2=CCH_3–C_6H_4–CH_3 (Ref. 8) have been observed to grow along the dimer rows, while only allyl mercaptan (ALM) CH_2=CH–CH_2–SH (Ref. 9) exhibited the line growth across the dimer rows. It is well known[6–17] that the reaction mechanism for the line growth along the dimer rows involves a chain reaction, beginning with the interaction of the C=C double bond with a Si dangling bond (DB) generated by the removal of an H atom from the H/Si(100)-2×1 surface using the scanning tunneling microscope tip.[5,18,19] Here, the terminal C atom of the C=C bond forms a Si–C bond, while the medial C atom of the C=C bond becomes a radical. This C radical can abstract an H atom from a neighboring Si dimer to create another Si DB, setting off a chain reaction to grow a 1D molecular line along the Si dimer row.[6]

A recent STM study of Hossain, Kato, and Kawai (HKK)[9] observed the growth of ALM lines across the dimer rows on the H/Si(100)-2×1 surface. In the observed[9] STM images of the ALM lines, each adsorbed molecule produces a bright protrusion which is located on one edge of a Si dimer in the adjacent dimer row. HKK interpreted the bright protrusion in terms of the SH group of the adsorbed ALM molecule. To account for the growth of ALM lines, HKK suggested that, after the initial reaction of the terminal C atom of the C=C bond with a single Si DB, the created radical at the medial C atom would be transferred to the S atom through the transfer of the H atom from the S to the C atom. The resulting S radical was proposed to abstract an H atom from the adjacent dimer row, followed by the H-atom diffusion on the adjacent dimer row for a chain reaction across the Si dimer rows.[9] However, our previous density-functional theory (DFT) calculations[20] showed that the reaction processes proposed by HKK are unlikely to occur because of their high activation barriers. Instead, we proposed a reaction mechanism where an ALM molecule adsorbing on a single H-empty site abstracts an H atom from a neighboring dimer on the same Si dimer row, similar to other alkene lines[6–8] growing along the dimer rows. The created H-empty site on the neighboring dimer abstracts an H atom from the SH group, and the resulting S-centered radical easily abstracts an H atom from a Si dimer in the adjacent dimer row, proceeding to a Si–S bond formation on one side of the adjacent dimer row with accompanying the associative desorption of H_2. This H_2-desorption process creates another H-empty site on the adjacent dimer row, setting off a chain reaction across the Si dimer rows. The resulting structure of the ALM line (termed the linear structure)[20] is displayed in Fig. 1(a).

However, a recent cluster DFT calculation[21] of Ferguson, Than, and Raghavachari (FTR) proposed that the so-called branched reaction mechanism would be more probable than our proposed[20] reaction mechanism forming the linear structure. According to the branched reaction mechanism, the medial C atom of the C=C bond initially reacts with a single Si DB and then the created radical at the terminal C atom is transferred to the S atom through the H transfer from the S to the C atom. In fact, these reaction processes were first considered by Pei *et al.*[22] Similar to the forementioned reaction pathway forming the linear structure, the S-centered radical abstracts an H atom from a Si dimer in the adjacent dimer row, followed by the Si–S bond formation and the associative H_2 desorption. This new reaction mechanism gives rise to the formation of the so-called branched structure[21] [see Fig. 1(b)]. Here, the initial reaction of the medial C atom of the C=C bond with a single Si DB is very unusual, in view of the experimental evidence[6–8] that the terminal C atom of the C=C bond initially reacts with a single Si DB.

In this Brief Report, using first-principles DFT calculations with a periodic slab geometry, we calculate the energy profile

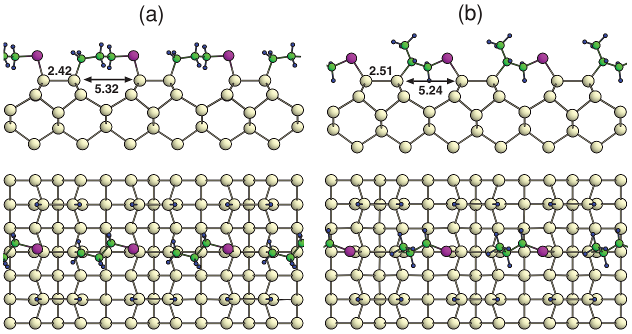

FIG. 1. (Color online) Side and top views of the optimized structure of the ALM line on the H-terminated Si(100) surface within (a) the linear structure and (b) the branched structure. The circles represent Si, S, C, and H atoms with decreasing size. The numbers denote the interatomic distances (in Å).

along the reaction pathway proposed by a recent[21] cluster DFT calculation. We find that the Si–C bond formation with the medial C atom of the C=C bond is kinetically and thermodynamically unfavored over that with the terminal C atom of the C=C bond. Unlike along the reaction pathway of the linear structure,[20] the Si–S bond formation and the associative H_2 desorption in the branched structure is found to be kinetically prohibited because of the absence of their concerted reactions. Moreover, we find that the simulated STM image of the branched structure shows the bright protrusion located on the initially reacted Si DB site, originating from the methyl group [see Fig. 1(b)]. These features for the position and origin of the bright protrusion in the branched structure are not consistent with those of the observed[9] STM data. Thus, the kinetics, thermodynamics, and STM image are unlikely to support the branched structure recently proposed[21] by FTR.

We performed the total-energy and force calculations by using first-principles density-functional theory[23] within the generalized-gradient approximation.[24] The Si, S, and H (C) atoms were described by norm-conserving[25] (ultrasoft[26]) pseudopotentials. The surface was modeled by a periodic slab geometry, where each slab contained six Si atomic layers plus adsorbed ALM molecules and the bottom Si layer was passivated by two H atoms per Si atom. The electronic wave functions were expanded in a plane-wave basis set using a cutoff of 25 Ry, and the electron density was obtained from the wave functions at four **k** points in the surface Brillouin zone of the 4×3 unit cell. All the atoms except the bottom two Si layers were allowed to relax along the calculated Hellmann-Feynman forces until all the residual force components were less than 1 mRy/bohr. Our calculation scheme has been successfully applied to the adsorption and reaction of various unsaturated hydrocarbon molecules on Si(100).[27]

As mentioned previously, formations of the branched and linear structures show the different features for the initial reaction of the C=C double bond with a single Si DB. In the branched (linear) structure, the medial (terminal) C atom of the C=C bond initially reacts with a single Si DB, thereby creating a radical at the terminal (medial) C atom. We first investigate the initial reaction of an ALM molecule with a single Si DB on an otherwise H-terminated Si(100) surface. In our calculations, this reaction is simulated by employing a 4×3 unit cell where adsorbed ALM molecules are separated by two H-terminated Si dimers along the dimer rows as well as by an additional dimer row perpendicular to the dimer rows. In order to find the minimum-energy pathway for such a Si–C bond formation, we optimize the structure by using the gradient projection method[28] where only the distance $d_{\text{Si-C}}$ between the medial (or terminal) C atom and its bonding Si atom is constrained. Hellmann-Feynman forces are used for the relaxation of all the atomic positions as well as the Si–C bond angles for the constrained Si–C bond length. In this way, we obtain the energy profile for the Si–C bond formation as a function of decreasing distance $d_{\text{Si-C}}$. The results for the branched and linear structures are displayed in Fig. 2, together with the atomic geometries of the transition and intermediate states. We find that in the case of the branched structure, the transition state (denoted as T_1) on going from the free molecule to the C radical intermediate (denoted as I_1) has a negative adsorption energy (E_{ads}) of -0.11 eV, yielding an energy barrier (E_b) of 0.11 eV for the Si–C bond formation, whereas in the case of the linear structure, there is no saddle point between the gas state and the C radical intermediate (denoted as I_{L1}), indicating a barrierless reaction for the Si–C bond formation. We also find that the I_1 (I_{L1}) state has $E_{\text{ads}} = 0.03$ (0.36) eV in the branched (linear) structure. On the basis of our results for the initial reaction of the C=C double bond, we can say that the Si–C bond formation with the medial C atom is not only kinetically but also thermodynamically unfavored over that with the terminal C atom. We note that the existing STM experiments[6–8] for various alkene lines on the H/Si(100)-2×1 surface reported the reaction of the terminal

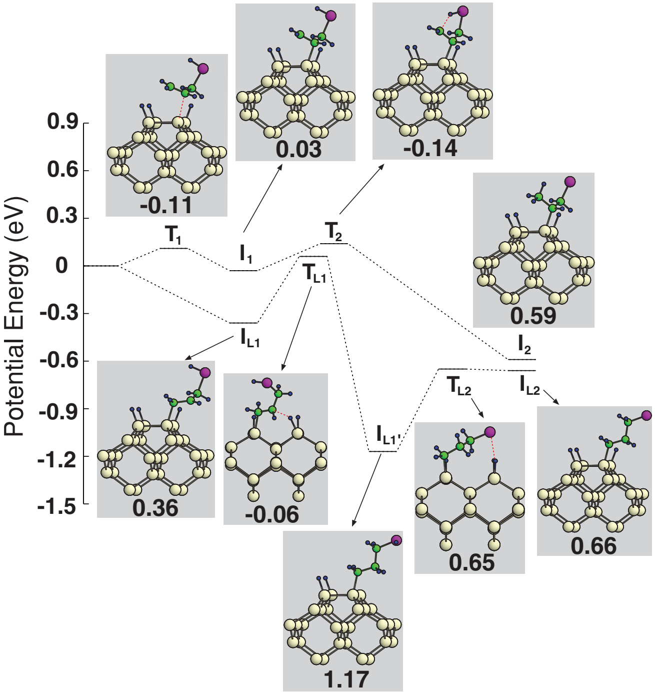

FIG. 2. (Color online) Calculated energy profiles for the initial reactions of the branched (upper) and linear (lower) structures. The atomic geometries of several transition and intermediate states are given together with their adsorption energies (in eV).

C atom with the single Si DB, including the ALM lines[9] as discussed below.

Along the reaction pathway for the branched structure, FTR proposed that the created radical at the terminal C atom can be stabilized by the transfer of the H atom from the SH group, thereby leaving an S radical.[21] As shown in Fig. 2, we find $E_{\mathrm{ads}} = -0.14$ eV for the T_2 state, yielding $E_{\mathrm{b}} = 0.17$ eV from the I_1 state to the S radical intermediate (denoted as I_2). On the other, along the reaction pathway for the linear structure, our previous DFT calculations[20] considered the two reaction steps on going from the I_{L1} state to the S radical intermediate (denoted as I_{L2}). The first step is to abstract an H atom from a neighboring Si dimer, which is the same as the previously[6–8] proposed H-abstraction pathway in the line growth of alkene molecules. Subsequently, the H atom in the SH group is transferred to the generated H-empty site on the neighboring dimer. As shown in Fig. 2, we obtained $E_{\mathrm{b}} = 0.42$ eV for the first step from I_{L1} to $I_{\mathrm{L1'}}$ and $E_{\mathrm{b}} = 0.52$ eV for the second step from $I_{\mathrm{L1'}}$ to I_{L2}. Here, it is notable that the S radical intermediate easily proceeds to formation of the I_{L3} state by abstracting the H atom from the neighboring dimer row, as discussed below. On the basis of the calculated energy barriers, we estimate that at room temperature the reaction rate from the $I_{\mathrm{L1'}}$ to I_{L3} state is $\sim 10^5$ sec^{-1}.[20] Thus, we can say that another ALM adsorption on the H-empty site at the $I_{\mathrm{L1'}}$ state is unlikely to occur, consistent with the experimental observations.[8,9]

Similar to the previously[20] proposed reaction pathway for formation of the linear structure, FTR[21] considered the following subsequent reaction processes for formation of the branched structure: (i) the S radical intermediate abstracts an H atom from the adjacent dimer row, forming the I_3 state, and (ii) the resulting SH group further reacts with a Si dimer in the adjacent dimer row to form the Si–S bond with accompanying the associative H_2 desorption. The calculated energy profiles together with the atomic geometries of the transition, intermediate, and final states are displayed in Fig. 3. We find that the H-abstraction process easily takes place with $E_{\mathrm{b}} = 0.02$ eV from I_2 to I_3, close to the corresponding one (0.01 eV) from I_{L2} to I_{L3} in the linear structure. However, for the second process (i.e., the Si–S bond formation and the associative H_2 desorption), we were unable to find the concerted reaction pathway, indicating a kinetically prohibited reaction. This result is consistent with the cluster DFT calculations[21] of FTR. Even though FTR could not find the concerted reaction pathway for the second process, they explored a complicated multistep process where (i) the S atom forms a bond with the surface Si atom, accompanying the S−H bond breaking, (ii) the dissociated H forms a weakly bound complex with the H on the same dimer, and (iii) the associative H_2 desorption occurs. FTR obtained larger energy barriers ($\sim$1.27 eV) from I_3 to the final (F) state compared to those ($\sim$0.88 eV in Ref. 21 and 1.08 eV in Ref. 20) from I_{L3} to the final (F_{L}) state in the linear structure.[21] These different behaviors in the second process between the branched and linear structures are possibly due to the fact that the branched structure containing the Si–C bond with the medial C atom is considerably more strained than the linear structure containing the Si–C bond with the terminal C atom, as pointed out by FTR.[21] As a matter of fact, the Si−Si distance between two Si dimers in the branched structure is 5.24 Å [see Fig. 1(b)], which is much shorter than 5.32 Å in the linear structure [see Fig. 1(a)]. Consequently, the dimer bond length in the branched structure becomes longer as 2.51 Å [see Fig. 1(b)], compared with 2.42 Å in the linear structure [see Fig. 1(a)].

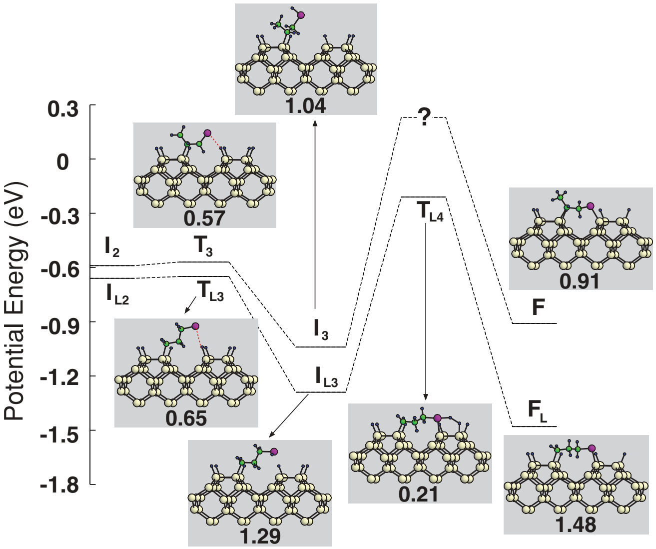

FIG. 3. (Color online) Calculated energy profiles along the reaction pathways for formations of the branched (upper) and linear (lower) structures. The atomic geometries of the transition, intermediate, and final states are given together with their adsorption energies (in eV).

It is worth noting that FTR[21] raised a problem for formation of the linear structure by pointing out that ALM and trimethylene sulfide (TMS) were experimentally observed[29] to exhibit the different line patterns even though both cases have the same S radical intermediate along their reaction pathways. Unlike the ALM line growing only across the dimer rows, TMS shows the line growth in a square wave pattern involving a chain reaction either across or along the dimer rows. However, it is notable that the different substrates, i.e., undoped[9] and n-type[29] Si(100) surfaces, were used in the experiments for the ALM and TMS line growths, respectively. Considering that the H-empty sites on undoped and n-type Si(100) surfaces contain an unpaired electron and two paired electrons, respectively, it is most likely that these different substrates would result in different reaction processes, leading to the different growth patterns as observed[9,29] in experiments. As a matter of fact, Pei, Ma, and Zeng[22] have already explained the different growth patterns in the ALM and TMS lines in terms of the attractive and repulsive electrostatic interactions of the S atom with a Si dimer in the adjacent dimer row, respectively, caused by undoped and n-type Si(100) substrates.

STM has proved to be a powerful tool for a direct view of adsorbed organic molecules on the Si(100) surface.[1–5] In their filled-state STM images of ALM lines, HKK[9] observed that each molecule produces the bright protrusion which is located on one edge of a Si dimer in the adjacent dimer row. Considering the fact that the C=C bond of the ALM molecule initially reacts with the single Si DB, HKK tentatively interpreted the observed bright protrusion in terms of the SH group.[9] For comparison with the STM measurements, we

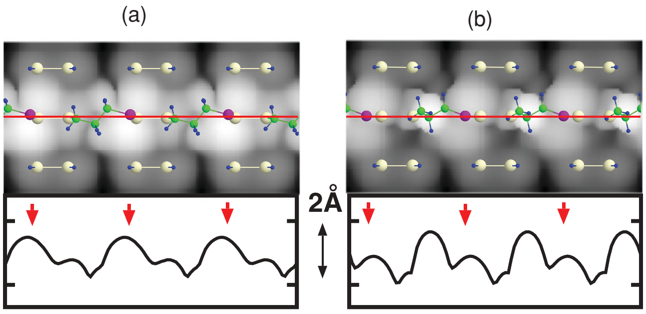

FIG. 4. (Color online) Simulated filled-state STM images of the infinite ALM line on the H-terminated Si(100) surface within (a) the linear structure and (b) the branched structure. The cross-sectional view along the ALM line is also included. The filled-state images were obtained by integrating the charge from occupied states within 1.2 eV of the highest occupied state. The images were taken at a charge density of 6.7×10^{-5} electrons/Å^3. The arrows in the cross-sectional view indicate the positions of the S atoms.

simulate the constant-current STM images for the filled states of the ALM line within the linear and branched structures using the Tersoff-Hamann approximation.[30] The results together with the cross-sectional view along the ALM line are displayed in Fig. 4. We find disparate features in the simulated filled-state STM images between the linear and branched structures. The linear structure produces the bright protrusion on one edge of a Si dimer in the adjacent dimer row [see Fig. 4(a)], originating from the lone pair of the S atom. On the other hand, the branched structure produces the bright protrusion on the initially reacted Si DB site [see Fig. 4(b)], originating from the methyl group. Thus, the linear structure well reproduces the features observed in the STM measurements,[9] such as the position and origin of the bright protrusion, whereas the branched structure fails to reproduce them.

In summary, we have investigated the growth mechanism and structure of ALM lines on the H-terminated Si(100)-2×1 surface using first-principles density-functional calculations. Our calculated energy profile along the reaction pathway showed that formation of the branched structure is kinetically unfavored over that of the linear structure. Moreover, the simulated STM image of the branched structure does not agree with the STM experiment.[9] Thus, we demonstrated that the branched structure recently proposed by a cluster DFT calculation[21] is not acceptable as a structural model of ALM lines.

This work was supported by National Research Foundation of Korea (NRF) grants funded by the Korean Government (KRF-314-2008-1-C00095 and KRF-2009-0073123).

---

[*] chojh@hanyang.ac.kr

[1] I. R. McNab and J. C. Polanyi, Chem. Rev. **106**, 4321 (2006).
[2] R. A. Wolkow, Annu. Rev. Phys. Chem. **50**, 413 (1999).
[3] S. F. Bent, Surf. Sci. **500**, 879 (2002) , and references therein.
[4] J. M. Buriak, Chem. Rev. **102**, 1271 (2002).
[5] M. A. Walsh and M. C. Hersam, Annu. Rev. Phys. Chem. **60**, 193 (2009).
[6] G. P. Lopinski, D. D. M. Wayner, and R. A. Wolkow, Nature (London) **406**, 48 (2000).
[7] P. Kruse, E. R. Johnson, G. A. DiLabio, and R. A. Wolkow, Nano Lett. **2**, 807 (2002).
[8] Md. Z. Hossain, H. S. Kato, and M. Kawai, J. Phys. Chem. B **109**, 23129 (2005).
[9] Md. Z. Hossain, H. S. Kato, and M. Kawai, J. Am. Chem. Soc. **127**, 15030 (2005).
[10] Md. Z. Hossain, H. S. Kato, and M. Kawai, J. Am. Chem. Soc. **130**, 11518 (2008).
[11] J.-H. Cho, D. H. Oh, and L. Kleinman, Phys. Rev. B **65**, 081310(R) (2002).
[12] J. K. Kang and C. B. Musgrave, J. Chem. Phys. **116**, 9907 (2002).
[13] P. Basu, N. P. Guinsinger, M. E. Greene, and M. C. Hersam, Appl. Phys. Lett. **85**, 2619 (2004).
[14] G. A. DiLabio, P. G. Piva, P. Kruse, and R. A. Wolkow, J. Am. Chem. Soc. **126**, 16048 (2004) , and references therein.
[15] J. L. Pitters, I. Dogel, G. A. DiLabio, and R. A. Wolkow, J. Phys. Chem. B **110**, 2159 (2006).
[16] Q. H. Wang and M. C. Hersam, J. Am. Chem. Soc. **130**, 12896 (2008).
[17] M. A. Walsh and M. C. Hersam, Chem. Commun. **46**, 1153 (2010).
[18] J. W. Lyding, T.-C. Shen, J. S. Hubacek, J. R. Tucker, and G. C. Abeln, Appl. Phys. Lett. **64**, 2010 (1994).
[19] T.-C. Shen, C. Wang, G. C. Abeln, J. R. Tucker, J. W. Lyding, Ph. Avouris, and R. E. Walkup, Science **268**, 1590 (1995).
[20] J.-H. Choi and J.-H. Cho, Phys. Rev. Lett. **102**, 166102 (2009).
[21] G. A. Ferguson, C. T. L. Than, and K. Raghavachari, J. Phys. Chem. C **113**, 18817 (2009).
[22] Y. Pei, J. Ma, and X. C. Zeng, J. Phys. Chem. C **112**, 16078 (2008).
[23] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. Sham, *ibid.* **140**, A1133 (1965).
[24] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396(E) (1997).
[25] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[26] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990); K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, *ibid.* **47**, 10142 (1993).
[27] J.-H. Cho and L. Kleiman, J. Chem. Phys. **121**, 1557 (2004); J.-H. Choi and J.-H. Cho, J. Am. Chem. Soc. **128**, 3890 (2006); J.-H. Lee and J.-H. Cho, Phys. Rev. B **76**, 125302 (2007); J.-H. Choi and J.-H. Cho, Phys. Rev. Lett. **98**, 246101 (2007).
[28] D. A. Wismer and R. Chattery, *Introduction to Nonlinear Optimization* (North-Holland, Amsterdam, 1978), pp. 174–178.
[29] S. A. Dogel, G. A. DiLabio, J. Zikovsky, J. L. Pitters, and R. A. Wolkow, J. Phys. Chem. C **111**, 11965 (2007).
[30] J. Tersoff and D. R. Hamann, Phys. Rev. Lett. **50**, 1998 (1983); Phys. Rev. B **31**, 805 (1985).