Theor Chem Account (2008) 120:79–83
DOI 10.1007/s00214-007-0296-4

REGULAR ARTICLE

Cluster study of surface radicals of Si(111)-7×7 reconstructed surface

Hee Soon Lee · Cheol Ho Choi

Received: 20 November 2006 / Accepted: 6 March 2007 / Published online: 21 April 2007

Abstract The Si(111)- 7 × 7 surface was theoretically investigated using four different QM/MM surface models. Although low-spin states turned out to be the ground states, there also exist low-lying high-spin states. The energy gap between the low-spin and the high-spin states per dangling bond is nearly constant (~4 kcal/mol) regardless of the number of dangling bonds in the model clusters, showing that no particular pattern of electron pairing among surface dangling bonds exists. Natural orbital occupation numbers showed that surface radicals due to dangling bonds have ideal open shell configurations. In addition to this, optimized geometries of the low-spin and the high-spin states are nearly identical with each other, suggesting the possibilities of intersystem crossings. So both low spin and high spin electronic configurations are important in the descriptions of the Si(111)- 7 × 7 reconstructed surface.

In contrast, geometric differences between pure QM and QM/MM models are significant especially near the adatom region, indicating that the QM/MM embedded model is necessary to adequately represent the Si(111)- 7 × 7 surface especially for small QM region models.

1 Introduction

Surface chemistry on semiconductor surfaces has gained enormous popularity recently and the interest is still growing. [1,2]. This may be partially due to the tremendous potential of the new functionalities of synthetically modified surfaces. From the chemical point of view, the well-ordered silicon surface provides a unique environment in which the traditional chemical knowledge can be applied.

One of the most well-studied and important silicon surfaces is Si(111)- 7 × 7 reconstructed surface [3]. Schlier and Farnsworth [4] first reported a 7 × 7 LEED (Low Energy Electron Diffraction) pattern for the clean Si(111) surface. After that, many structural models were proposed to account for this observation. The widely accepted structural model for this 7 × 7 reconstruction is DAS (Dimer-Adatom Stacking Fault Model) [5]. It involves large reconstructions of atoms within one (111) double layer. Before the reconstruction, the bulk-terminated (111) surface has one dangling bond per surface Si atom. The 7 × 7 reconstruction reduces these tricoordinated Si atoms from 49 to 19 in each unit cell yielding two triangular subunits (faulted and unfaulted halves). The remaining 19 dangling bonds for each unit cell are composed of 12 adatoms, 6 rest atoms and 1 corner atom. The adatoms are divided into two classes according to their position in the subunits: the corner adatoms sit in the corners of the subunits and the center adatoms sit in the center of the subunits. Each center adatom has two neighboring rest atoms, but only one for each corner adatom. A model of the adatom and the rest atom is presented in Fig. 1. The rest atom is in *para*-position of the adatom. As compared to rest atom, the adatom involves three highly strained 4-membered rings which would reduce its stability.

A considerable movement of atoms from their normal lattice positions in the unreconstructed surface to the positions in the (7 × 7) structure results in the surface being highly strained. In spite of this, the (7 × 7) structure is very stable and the transformation from the (2 × 1) cleaved surface is irreversible.

Since the resulted (7 × 7) surface provides a number of spatially and electronically nonequivalent reactive sites, the

---

Contribution to the Mark S. Gordon 65th Birthday Festschrift Issue.

H. S. Lee · C. H. Choi (✉)
Department of Chemistry, College of Natural Sciences,
Kyungpook National University, Taegu 702-701, South Korea
e-mail: cchoi@knu.ac.kr

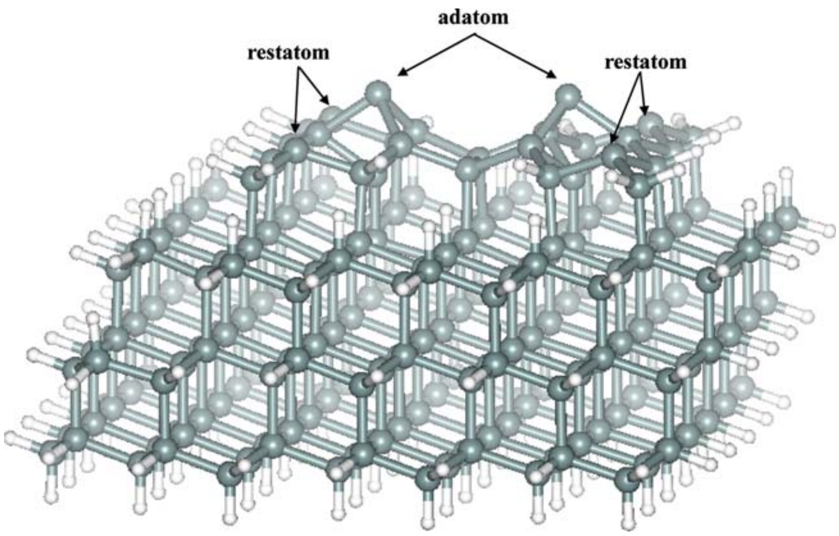

Fig. 1 The SIMOMM cluster model of Si(111)- 7 × 7 surface used in this paper

surface is expected to display diversities of adsorption configurations. Among these, an adatom coupled with one adjacent rest atom has been considered an important paired reactive site that can act as a strong dipole, making addition reactions of alkenes with Si(111)- 7 × 7 possible [6].

In the case of Si(100)-2 × 1 surface where the surface Si atoms dimerize with their neighboring atom yielding 2 × 1 reconstructed rows, a great deal of theoretical studies were performed to understand the characteristics of these dimer bonds. Redondo and Goddard [7] first showed that the dimerized bond of 2 × 1 reconstructed surface should be considered as a singlet diradical. Therefore, a qualitatively correct description of the surface dimer requires at least a generalized valence bond, GVB-PP (1) [8]. These conclusions were further supported by high level multi-reference calculations [9,10].

Detailed understanding of the characteristics of Si(111)- 7 × 7 surface is a prerequisite to properly study the surface chemical adsorption reactions. In addition, appropriate cluster design of the Si(111)- 7 × 7 surface is also important to correctly describe the surface chemistry. In this paper, the geometrical and the electronic structures of Si(111)- 7 × 7 surface were studied focusing on its multiconfigurational aspects. Various combinations of the surface-reactive dangle bond sites were systematically tested to analyze possible interactions among the surface-dangling bonds and their surface model dependencies.

2 Computational details

All-electron 6–31G(d) [11] basis set which has shown to provide quantitatively correct results in the studies of the similar surface systems [12–15] was used throughout this work. As discussed in the introduction, Si(111)- 7 × 7 surface carries radicals due to dangle bonds. Therefore, ROHF (Restricted Open Shell HF) and CASSCF (complete active space SCF) theories [16,17] were used as a reference wavefunctions for the correct high-spin and low-spin states, respectively. Since minimal active spaces for CASSCF are adopted, the wavefunction of the high-spin state becomes single configurational. This is why ROHF wavefunctions were chosen for the descriptions of the high-spin states. The active space was designed such that all dangling bonds are included. In order to recover the dynamic electron correlation, and to ensure that all parts of the reaction path are treated equivalently, single point energy evaluations with MP2 and multi-reference second order perturbation theories were performed for ROHF and CASSCF reference wavefunctions, respectively [18–21]. The GAMESS (General atomic and molecular electronic structure system) [22,23] program was used for all of the computations.

In order to study surface size-effects, a hybrid quantum mechanics/molecular mechanics (QM/MM) method called SIMOMM [24] (surface integrated molecular orbital molecular mechanics) was used. This approach embeds a smaller QM cluster in a much larger MM cluster in order to reduce or eliminate possible edge effects. MM3 [25–27] parameters were used for the molecular mechanics optimization part of the computations. All of the full geometry optimizations were done without imposing symmetry unless otherwise specified.

3 Results and discussions

As discussed in the introduction, the Si(111)- 7 × 7 surface contains a number of nonequivalent reactive dangling bond sites. Among these, dangling bonds in close proximity to each other can have the possibilities of pair interactions, which would affect the surface characteristics. Accordingly, four different QM models and their corresponding SIMOMM models of the Si(111) 7 × 7 surface were designed to systematically analyze these effects. The results of each model are discussed in order. The reference MM region of SIMOMM model for all the calculations is presented in Fig. 1. The corresponding QM regions are presented in Fig. 2.

3.1 9-Si model: one adatom + one rest atom

A simplest possible model that represents an adatom and a rest atom pair is 9-Si model as shown in Fig. 2a. This model shall be referred to as 9-QM, which can be considered as the corner adatom and its rest atom pair model. In addition to this purely quantum mechanical 9-Si model, a SIMOMM model is designed, where the 9-Si QM region is embedded in $Si_{247}H_{140}$ MM region (see Fig. 1). This is referred to as 9-SIMOMM. Since these two models contain two dangling bonds, 2 electrons and 2 orbitals CASSCF was used for the correct-singlet spin state. ROHF wavefunction were adopted for the description of triplet state, since only one configuration state function is possible out of two orbitals. Corresponding MRMP2 and MP2 single point energy evaluations were done, respectively, to recover dynamic electron correlations and the results are presented in Table 1. The two second-order Perturbation theories shall be referred to as PT2. The PT2 singlet-triplet energy gaps (ΔE_{S-T}) of 9-QM and 9-SIMOMM models are calculated to be 7.28 and 7.34 kcal/mol, respectively, with the singlet state being the ground state. Note that PT2 usually recover more electron correlations from the lower spin states than the higher ones due to the intrinsic correlations of the same spin electrons in the higher spin states. Since the singlet–triplet gap is small, the intersystem crossing between these two different spin states can be an important effect on the surface chemical reactions. Since ΔE_{S-T} of the 9-QM and the 9-SIMOMM are nearly identical, the effect of SIMOMM cluster on relative energies is minimal.

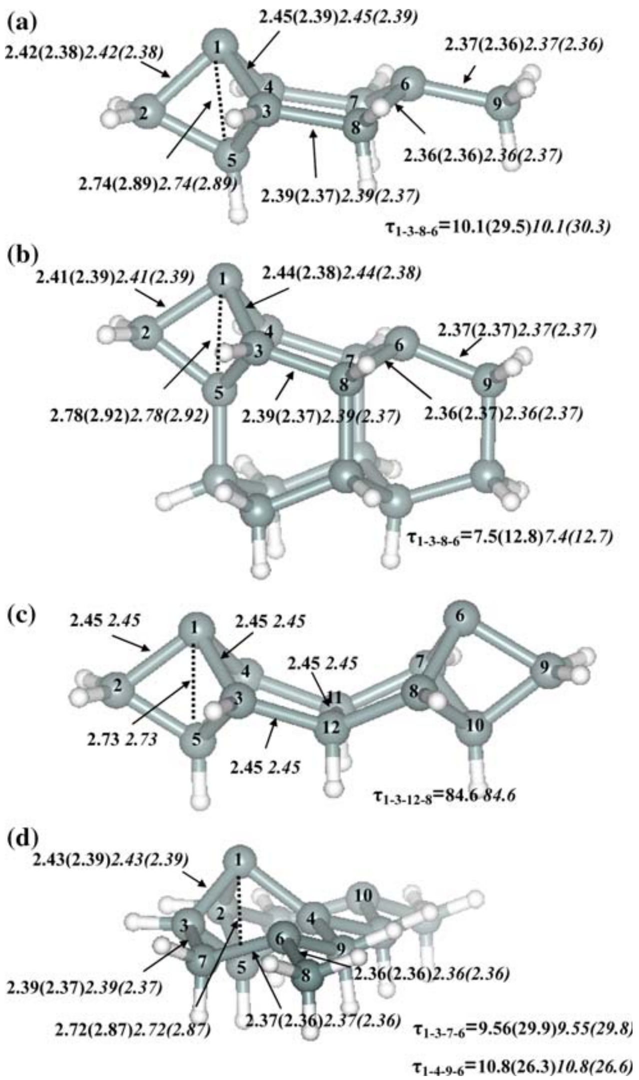

Fig. 2 QM part of SIMOMM models. The numbers and the numbers in *parenthesis* are from SIMOMM and pure QM calculations, respectively. The numbers in *italic* are the values of high-spin states. Bond lengths and torsional angles are in Angstrom and degree, respectively. **a** 9-Si model, **b** 16-Si model, **c** 12-Si model, **d** 13-Si model

However, the effect of SIMOMM on structure is significant. The three bonds directly attached to the adatom, Si_1 are increased by 0.04 Å, while the distance between Si_1 and Si_5 is reduced by 0.15 Å in 9-SIMOMM. Furthermore, the torsional angle of Si_1–Si_3–Si_8–Si_6 is reduced by 19.4° in 9-SIMOMM model. As compared to these, the differences in geometric data near the rest atom are minimal. These results can be expected, since the adatom is more strained than the rest atom so that it is more affected by SIMOMM model. In short, such large QM/MM effects on adatom geometries suggest that QM/MM model is equally necessary

Table 1 Relative energetics in kcal/mol between the low-spin and the high-spin states

	ΔE (CASSCF − ROHF)	ΔE (MRMP2 − MP2)
9-QM	0.029	−7.28 (3.64c)
9-SIMOMM	0.045	−7.34 (3.67)
16-QM	−0.063	−8.93 (4.46)
16-SIMOMM	0.014	−8.82 (4.41)
12-QM	–	–
12-SIMOMM	0.0087	−8.60 (4.3)
13-QM	0.017	−10.75 (3.58)
13-SIMOMM	0.024	−10.88 (3.63)

CASSCF wavefunction and MRMP2 energy correction were adopted to describe the low-spin states, while ROHF wavefunction and MP2 were adopted for the high-spin states

CASSCF (2,2)/6–31G(d) was used in all the model systems except 13-QM and 13-SIMOMM, where CASSCF (3,3)/6–31G(d) was used

Numbers in the parenthesis are EGPD (Energy Gap per Dangling bond) when one also deals with the chemical adsorption reactions at this particular site. The CASSCF (2,2) NOON(Natural Orbital Occupation Number) values of the singlet state of 9-SIMOMM, which is a good measure of multi-configurational character, are 1.00 and 1.00. These values clearly indicate that the two dangling bonds are ideal radicals with singlet configuration being slightly more stable than the triplet, further substantiating that CASSCF (2,2) is the minimal correct wavefunction for the singlet ground state of this model. As a result of small ΔE_{S-T}, the geometric data between the singlet and the triplet states are nearly identical within the same model, further increasing the possibilities of intersystem crossing. It can be also concluded that the surface radicals are highly local so that their spin configurations would not affect surface geometries.

The Mulliken population analysis shows that the charges on the adatom and the rest atom of 9-SIMOMM are −0.04 (−0.05) and −0.14(−0.20), respectively (see Table 2). Note that the numbers in the parenthesis are the corresponding values of 9-QM. The adatom is nearly neutral, while the rest atom is negatively charged. The bare 9-QM model overemphasizes the negative charge on the rest atom, which would significantly distort the surface reactivity toward the incoming adsorbates.

3.2 16-Si model: double layer model of one adatom + one rest atom

An improved model for the pair of an adatom and a rest atom would be the double layer model as shown in Fig. 2b, where the next layer is also included in the model as compared to Fig. 2a. This model is denoted as 16-QM. The corresponding 16-SIMOMM model is designed where the 16-Si QM region embedded in $Si_{247}H_{140}$ MM region. Again, the same CASSCF (2,2) wavefunction was adopted to describe the two dangling bonds.

Table 2 Mulliken Charges of adatoms and rest atoms in their low-spin states

	Adatom	Rest atom
9-QM	−0.05	−0.2
9-SIMOMM	−0.04	−0.14
16-QM	−0.01	−0.09
16-SIMOMM	0.0	−0.06
12-QM	–	–
12-SIMOMM	−0.04	−0.04
13-QM	0.0	−0.18
13-SIMOMM	0.04	−0.13

CASSCF (2,2)/6–31G(d) was used in all the model systems except 13-QM and 13-SIMOMM, where CASSCF (3,3)/6–31G(d) was used

The PT2 ΔE_{S-T} of 16-QM and 16-SIMOMM are calculated to be 8.93 and 8.82 kcal/mol, respectively, with the singlet state being the ground state. These energy differences are slightly increased by about 1 kcal/mol as compared to the 9-Si model.

Again, the effect of SIMOMM on structure is significant. The distance between Si_1 and Si_5 and the torsional angle of Si_1–Si_3–Si_8–Si_6 are reduced by 0.14 Å and 5.3 °, respectively, in 16-SIMOMM.

Overall, the improvements by 16-SIMOMM models over 9-SIMOMM are not significant indicating that 9-SIMOMM can be considered as already a good model for the adatom-rest atom pair. However, the improvements by 16-QM over 9-QM are relatively great showing that a large model is required, when only pure QM model is adopted.

3.3 12-Si model: two adatoms

The closest adatom pair appears at the junction of the faulted and the unfaulted halves of DAS model. A 12-QM model was designed to represent this pair as shown in Fig. 2c. The corresponding 12-SIMOMM model was also designed, where the 12-Si QM region embedded in $Si_{247}H_{140}$ MM. CASSCF (2,2) for singlet state geometry optimizations on the pure 12-QM model yielded unphysical structures, in which the two radicals Si_1 and Si_6 formed a σ bond. In contrast, the same geometry optimizations with 12-SIMOMM yielded proper structures for the two adatoms. The three directly attached bonds to the adatom as well as the Si_1–Si_5 distances are nearly identical to those of 9-SIMOMM and 16-SIMOMM indicating that SIMOMM method provides consistent models regardless of the design of SIMOMM model.

Again, the singlet and the triplet structures are nearly identical due to the energetic near degeneracy. The PT2 ΔE_{S-T} of 12-SIMOMM models are calculated to be 8.60 kcal/mol with the singlet state being the ground state. It is slightly increased by about 1 kcal/mol as compared to the pair of an adatom and a rest atom of 9-SIMOMM. Nonetheless, they are quite similar indicating that regardless of adatom or rest atom, the ΔE_{S-T} mostly depends on the number of dangling bonds.

In this particular model for the two adatoms, pure QM model failed to provide physically meaningful structure, while it is seen that the SIMOMM model consistently yielded proper geometries regardless of types of dangling bonds.

3.4 13-Si model: one adatom + two rest atoms

As compared to the the corner adatom that has only one near-by rest atom, the center adatom has two rest atoms. 13-QM model was designed to model this situation (see Fig. 2d). The corresponding 13-SIMOMM was also designed. Since these two models contain three dangling bonds, three electrons and three orbitals active space was used for the correct-doublet spin state. For the calculation of quartet state, ROHF quartet calculations were performed. The PT2 $\Delta E_{D\text{–}Q}$ of 13-QM and 13-SIMOMM models are calculated to be 10.75 and 10.88 kcal/mol, respectively, with the doublet state being the ground state. The doublet state CASSCF (3,3) NOON of the 13-SIMOMM are 1.01, 1.00 and 0.99. As in the other model studies, these values further indicate that the three dangling bonds are ideal radicals with doublet configuration being slightly more stable than the quartet. In order to compare these results with other models, it would be more useful to consider the energy gap per dangle bond (EGPD). Accordingly, the EGPD of the 9-SIMOMM and 13-SIMOMM are 3.68 and 3.63 kcal/mol, respectively. The values show that the energy gap due to the dangling bonds is nearly additive indicating that the paring interactions among dangling bonds are negligible.

As seen in the earlier models, the effect of SIMOMM on structure is significant. The three bonds directly attached to the adatom, Si_1 are increased by about 0.04 Å, while the distance between Si_1 and Si_5 is reduced by 0.15 Å in 13-SIMOMM. Furthermore, the torsional angle of Si_1–Si_3–Si_7–Si_6 is reduced by 20.34° in 13-SIMOMM model.

4 Conclusions

The reconstructed Si(111)- 7 × 7 surface was theoretically investigated using four surface QM/MM models, focusing on possible pair interactions among the surface dangling bonds. Although low-spin states turned out to be ground states, the energy gap between the low-spin and high-spin states is minimal in all of the model calculations. The EGPD (Energy Gap per Dangling bonds) from all model calculations is about 4 kcal/mol showing that the energy gap due to the dangling bond is nearly additive. All CASSCF calculations yielded nearly half-filled orbitals of active space showing that the dangling bonds have ideal open shell configurations.

The optimized geometries between the low-spin and the high-spin states is nearly identical, increasing the chance of intersystem crossing between different spin states, which may become an important factor in certain surface chemical reactions. So both low spin and high spin electronic configurations are important in the descriptions of surface chemical reactions.

In contrast, geometric differences between pure QM and QM/MM models are significant especially near the adatom region. In some test calculations, the small QM model failed to yield physically meaningful structures, showing that proper design of the cluster model is important. The geometric data among the four different SIMOMM models are nearly identical showing that the SIMOMM model is able to provide the geometric constraints of sub-surface layer to the top most layer consistently regardless of the QM/MM model.

Acknowledgments This work was supported by [R01-2004-000-10173-0(2006)].

References

1. Choi CH, Gordon MS (2001) Chemistry on silicon surfaces. In: Rappoport Z, Apeloig Y (eds) The chemistry of organic silicon compounds, vol 3. Chap. 15. Wiley, London, pp 821–852
2. Choi CH, Gordon MS (2004) Theoretical studies of silicon surface reactions with main group absorbates. In: Curtiss LA, Gordon MS (eds) Computational materials chemistry: methods and applications, Chap. 4. Kluwer, Dordrecht, pp 125–190
3. Walternburg HN, Yates JT Jr (1995) Chem Rev 95:1589
4. Schlier RE, Farnsworth HE (1959) J Chem Phys 30:917
5. Takayanagi K, Tanishiro Y, Takahashi S, Takahashi M (1985) Surf Sci 164:367
6. Tao F, Xu GQ (2004) Acc Chem Res 37:882
7. Redondo A, Goddard WA III (1982) J Vac Sci Technol 21:344
8. Bobrowicz FW, Goddard III WA Modern theoretical chemistry, vol. 3. Schaefer III HF (ed) Chapt. 4
9. Shoemaker J, Burggarf LW, Gordon MS (2000) J Chem Phys 112:2994
10. Gordon MS, Shoemaker J, Burggraf L (2000) J Chem Phys 113:9355
11. Hehre WJ, Ditchfield R, Pople JA (1972) J Chem Phys 56:2257
12. Choi CH, Gordon MS (2002) J Am Chem Soc 124:6162
13. Jung Y, Choi CH, Gordon MS (2001) J Phys Chem B 105(18): 4039–4044
14. Jung Y, Gordon MS, Doren DJ, Head-Gordon MJ (2003) Chem Phys 119:10917
15. Rintelman JM, Gordon MS (2004) J Phys Chem 108:7820
16. Ruedenberg K, Schmidt M, Gilbert MM, Elbert ST (1982) Chem Phys 71:41
17. Schmidt MW, Gordon MS (1998) Annu Rev Phys Chem 49:233
18. Werner H-J (1996) Mol Phys 89:645
19. Glaesemann KR, Gordon MS, Nakano H (1999) PCCP 1:967
20. Nakano HJ (1993) Chem Phys 99:7983
21. Nakano H (1993) Chem Phys Lett 207:372
22. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su S, Windus TL, Dupuis M, Montgomery JA Jr (1993) J Comp Chem 14:1347
23. Fletcher GD, Schmidt MW, Gordon MS (1999) Adv Chem Phys 110:267
24. Shoemaker JR, Burgraff LW, Gordon MS (1999) J Phys Chem A 103:3245
25. Allinger NL, Yuh YH, Lii JH (1989) J Am Chem Soc 111:8551
26. Lii JH, Allinger NL (1989) J Am Chem Soc 111:8566
27. Lii JH, Allinger NL (1989) J Am Chem Soc 111:8576