Honeycomb chain structure of the Au/Si(111)-(5×2) surface reconstruction: A first-principles study

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Models with a honeycomb chain feature for the Au/Si(111)-(5×2) surface reconstruction are systematically examined using first-principles calculations. The atomic and electronic structures of these models are analyzed in detail. Our calculation shows that one of these models has a lower surface energy than the previously proposed models by Erwin [Phys. Rev. Lett. **91**, 206101 (2003)] and by Riikonen and Sánchez-Portal [Phys. Rev. B **71**, 235423 (2005)]. This newly identified model also reproduces certain key features in the angle-resolved photoemission measurement and experimental scanning tunneling microscopy images.

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One-dimensional metal atomic wires on a semiconductor surface have generated huge research interests in recent years due to potential applications in the microelectronics industry. One of the prototypical systems under intensive studies is the gold-induced surface reconstructions on Si(111). Among the numerous Au-induced reconstruction phases on the Si(111), the (5×2) has attracted the most attention and has been extensively studied by experiment.[1–18] Although experimental measurements alone may not be enough for resolving the atomistic structure of the reconstruction, they impose a set of critical criteria that must be satisfied by any theoretical structural model.[19] One such criterion is that the simulated scanning tunneling microscopy images (STM) images of the theoretical models should exhibit bright protrusions with Y-shaped atomic features.[7–10] Another criterion requires agreement between the band structures of the models and the angle-resolved photoemission spectra (ARPES) data, which show a strong surface band beginning at the (5×2) zone boundary and disperses toward the (5×1) zone boundary.[12–15] In addition to satisfying the constraints imposed by experimental data, the correct theoretical structural model should also have lowest energy according to first-principles total energy calculations.

Technological advances in this field have made it possible for precisely calibrated experiments to determine the Au coverage of 0.4 ML when the (5×2) phase appears. This has allowed researchers to eliminate certain models outright and thus significantly reduce the number of candidate models to be considered. Two models at this coverage were proposed by Marks and Plass (MP)[18] and Hasegawa, Hosaka, and Hosoki (HHH)[6] based on their experimental data. However, theoretical studies show that neither model was found to be consistent with either STM or ARPES data.[19,20] Nevertheless, without an extra adatom, the underlying structure of the MP model is basically that of the honeycomb chain (HC) structure (see Fig. 4 in Ref. 18). An alternative structure—the Erwin model (E)—was obtained via a 180° rotation (with respect to the underlying substrate) of the honeycomb chain in the MP model.[18,19,21] Erwin noticed the presence of some overcoordinated Si atoms in the rhombic-shaped joint and suggested a (5×2) variant ($E(5\times2)$), which then removes some Si atoms in order to relieve overcoordination. In addition to having a lower surface energy than the MP and HHH models, the $E(5\times2)$ variant seems to satisfy some of the constraints imposed by experimental data. Recently, two structural models, one by Riikonen and Sánchez-Portal (RS)[21] and another by Chuang,[22] were proposed independently for the (5×2) surface reconstruction. These two models not only show the clear double honeycomb chain feature with different alignments of the two Au rows, but both are also energetically more favorable than the Erwin structure. Ren *et al.* also proposed an alternative (5×2) model based on the structure suggested by RS.[21,23] They found that the presence of Si adatom on the newly derived (5×2) model significantly improved the band structure.

Despite the numerous models that have been proposed previously, differences in surface energies among these models are found to be rather small.[18–23] Furthermore, all of these models exhibit a HC feature. Thus, a question arises as to what kind of optimal atomic arrangement the lowest energy model should have. It is therefore highly desirable to perform a comprehensive study on the honeycomb chain feature and thus resolve this issue definitively.

In this Brief Report, we systematically examine the atomic and electronic structures of the honeycomb chain models for Au/Si(111)-(5×2) surface by using first-principles calculations. First, the gold chains are combinatorially assigned on the honeycomb chain structure in order to generate a series of (5×1) HC models. Overall, 36 ($C_2^9=\frac{9!}{2!\times7!}=36$) models are generated using this method and further optimized. Among these 36 models, we are able to identify four previously proposed models (Marks and Plass, Erwin, Chuang, and Riikonen and Sánchez-Portal). In addition, we have identified a new model, which is lowest in surface energy but has not been reported yet in the literature. Next, we use this newly identified (5×1) model to derive up to 40 (5×2) models using several known methods. Then, these models are further optimized, out of which one turned out to have lowest surface energy. Finally, the band structures of the lowest energy model and the corresponding simulated STM images are presented.

The calculations were carried out within the generalized

TABLE I. The relative surface energies ΔE_s with respect to the HC16(5×1) model [meV per (5×2) cell] and the separations D (Å) between the two gold rows of the various structural models. MP, E, RS, and HC15 and HC16 represent the models proposed by Mark and Plass (Ref. 18), Erwin (Ref. 19), Riikonen and Sánchez-Portal (Ref. 21), Chuang (Ref. 22), and the newly identified model in this study, respectively. RS′ is similar to the RS model proposed by Ren *et al.* (Ref. 23). The numbers in parentheses are the relative surface energies calculated with a finer k-point grid of 3×7 and a higher energy cutoff of 312.5 eV.

Label	Model	ΔE_s	D (Å)	Model	ΔE_s
HC16	HC16(5×1)	0	7.47	HC16(5×2)	−178(−180)
HC13	RS(5×1)	+208(+261)	3.10	RS′(5×2)	+690(+567)
HC15	HC15(5×1)	+402(+404)	6.87	HC15(5×2)	+469(+484)
HC18	E(5×1)	+661(+640)	3.80	E(5×2)	+567(+563)
HC35	MP(5×1)	+883	3.80	MP(5×2)	+2366

gradient approximation as parametrized by Perdew, Burke, and Ernzerhof[24] to density functional theory[25] using projector-augmented-wave (PAW) potentials,[26] as implemented in Vienna *ab initio* Simulation package.[27] The reference configuration $6s^1 5d^{10}$ (to indicate valence electrons) is used for generating the Au PAW potential. The kinetic energy cutoff was set to 250 eV and the 2×4 Monkhorst–Pack grid was used to sample the surface Brillouin zone (BZ). Moreover, for all our surface calculations, the theoretical Si bulk lattice constant of 5.465 Å was used consistently throughout. The Au/Si(111)-(5×2) surface was modeled by a periodically repeating slab consisting of three Si bilayers, a reconstructed layer, and a vacuum gap of ~12 Å. In order to arrive at an optimum value for the vacuum gap of 12 Å, we have also calculated the energies for eight low energy models (listed in Table I) using 10 and 14 Å for the vacuum gaps and found that the differences in energies are all well within acceptable range [less than 1.1 meV per (5×2) cell]. Hydrogen atoms were used to passivate the Si dangling bonds at the bottom of the slab at a Si-H distance of 1.509 Å along the ideal crystalline directions and their positions were kept fixed. Similarly, the silicon atoms of the bottom bilayer were kept fixed at the bulk crystalline positions. All the models considered here were examined using a (5×2) supercell. The remaining Si and Au atoms were relaxed until the residual force was smaller than 0.01 eV/Å.

After computing the total energies of the models, the relative surface energy with respect to the HC16(5×1), ΔE_s, is calculated next using $\Delta E_s = E_{model} - E_{HC16} - \Delta N_{Si} \times E_{Si}$, where E_{HC16} and E_{model} are the total energies of the HC16(5×1) and other proposed models, respectively. E_{Si}, on the other hand, represents the chemical potential of Si bulk phase, while ΔN_{Si} is the difference in the number of the Si atoms with respect to the HC16(5×2) model. All models considered here are at the same Au coverage of 0.4 ML, and thus the relative surface energies will not depend on the choice of the Au chemical potential.

The atomic structure of the HC model is illustrated in Fig. 1(a). The numbers in the figure are used to label the positions of two gold chains along the $[\bar{1}10]$ direction. The (5×2) unit cell is outlined with red dotted lines. Gold, surface silicon, and the underlying silicon atoms are illustrated in blue, yellow, and white, respectively. To explore all the honeycomb chain models, the gold chains are first combinatorially assigned on the honeycomb chain structure to generate a series of (5×1) HC models. This method yielded 36 ($C_2^9 = \frac{9!}{2!\times 7!} = 36$) models, which are subject to further optimizations. The relative surface energies of selected important models are plotted in Fig. 1(b). The lowest energy honeycomb chain model turns out to be HC16, whose atomic structure is illustrated in Fig. 1(a). We are also able to identify

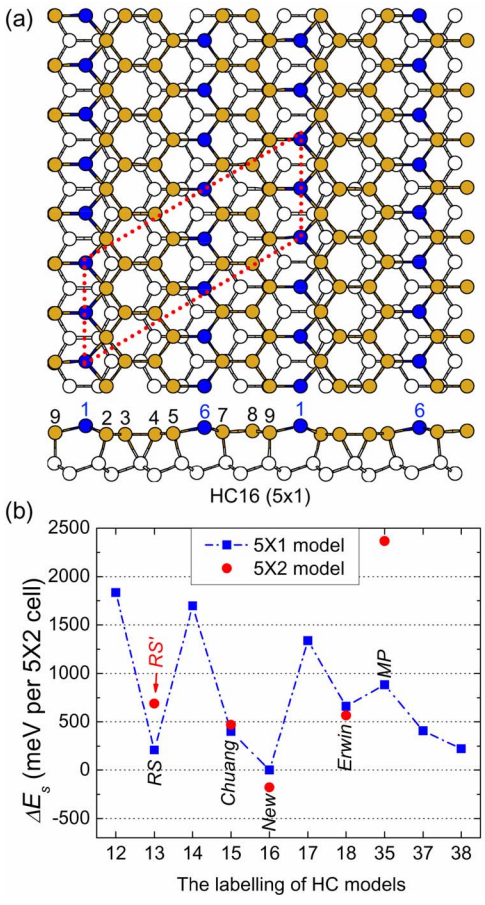

FIG. 1. (Color online) (a) Atomic structure of the double honeycomb chain model. The numbers in the figures are used to label the positions of gold chains along the $[\bar{1}10]$ direction. The (5×2) unit cell is outlined in red. (b) The relative surface energy with respect to the HC16 (5×1) model, ΔE_s [meV per (5×2) cell], as a function of various known models.

four earlier proposed models, namely, HC35, HC18, HC15, and HC13 which stand for Marks and Plass,[18] Erwin,[19] Chuang,[22] and Riikonen and Sánchez-Portal,[21] respectively. However, they all have higher surface energy than the HC16(5×1) model. A prior study indicated that the MP model (HC35) and Erwin model (HC18) are of different orientations with respect to the underlying substrate. Our own model nomenclature also allows us to label models, which have the same motif but different orientations with respect to the substrate.

Our calculations show that the substitution of Si atoms with Au atoms for all the models basically preserves the honeycomb structure. The relative surface energies (ΔE_s's), as well as the separations (D's) between the left (L) and the right (R) gold rows in the (5×1) phase are summarized in Table I. We note that the separation of the two gold rows in the HC16 model is the largest (7.47 Å) while that in the RS is the smallest (3.10 Å).

Having identified the (5×1) model, the (5×2) models can be created using the following schemes. First, following Marks and Plass' procedure, the (5×2) phase is created by adding one Si atom on every other (5×1) cell,[18] noting that for each of the (5×1) models there are four honeycomb sites on which to place the Si adatoms. Second, using Erwin's prescription, we remove a Si atom in every other (5×1) cell in order to create a (5×2) model.[19] Since there are seven Si atoms in each (5×1) cell, seven models for (5×2) can be created using the latter technique of removing Si atoms. Third, instead of atom removal, the (5×2) model is artificially produced via the creation of an asymmetric bulge of silicon atoms in the row as was employed by Riikonen and Sánchez-Portal.[21] Based on this idea, it is possible to create a new (5×2) model by displacing or distorting some atoms in two (5×1) cells. Last, one can combine these three methods to create the (5×2) cell as was done in our previous study.[23] In short, we have applied the above approaches to the newly identified HC16(5×1) model and have generated up to 40 (5×2) models out of it. Of these, we are able to identify one (5×2) model that is the lowest energy model and which has not been previously reported.

We found that though the removal of Si atom effectively preserves the honeycomb structure, a rebonded motif of a trimer and a pentamer ring with neighboring atoms is observed in some cases. This pattern has also been seen in a previous study.[23] We also found that the removal of a silicon atom in the Erwin model lowers the surface energy by 94 meV per (5×2) cell in agreement with the previous work by Erwin,[19] as shown in Table I. In some cases, removing every other Si atoms in a row increases the surface energies. Likewise, adsorption of an adatom could also result in lower or higher surface energy depending on the location of the adsorption site.

The surface energies of the HC16(5×1) and HC16(5×2) models are found to be lower than that of Erwin's. More significantly, the present results indicate that among the models considered here the HC16(5×2) variant is the most stable in energy. The rearrangement of one gold row in the HC16(5×2) leads to a 178 meV per (5×2) cell lowering of total energy with respect to the HC16 (5×1) case. See Table I and Figs. 3 and 1(a). This type of rearrangement has already been seen in the Ag/Si(111)-(3×1) case.[22] To verify that the HC16(5×2) model is indeed lowest in energy, the energies of the eight lowest energy models in the table are further calculated using a finer k-point grid of 3×7 for the surface BZ integration as well as a larger kinetic energy cutoff of 312.5 eV. We found that the energy ordering is mostly retained. The lone exception is in the RS′ (5×2) case, where we saw a big decrease in energy of about ~123 meV per (5×2) cell, thus taking it closer to the energy of E(5×2).

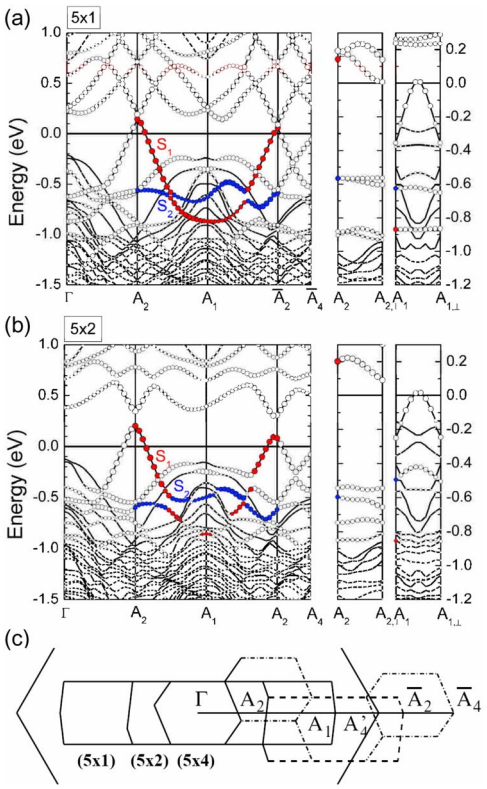

FIG. 2. (Color online) Band structures of the HC16 models for (a) (5×1) and (b) for (5×2). (c) Surface Brillouin zone for the Si(111)-(5×2)-Au surface reconstruction. Certain special points are indicated.

Having identified the lowest energy models HC16(5×2) and HC16(5×1), we now turn to the electronic structures of these two models. The electronic band structures of the HC16 models are plotted in Figs. 2(a) and 2(b). The symmetry line segments in the surface BZ are illustrated in Fig. 2(c). Obviously, besides the aforementioned stabilization in energy, the HC16(5×2) model reveals a clear surface band S_1 dispersing downward from the (5×2) zone boundary (A_2) toward the (5×1) zone boundary (A_1). Compared to the $E(5\times2)$ case, the corresponding S_1 bandwidth of about 1.0 eV is much closer to the experimental data.[12] The surface character of the S_1 band is even more pronounced in the HC16(5×1). In addition, we have also assigned the S_2 band, as shown in Figs. 2(a) and 2(b). The right panels of Figs. 2(a) and 2(b) demonstrate that neither the HC16(5×1) nor its (5×2) variant shows continuous dimensionality transition of the main surface band S_1.[12,15]

One of the key topographs in the experimental STM image for the (5×2) surface reconstruction is an array of

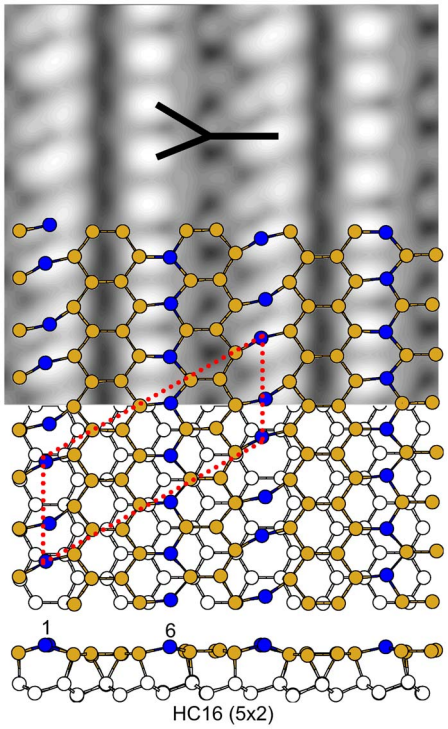

FIG. 3. (Color online) Simulated filled-state STM image with a sample bias of −0.8 eV and atomic structure of the HC16 (5×2) model.

Y-shaped features consisting of a pair of arms and one bright tail with a well-defined crystallographic orientation with respect to the underlying substrate.[6–10] The simulated STM image shown in Fig. 3 for the HC16(5×2) model with a sample bias of −0.8 V was calculated according to the theory of Tersoff and Hamann.[28] To help us highlight and identify the Y-shaped feature, a Y-shaped symbol is employed in the STM image in Fig. 3.

The calculated band structures and the simulated STM image only partly agree with experimental data. This raises the possibility that the model we have identified might not be the lowest energy model among the models with the honeycomb feature. Since our search was only limited to (5×1) with two Au rows, it is also possible that the Au atoms in two neighboring (5×1) cells do not lie in the same row. If this is indeed the case, a more exhaustive search is needed. Furthermore, this requires that the gold atoms be combinatorially assigned on the (5×2) honeycomb models. Thus, instead of 36 models, there are now additional 1512 models for the (5×2) phase to be optimized.[29] Compared with the initial number of models we have examined in this Brief Report, computing time requirement is 42 times greater, making it impractical to perform first-principles calculations. Instead, we have performed this combinatorial search using a Ag-Si tight-binding potential[22] and came up with the same result—HC16 is the model with the lowest energy.

In summary, models with the honeycomb chain feature for the Au/Si(111)-(5×2) surface reconstruction were systematically examined using first-principles calculations. Our calculations showed that the HC16(5×2) model is energetically more stable than any proposed models in the literature. More importantly, the strong surface band observed in angle-resolved photoemission was well reproduced in the HC16(5×2) model. Additionally, the simulated STM image of this model also recovered the Y-shaped feature seen in the experimental STM images.

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[1] H. E. Bishop and J. C. Riviere, J. Phys. D: Appl. Phys. **2**, 1635 (1969).
[2] H. Lipson and K. E. Singer, J. Phys. C **7**, 12 (1974).
[3] G. LeLay and J. P. Faurie, Surf. Sci. **69**, 295 (1977).
[4] C. Schamper *et al.*, Phys. Rev. B **43**, 12130 (1991).
[5] A. A. Baski *et al.*, Phys. Rev. B **41**, 10247 (1990).
[6] T. Hasegawa *et al.*, Surf. Sci. **357**, 858 (1996).
[7] J. D. O'Mahony *et al.*, Phys. Rev. B **49**, 2527 (1994).
[8] J. R. Power *et al.*, Phys. Rev. B **56**, 3587 (1997).
[9] H. S. Yoon *et al.*, Phys. Rev. Lett. **92**, 096801 (2004).
[10] H. S. Yoon *et al.*, Phys. Rev. B **72**, 155443 (2005).
[11] I. R. Collins *et al.*, Surf. Sci. **325**, 45 (1996).
[12] R. Losio *et al.*, Phys. Rev. Lett. **85**, 808 (2000).
[13] I. Matsuda *et al.*, Phys. Rev. B **68**, 195319 (2003).
[14] K. N. Altmann *et al.*, Phys. Rev. B **64**, 035406 (2001).
[15] J. L. McChesney *et al.*, Phys. Rev. B **70**, 195430 (2004).
[16] I. G. Hill and A. B. McLean, Phys. Rev. B **55**, 15664 (1997).
[17] H. M. Zhang *et al.*, Phys. Rev. B **65**, 035314 (2001).
[18] L. D. Marks and R. Plass, Phys. Rev. Lett. **75**, 2172 (1995); R. Plass and L. D. Marks, Surf. Sci. **380**, 497 (1997).
[19] S. C. Erwin, Phys. Rev. Lett. **91**, 206101 (2003).
[20] M. H. Kang and J. Y. Lee, Surf. Sci. **531**, 1 (2003).
[21] S. Riikonen and D. Sánchez-Portal, Phys. Rev. B **71**, 235423 (2005).
[22] F. C. Chuang, Ph.D. thesis, Iowa State University, 2005.
[23] C.-Y. Ren *et al.*, Phys. Rev. B **76**, 075414 (2007).
[24] J. P. Perdew *et al.*, Phys. Rev. Lett. **77**, 3865 (1996).
[25] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1135 (1965).
[26] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[27] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); G. Kresse and J. Furthmuller, *ibid.* **54**, 11169 (1996).
[28] J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985).
[29] For the (5×2) cell, there are 3060 ($C_4^{18}=\frac{18!}{4!\times14!}=3060$) models. Taking translational symmetry further into account and excluding previous 36 (5×1) models, only 1512 models are unique. ($\frac{3060-36}{2}=1512$.)