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Comparative study of adatom induced relaxations and energetics for Si, Ge and carbon adsorption on a (2 × 1) Si(001) surface

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Abstract. Surface complexes involving silicon, germanium and carbon adatom on predefined adsorption sites of the 2 × 1 reconstructed Si(001) surface are investigated for their energetics and associated structural relaxations. Tersoff's semi-empirical potential is used and the relaxations are obtained by employing the Monte Carlo simulated annealing technique. The results for the cases of Si, Ge and carbon adsorptions are compared. It is found that Si and Ge as adatoms on Si(001) 2 × 1 reconstructed surface behave in a similar fashion but the carbon adatom behaves in a markedly different way. Specifically, the carbon adatom induces a Si–C–Si chain configuration. It is also found that the adsorption sites between two dimer rows are the most favourable ones.

Keywords. Adatom adsorption; surface reconstruction.

1. Introduction

Simulations of crystal growth and surface kinetic phenomena have acquired an important place in materials research because they help in analysing the role played by different key parameters in the complex growth evolution process. With the advent of scanning tunneling microscopy, it has now become possible to confirm and validate the predictions made by such simulation results, which has given a further boost to research in this field. In order to understand the epitaxial growth on Si(001) surface which is a technologically important material, many theoretical/computational and experimental (Chadi 1979; Pandey 1982; Yin and Cohen 1982; Northrup 1985; Stillinger and Weber 1985; Dodson and Taylor 1986; Khor and Das Sarma 1987; Brocks *et al* 1991; Srivastava *et al* 1991; Toh and Ong 1991; Ronald and Gilmer 1992; Max Lagally 1993; Smith *et al* 1995) studies have been made over the past decades. The Si(001) surface is observed to reconstruct (dimerize) in a 2 × 1 atomic arrangement after annealing over the temperature range between 400 K and 0 K. Various groups have portrayed a clear picture of dimerized silicon surface and silicon adatom diffusion mechanism on it. To study such surface reconstruction and adatom diffusion on silicon surface, Monte Carlo and molecular dynamics approaches have been developed.

In this paper, we have used the Tersoff's (1989) semi-empirical potential to study adsorption of Si, Ge and C on Si(001) 2 × 1 reconstructed surface. We proceed to get a clean Si(001) 2 × 1 reconstructed surface using the known data about atomic displacements (Wang and Rockett 1991) and then allow a Si, Ge or C adatom to adsorb. We have used Monte Carlo simulated annealing because of its well established merits in the context of such problems.

2. Methodology

We used various adsorption sites on the Si(001) 2 × 1 reconstructed surface based on the works of Brocks *et al* (1991) and Toh and Ong (1991) (figure 1). The sample size was of eight layers with 64 atoms (8 × 8) in each layer, out of which, three layers of the bottom were held fixed and the atoms in the remaining five layers were allowed to move under Monte Carlo process. Periodic boundary conditions were applied in the lateral directions to simulate an infinite structure. The entire system was then allowed to relax and cool from 400 K to 0 K with the temperature reduction factor $\alpha = 0{\cdot}9$, as per Kirkpatrick *et al* (1983), for every ten thousand Monte Carlo steps, each Monte Carlo step being equivalent to four moves per atom. A 2 × 1 surface reconstruction was thus obtained by this simulated annealing technique. An adatom (Si, Ge or C) was then placed 1 Å above the relaxed reconstructed surface and the energy minimization process was repeated in each case.

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In the process, we obtained the energy of the adatom, its height relative to the relaxed surface and the dimer bond length for the final relaxed equilibrium state. Further we obtain the geometric structure for these equilibrium states.

3. Results and discussion

3.1 *Si(001) surface reconstruction*

Using the Monte Carlo simulated annealing technique with Tersoff's potential, we obtained defected 2×1 reconstructed surface (figure 2) having a mixture of symmetric and asymmetric dimerization for a variety of annealing schedules. To get a clean Si(001) 2×1 reconstructed surface, we used the known data about atomic displacements by Wang and Rockett (1991). It was observed that the dimerization took place by displacing atoms from their ideal bulk positions by 0·76 Å along the dangling bond direction (y-direction) resulting in the dimer bond length of 2·27 Å. We found that alongwith the dimerization a large inward relaxation of the topmost layer occurred into the bulk material. This inward relaxation which was distributed over five underlayers was found to be 16·25% (table 1).

Different groups (Pandey 1982; Yin and Cohen 1982; Dodson and Taylor 1986; Khor and Das Sarma 1987; Brocks *et al* 1991) have reported a (2×1) reconstruction energy/dimer of 1·7–2·2 eV and a dimer length in the range 2·22–2·41 Å with inward relaxation of about 17·5% of the top layer into the bulk. Our results are in good agreement with all these results.

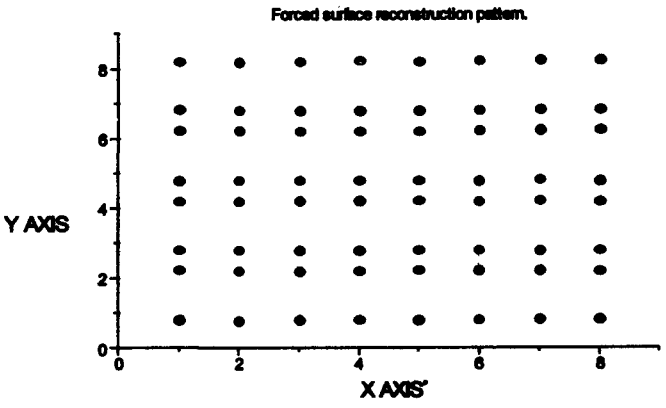

Figure 1. Si(001) 2×1 surface reconstructed pattern.

3.2 *Si, Ge and carbon adsorption*

The different adsorption sites namely F, D, B and A are defined in figure 1.

3.2a *Site F*: When a Si adatom is placed at this site F and the system is allowed to relax, it is observed that, adatom gets adsorbed at a distance of 0·55 Å below the surface at the same site (figures 3a and b). The germanium adatom placed at this site F also gets adsorbed but at a distance of 0·65 Å below the surface and 0·4 Å above the surface in few cases (figure 4). These results along with other results such as adatom–dimer atom bond lengths, dimer bond lengths, and other bondings are tabulated in tables 2 and 3 for Si and Ge respectively. Adatom–dimer bond lengths A–D1 and A–D2, in both the cases are large as compared to Si–Si and Si–Ge bond lengths which is in good agreement with the results reported by Brocks *et al* (1991) as well as Roland and Gilmer (1992). The energies of silicon adatom and that of germanium are found to be −3·62 eV and −3·56 eV, respectively and these are minimum amongst all adsorption sites studied here.

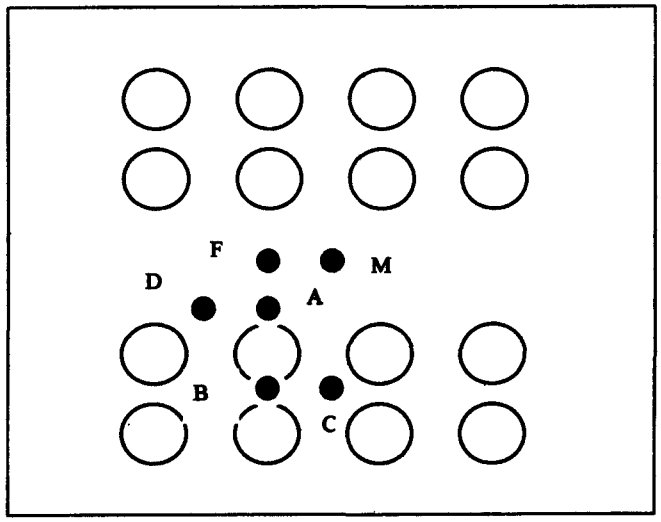

Figure 2. The Si(001) 2×1 surface with adatom binding sites labelled (sites are represented by dark circles).

Table 1. Si(001) 2×1 surface reconstruction.

Energy eV/dimer	Dimer length (l)	Inter dimer separation (w)	Separation betn dimer rows (n)	% Inward relaxation
−2·13 eV	2·27 Å	3·83 Å	7·68 Å	16·25

Carbon adatom at this site exhibits a markedly different behaviour. It migrates to site A forming a single bond with the dimer silicon (figures 5a and b) with bond length of 1·75 Å. Energy of the carbon adatom is – 1·96 eV which is due to formation of a single Si–carbon bond. The other geometric details are given in table 4.

3.2b *Site D*: When a Si adatom is placed at site D, it forms three bonds, out of which two are with dimer atoms which belong to the same dimer row and one with the subsurface atom. The peculiar behaviour to be noted for this site in case of Si adatom is that, when adatom forms bonds with dimer atoms, it pulls the front two dimer atoms by 0·5 Å towards each other (figures 6a and b). The adatom–dimer atom bond lengths are 2·36 Å and 2·34 Å, respectively (table 5). These are in good agreement with the results previously reported by Brocks *et al* (1991) and Smith *et al* (1995). Similar behaviour is observed in the case of Ge adatom. Germanium forms two bonds with dimer atoms of the same dimer row. The adatom–dimer bond length is 2·47 Å (table 6, figures 7a and b). No dimer opening is seen for the cases of both Si as well as Ge adatom. Adatom energies are – 2·16 eV and – 1·93 eV for Si and Ge, respectively.

In the case of carbon, it migrates to site M (figure 8) and forms a Si–C–Si chain with Si–C bond length of 1·82 Å (table 7). It is found that the neighbouring dimers do not open up. Adatom energy in this case turns out to be minimum i.e. – 3·89 eV, which suggests the tendency of carbon adatom to form silicon carbide stable structure.

3.2c *Site B*: In the case of both the Si and Ge adatoms, it is observed that when placed at this B site and allowed to move freely on the relaxed surface, they migrate to site C (figures 9a and b). In each case the adatom forms four bonds with the neighbouring dimer atoms with average bond length of 2·47 Å. Due to this type of bonding, dimers open up with bond length of 2·39 Å and 2·52 Å for silicon and germanium, respectively. Such type of migration and bond formation is also reported by Brocks *et al* (1991) and Srivastava and Garrison (1991). The energy of silicon adatom is – 2·89 eV and that of germanium is – 2·66 eV (tables 8 and 9).

In the case of a carbon adatom, it migrates from site B to site A and forms a bond with the dimer silicon

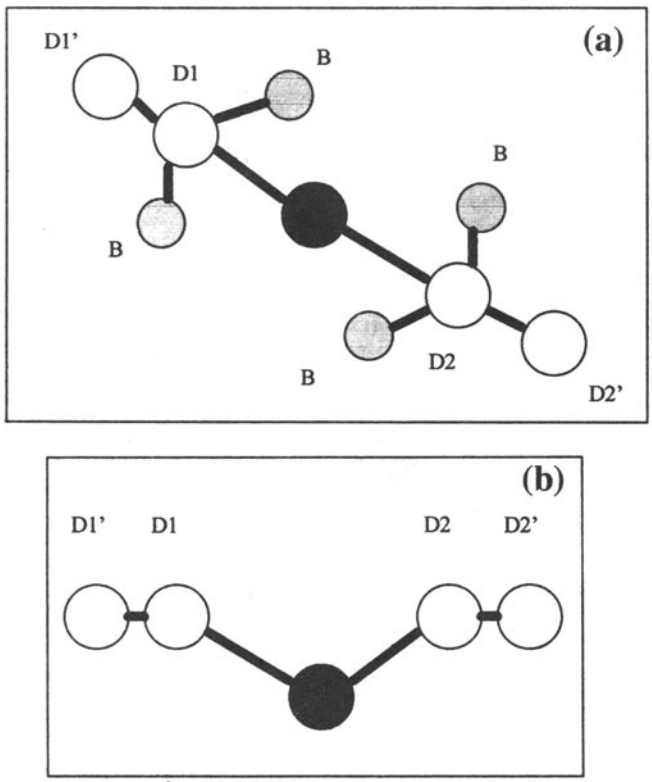

Figure 3. (**a**) Adsorption at site F and (**b**) adsorption below the surface layer.

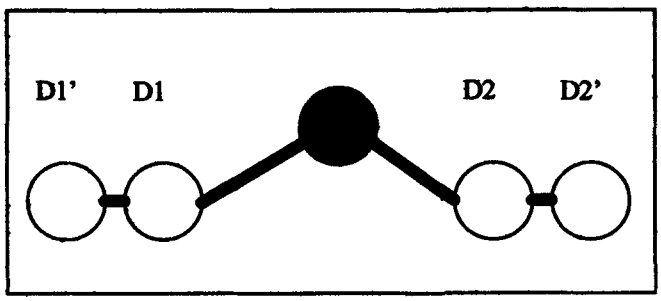

Figure 4. Adsorption above the surface layer.

Table 2. Silicon (site F).

Adatom energy	Adatom height	A–D1	A–D2	D1–D1′	D2–D2′
– 3·62 eV	– 0·55 Å	2·83 Å	2·76 Å	2·24 Å	2·27 Å

Table 3. Germanium (site F).

(a)

Adatom energy	Adatom height	A–D1	A–D2	D1–D1′	D2–D2′
– 3·56 eV	– 0·66 Å	2·76 Å	2·46 Å	2·35 Å	2·35 Å

(b)

Adatom energy	Adatom height	A–D1	A–D2	D1–D1′	D2–D2′
– 2·69 eV	0·4 Å	3·18 Å	2·69 Å	2·47 Å	2·26 Å

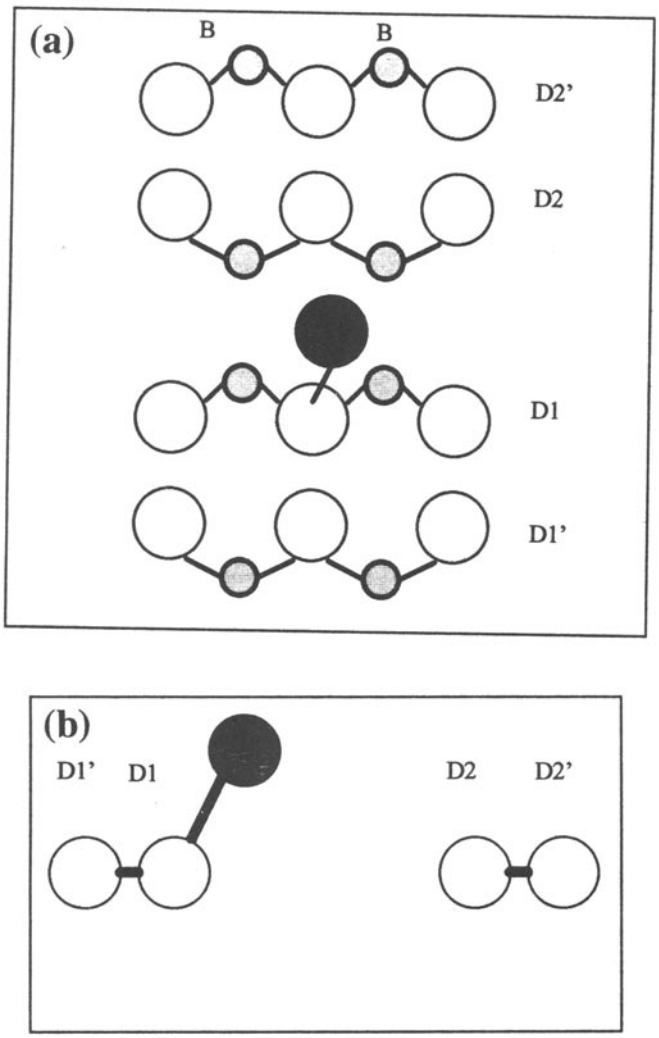

Figure 5. (**a**) Binding at site A and (**b**) adsorption above the surface at site A.

Table 4. Carbon (site F).

Adatom energy	Adatom height	A–D1	A–D2	D1–D1′	D2–D2′
– 1·96 eV	1·3 Å	1·75 Å	4 Å	2·27 Å	2·29 Å

atom with bond length 1·80 Å (figures 5a and b and table 10). The adatom energy in this case is – 1·96 eV.

3.2d *Site A*: When a silicon adatom is placed at this dangling bond site A (figure 10), it is seen that it migrates to site F (see figure 4) which is the minimum energy site amongst all the other sites. The energy of

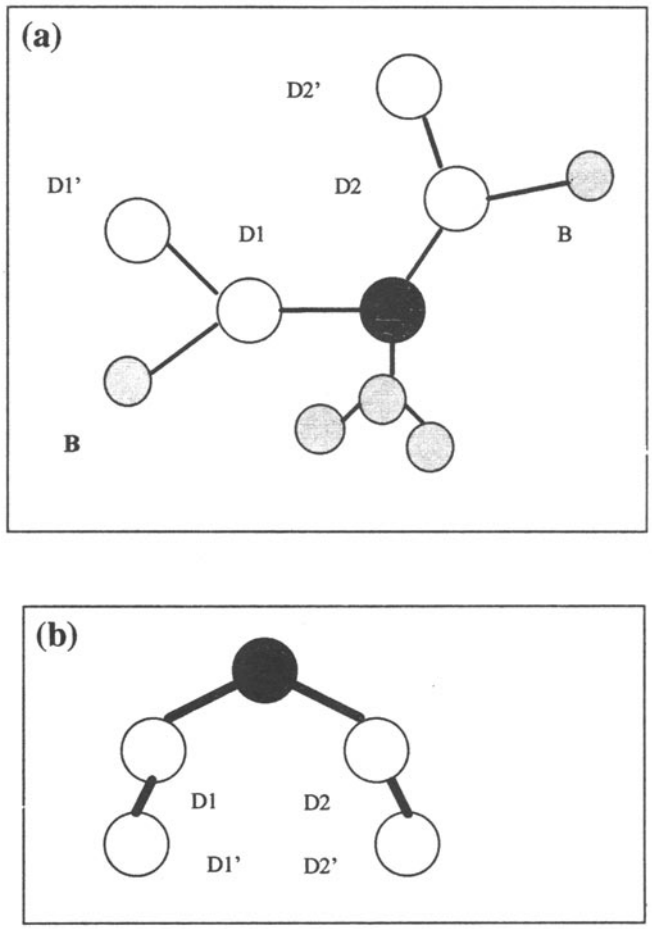

Figure 6. (**a**) Adsorption at site D, three bonds, two with neighbouring dimer atoms and one with subsurface atom and (**b**) adsorption at site D, adatom pulls front two dimer atoms towards each other.

Table 5. Silicon (site D).

Adatom energy	Adatom height	A–D1	A–D2	D1–D1′	D2–D2′	D1–D2	D1′–D2′	A–B
– 2·16 eV	1·63 Å	2·36 Å	2·34 Å	2·23 Å	2·23 Å	3·34 Å	3·76 Å	2·97 Å

Table 6. Germanium (site D).

Adatom energy	Adatom height	A–D1	A–D2	D1–D1′	D2–D2′	D1–D2	D1′–D2′	A–B
– 1·93 eV	1·99 Å	2·47 Å	2·47 Å	2·25 Å	2·24 Å	3·91 Å	3·83 Å	2·49 Å

the adatom at this site is – 3·64 eV with adatom–dimer atom separation of 2·63 Å and 2·82 Å (table 11). Germanium shows two different migrations: (i) it migrates from site A to site D (figures 6a and b) with energy – 2·0 eV and adatom–dimer atom bond length 2·43 Å (table 12a) and the front dimer atoms get pulled by 0·3 Å towards each other, and (ii) it migrates from site A to site M (figure 8) with an energy – 2·09 eV and adatom–subsurface atoms bond length of 2·36 Å (table 12b).

In the case of a carbon, the adatom forms a single Si–carbon bond with a bond length of 1·80 Å and energy of the adatom is – 1·96 eV (table 13 and figures 5a and b).

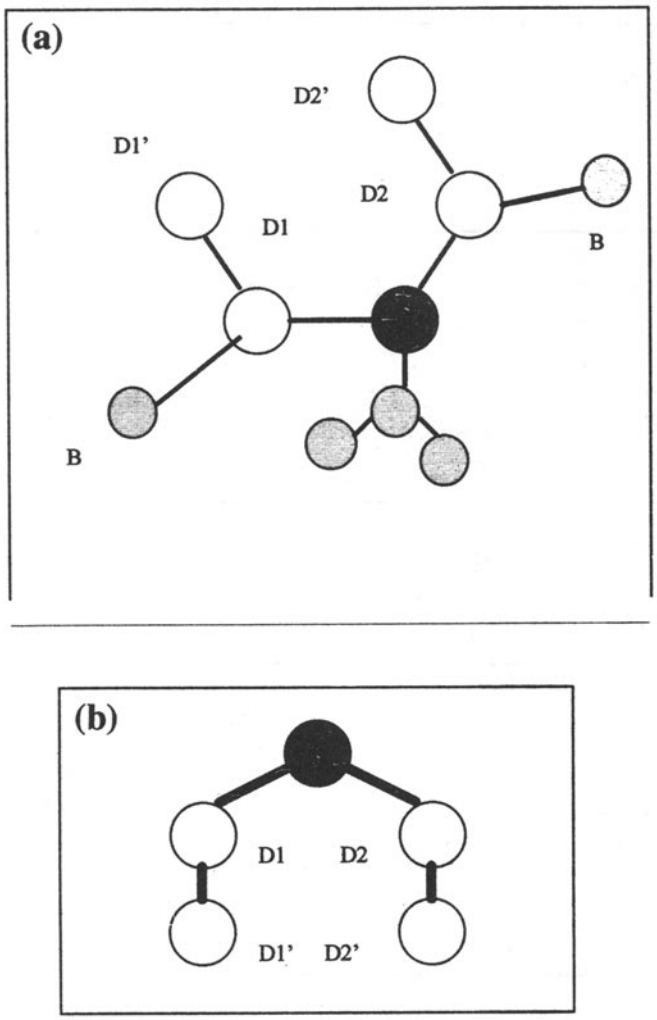

Figure 7. (a) Adsorption at site D, adatom do not pull front two dimer atoms and (b) top view of adsorption at site D.

4. Conclusion

In this paper, we have studied different adsorption mechanisms for Si, Ge and C adatoms and their energetics. It is found that, in case of both the silicon and germanium adatoms, site F is the minimum energy site. A somewhat different behaviour is observed for Si and Ge at site D; silicon pulls the dimer atoms towards each other to get adsorbed at that site, while this is not seen in the case of germanium. No dimer opening is observed except at site B and this may be due to migration to the site C (which is not an adsorption site).

As discussed earlier the carbon adatom at site D migrates to site M to form a Si–C–Si chain. This markedly different behaviour of carbon in comparison with that of Si and Ge, may get explained on the basis of the difference in the bond lengths of Si–C and Si–Ge or Si–Si. The bond length of Si–C is just 1·88 Å which

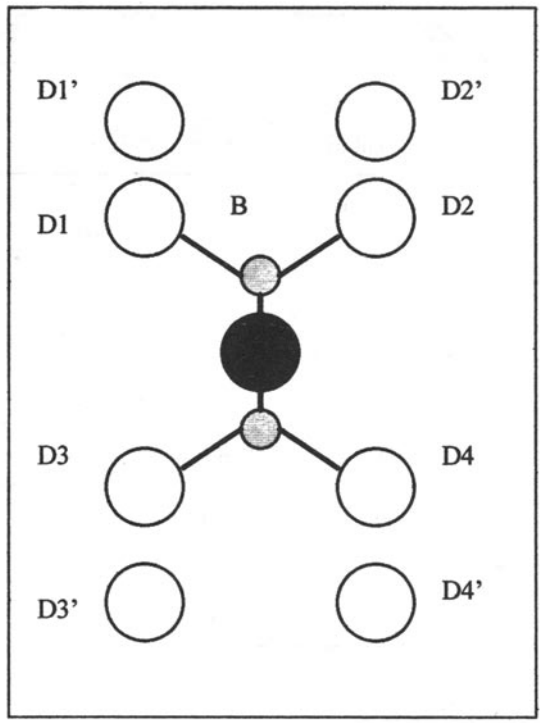

Figure 8. Adsorption at site M to form Si–C–Si chain.

Table 7. Carbon (site D).

Adatom energy	Adatom height A	A–B1	A–B1′	B1–D1	B1–D2	B1′–D3	B1′–D4	D1–D1′	D2–D2′	D3–D3′	D4–D4′
– 3·89 eV	0·16 Å	1·82 Å	1·82 Å	2·27 Å	2·32 Å	2·28 Å	2·32 Å	2·27 Å	2·26 Å	2·25 Å	2·26 Å

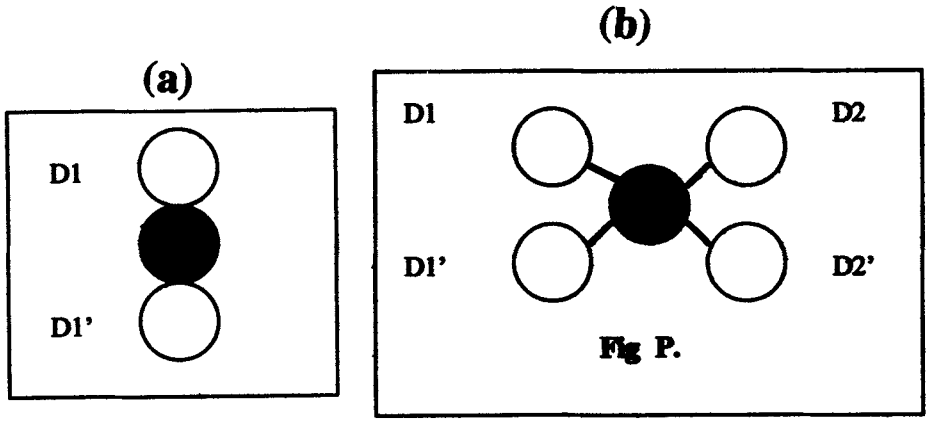

Figure 9. (a) Adsorption at site B and (b) site C with four bonds with neighbouring dimer atoms.

Table 8. Silicon (site B).

Adatom energy	Adatom height	A–D1	A–D1′	A–D2	A–D2′	D1–D1′	D2–D2′
– 2·89 eV	1·32 Å	2·46 Å	2·47 Å	2·47 Å	2·47 Å	2·38 Å	2·38 Å

Table 9. Germanium (site B).

Adatom energy	Adatom height	A–D1	A–D1′	A–D2	A–D2′	D1–D1′	D2–D2′
– 2·66 eV	1·60 Å	2·46 Å	2·47 Å	2·47 Å	2·47 Å	2·52 Å	2·45 Å

Table 10. Carbon (site B).

Adatom energy	Adatom height	D1–D1′	A–D1	A–D1′	D1–B	D1′–B
– 1·96 eV	1·9 Å	2·31 Å	1·80 Å	3·33 Å	2·29 Å	2·26 Å

is so small that carbon at site D is energetically unable to pull two front atoms of the two neighbouring dimers in order to form Si–C bonds on the surface. Also it is interesting to note that the site F, which is the lowest energy site for Si as well as Ge, is not a favourable site for carbon. It cannot form bonds with neighbouring dimer atoms of the adjacent dimer rows, again because of the short bond length of Si–C. However, after migrating to site M, it can form Si–C–Si bonds with subsurface Si atoms.

Table 11. Silicon (site A).

Adatom energy	Adatom height	A–D1	A–D2	D1–D1′	D2–D2′
– 3·64 eV	0·46 Å	2·63 Å	2·82 Å	2·31 Å	2·25 Å

Our calculations reveal that another possible adsorption site for carbon is site A, where carbon forms a single

Table 12. Germanium (site A).

(a)

Adatom energy	Adatom height	A–D1	A–D2	D1–D1′	D2–D2′	D1–D2	D1′–D2′
– 2·0 eV	1·7 Å	2·43 Å	2·43 Å	2·21 Å	2·23 Å	3·58 Å	3·81 Å

(b)

Adatom energy	Adatom height	A–B1	A–B2	D1–D1′	D2–D2′
– 2·09 eV	0·65 Å	2·36 Å	2·36 Å	2·27 Å	2·27 Å

Table 13. Carbon (site A).

Adatom energy	Adatom height	A–D1	D1–D1′	D1–B1	D1–B2	A–B1	A–B2
– 1·96 eV	1·14 Å	1·78 Å	2·32 Å	2·32 Å	2·34 Å	3·29 Å	3·08 Å

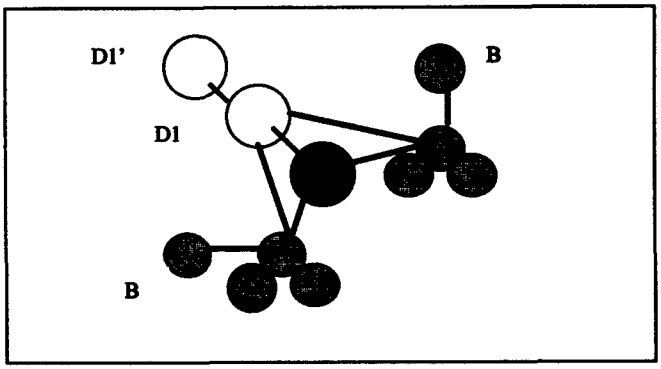

Figure 10. Top view of adsorption at site A (shaded circles represent sub surface atoms).

Si–C bond. Obviously this is a higher energy configuration as compared to site M, where it forms a most stable configuration with formation of Si–C–Si chain.

In conclusion, we have compared the adsorption of Si, Ge and C adatoms on the (2 × 1) reconstructed Si(001) surface using Monte Carlo simulated annealing procedure and Tersoff semi-empirical potential. The behaviour of C adatom is seen to be distinctly different as compared to that of Si and Ge adatoms.

The configurations and energies identified in this work could be useful in the problem of crystal growth from vapour phase.

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