A correlation study of sodium atom chemisorption on the silicon surface

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Abstract. Different possible adsorption sites of sodium atoms on a silicon surface have been investigated using *ab initio* self-consistent unrestricted Hartree–Fock total-energy cluster calculations with Hay–Wadt effective core potentials. The effects of electron correlation have been included by invoking the concepts of fourth-order many-body perturbation theory and are found to be highly significant. Bare silicon and hydrogen-bonded silicon cluster models have been employed to represent the silicon surface. We find that the Na atom adsorption across a dimer bond at the pedestal site modelled with an $NaSi_7(4, 2, 1)$ cluster is most favoured energetically, followed by Na adsorption at the cave site modelled with $NaSi_8(4, 2, 2)$. The effects of the charge transfer from Na to the silicon surface are also analysed and discussed.

1. Introduction

Alkali metal/silicon interfaces have been studied extensively both experimentally and theoretically because they present pertinent models for the study of chemisorption and because of their potential for important tehnological applications [1]. Most of the studies have concentrated on the chemisorption of K and Cs on the Si(001) surface [2–16] with several studies on the Na/Si interface. In this paper, we report on our continuing work on alkali metal chemisorption on semiconductor surfaces, namely the Na/Si system, with a summary of the relevant literature first.

Glander and Webb [17] have studied the adsorption of Na on Si(001) using two types of experiments, called the 'dosing' and 'equilibrium' experiments. They initially produced a well ordered 4×1 structure, which reverted to a 2×1 structure as the coverage increased. The saturation coverage is 0.68 of a monolayer (ML), but for low enough temperatures and a high enough Na pressure, bulk Na can grow in islands on the surface. Angle-resolved photoemission studies of Enta *et al* [18] showed that this 2×1 phase is preserved for alkali metal atoms adsorbing on the Si(001) surface and that the 2×1 surface consists of buckled dimers. Soukiassian *et al* [19], in a photoemission spectroscopy study, also considered the adsorption of Na and Cs on the Si(001) 2×1 surface. They found that the alkali metal atom induces an electronic interface state near the Fermi level and hybridization between Na 's' and Si 'p' valence electrons occurs. The alkali metal/silicon bonding was interpreted to be weak, polarized and covalent in nature and adsorbate metallization was implied.

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Theoretically, Northrup [20] in a study of the surface states of Na/Si(111) 1×1, using self-consistent pseudopotential total-energy calculations and the local density approximation, found the bonding between Na and surface Si atoms to be ionic with an Si–Na bond length of 2.71 Å. The bonding is apparently formed by the Na 3s orbitals and the dangling-bond orbitals on the Si surface. For 1.0 ML coverage, Na adsorption was found most likely to occur in the threefold hollow site. Batra [21], using a self-consistent pseudopotential method, has studied the electronic structures for Na adsorbed on Si(001) (2×1) at two different coverages. This study concluded that the bonding is ionic and that both the (hollow) pedestal and the bridge sites are favoured energetically at room temperature for Na adsorption at coverages of 0.5 ML and 1.0 ML, respectively. Kobayashi *et al* [22], using the local density approximation and the norm-conserving pseudopotential, found the most stable configuration to be the pedestal and the (trough) cave sites, with an earlier argument that the polarized covalent bond picture is more appropriate than strong ionic bonding. There does not appear to be a consensus for the adsorption of Na on the Si surface in terms of the preferred chemisorption sites, the extent of coverage and the nature of bonding.

All the theoretical studies have basically employed the local density approximation within the formalism of density functional theory. In our work, we propose to use an alternative formalism, namely *ab initio* unrestricted Hartree–Fock (UHF) theory to study the chemisorption of Na on Si by simulating the surface with finite Si clusters and hydrogen-bonded Si (SiH) clusters. It is well known that clusters are well suited for the study of semiconductor surfaces [23], and in general can yield accurate results of such properties as the chemical nature of a bond, bond length and other geometrical data [24]. In as much as the effects of electron correlation can be very significant, we have studied these by invoking the concepts of fourth-order many-body perturbation theory, as in our previous works on chemisorption [25–27].

This paper is organized as follows: in section 2 we discuss the basic theory and the computational method used, followed by the cluster models in section 3. The results of Na chemisorption on the clusters are presented in section 4, and in section 5 the bonding nature and charge density of the energetically preferred adsorption sites are discussed. A summary of the results and conclusions are presented in the final section.

2. Theory and the computational method

Both the unrestricted Hartree–Fock (UHF) theory and the many-body perturbation theory (MBPT), as used in this work, are well documented in the literature [28–33]. Here we present only a basic equation to define some terms. In MBPT, the energy is given by the linked diagram expansion

$$\Delta E = E - E_0 = E_1 + E_{\text{corr}} = \sum_{n=0}^{\infty} \langle \phi_0 | V[(E_0 - H_0)^{-1} V]^n | \phi_0 \rangle_{\text{L}} \tag{1}$$

where ϕ_0 is taken to be the UHF wavefunction, H_0 is the sum of one-electron Fock operators, E_0 is the sum of UHF orbital energies and $V = H - H_0$ is the perturbation, where H is the usual electronic Hamiltonian. The subscript L indicates the limitation to linked diagrams. Though one can include various categories of infinite-order summations from (1), the method is usually limited by termination at some order

of perturbation theory. In this study, we have carried out fourth-order calculations which consist of all single-, double- and quadruple-excitation terms.

Now one of the primary considerations involved in *ab initio* HF/MBPT calculations is the determination of the type of basis set to be used [34]. Basis sets used in *ab initio* molecular orbital computations usually involve some compromise between computational cost and accuracy. Keeping in mind the tremendous cost of *ab initio* calculations, specifically for large systems like sodium and silicon, we have elected to represent them by effective core potentials (ECP) or pseudopotentials (PP). In particular, we have used the Hay–Wadt effective core potential (HWECP) [35–36], which is known to provide almost exact agreement with all electron results, and for hydrogen the 3-21G basis set [29] has been used. All computations were done using the programs GAMESS [37] and GAUSSIAN 88 [38].

3. Si and SiH clusters

The clusters considered for this study, as shown in figure 1, are the bare silicon clusters, $Si_7(4, 2, 1)$, $Si_8(2, 4, 2)$ and $Si_8(4, 2, 2)$, which have been derived from the structural models of the top three Si surface layers around an adsorption site in a slab geometry [21], and the hydrogen-bonded silicon clusters, $Si_7(4, 2, 1)H_8$, $Si_7(4, 2, 1)H_{12}$, $Si_9(2, 5, 2)H_{12}$ and $Si_9(2, 5, 2)H_{14}$, which had been considered earlier for K chemisorption [4]. The numbers in parentheses represent Si atoms in each layer; the first number refers to the layer closest to the adsorbate atom. All atomic positions were completely optimized (no constraints); a significant improvement over the fixed symmetric dimer model previously reported in the literature. The bond length between the surface and subsurface atoms (interlayer bonds) for the various clusters are shown in table 1, and the total energies are given in table 2.
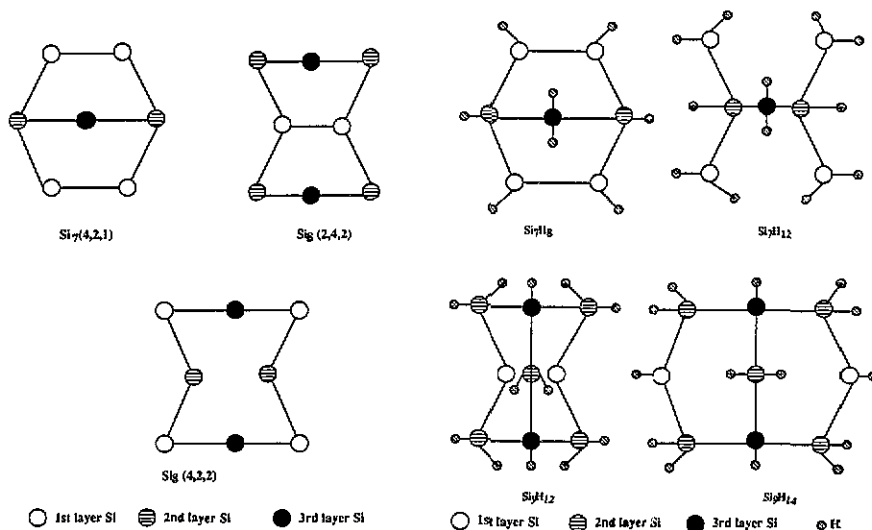

Figure 1. Si and SiH clusters.

The three-layer bare Si cluster, namely $Si_7(4, 2, 1)$, is appropriate for the pedestal (hollow) site chemisorption, and for the hydrogen-bonded cluster Si_7H_8, four hydrogen atoms are used to tie up the dangling bonds above the surface. The surface

Table 1. Optimum geometries of Si and SiH clusters.

Cluster	d (Å)						
	Si_7	Si_7H_8	Si_7H_{12}	$Si_8(2,4,2)$	$Si_8(4,2,2)$	Si_9H_{12}	Si_9H_{14}
Si_1–Si_1	2.61	2.13	2.44/3.41	2.52	2.91	2.34	3.81
Si_1–Si_2	2.37	2.35	2.34/2.42	2.42	2.30	2.34/2.42	2.38
Si_2–Si_3	2.38	2.37	2.34	2.42	2.30	2.34/2.35	2.37

Table 2. Total energies (au) of Si and SiH clusters.

Cluster	SCF	MP2	MP3	MP4
Si_7	−25.944 81	−26.265 18	−26.294 20	−26.311 54
Si_7H_8	−30.784 84	−31.131 17	−31.190 70	−31.207 49
Si_7H_{12}	−32.994 59	−33.337 45	−33.411 73	−33.432 19
$Si_8(2, 4, 2)$	−29.653 39	−30.193 00	−30.140 44	−30.176 07
$Si_8(4, 2, 2)$	−29.608 86	−29.962 14	−29.999 85	−30.022 39
Si_9H_{12}	−40.628 76	−41.066 82	−41.147 41	−41.170 13
Si_9H_{14}	−41.759 03	−42.200 13	−42.288 67	−42.312 30

dimer bond length of 2.61 Å for the bare silicon cluster is in good agreement with the low-lying triplet geometry of an earlier cluster calculation [23] that obtained a value of 2.66 Å. For the SiH cluster, the optimized Si surface dimer has a bond length of 2.13 Å and the Si–H bond length is 1.47 Å. The interlayer bond lengths for both clusters, however, are about the same, as can be seen from table 1, and approach the bulk Si nearest-neighbour distance. The binding energy obtained for Si_7 is 3.06 eV per atom. For a pentagonal bipyramidal geometry of this cluster size, Rohlfing and Raghavachari [39], using the same HWECP but with a contracted basis and a d function added, obtained a binding energy of about 3.80 eV.

The cluster Si_7H_{12}, appropriate for valley bridge site chemisorption, has four surface-layer Si atoms and eight hydrogen atoms to saturate the dangling bonds. The surface Si–Si bond lengths of the dimers are very much elongated (2.44 Å and 3.41 Å) but the interlayer bonds are close to the bulk Si bond length. The Si–H bond lengths at the lower layers are 1.47 Å and become more relaxed at the surface (1.48–1.51 Å).

For the bare Si cluster $Si_8(2, 4, 2)$, appropriate for bridge site chemisorption, the optimized structure has a surface-symmetric dimer bond of 2.52 Å with interlayer bonds of 2.42 Å. The bare Si cluster $Si_8(4, 2, 2)$, appropriate for cave site adsorption, has two symmetric surface dimers at the hollow site. The surface dimer bond lengths of 2.91 Å are much longer, however, and are close to the dimensions of the cave apertures of 2.98 Å given by Levine [40]. Interlayer bonds of 2.30 Å are shorter than in any of the clusters considered. We observe here that the total energies for the Si_8 clusters used to model the bridge and cave adsorption geometries compare favourably with those of the optimized ideal, bulk-terminated lattice of the Si(001) 2×1 surface [41], the symmetric model of Batra [42] or the asymmetric model of Yin and Cohen [43]. For the bicapped octahedral structure of Si_8, Rohlfing and Raghavachari obtained a binding energy of about 2.2 eV, while our values are 3.42 and 2.89 eV per atom for $Si_8(2, 4, 2)$ and $Si_8(4, 2, 2)$, respectively.

The atomic positions of the optimized cluster for the hydrogen-bonded cluster Si_9H_{12} are totally asymmetric. In this case, one Si atom of the surface dimer protrudes
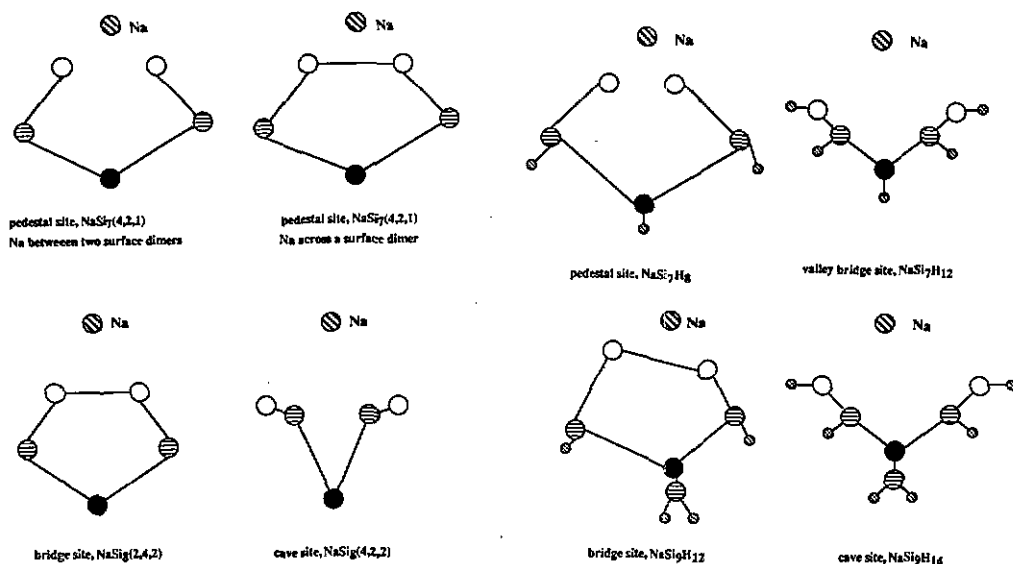
Figure 2. Side view of optimized chemisorption sites.

out of the surface while the other moves away from the surface resulting in an asymmetric surface dimer with a bond length of 2.34 Å. This is in agreement with an earlier MINDO (modified intermediate neglect of differential overlap) calculation that found the minimum energy configuration for this cluster to be the asymmetric dimer [44]. Interlayer bonds vary between 2.34 Å and 2.42 Å with Si–H bond lengths of about 1.48 Å. For the hydrogen-bonded silicon cluster Si_9H_{14}, interlayer bonds of 2.37 Å and 2.38 Å again approach that of bulk Si bond length, while the Si–H bonds of 1.48 Å are in agreement with MINDO [45] and *ab initio* [46] calculations for this cluster. The surface symmetric dimer bond length of 3.81 Å compares with the value of 3.84 Å for an ideal Si(001) lattice [41].

4. Na chemisorption

Several possible chemisorption sites were investigated by placing the Na adatom at different approach positions above the surface-layer Si atoms of the optimized clusters, as shown in figure 2. The total energies for the interaction of the Na atom with the clusters are calculated as a function of the vertical height of the Na atom above the surface-layer Si atoms, yielding the optimum vertical height. Substrate relaxation due to the adatom was not considered. This optimum geometry was then used to calculate the fourth-order perturbation theory energy eigenvalues shown in table 3. To determine the relative stability of chemisorption at the different sites, the chemisorption energies E_c are calculated from

$$E_c(Si_m/Si_mH_n) = E(Na) + E(Si_m/Si_mH_n) - E(Na\text{–}Si_m/Si_mH_n) \qquad (2)$$

and shown in table 4. We had successfully applied this technique to the Li atom chemisorption on the Si surface [47] to clearly identify the chemisorption site that a scanning tunnelling microscopy study [7, 8] had proposed.

Table 3. Total energies (au) of NaSiH clusters.

Cluster	SCF	MP2	MP3	MP4
NaSi$_7$	−26.198 69	−26.521 50	−26.548 03	−26.567 37
NaSi$_7$ [a]	−26.185 09	−26.531 02	−26.551 16	−26.569 63
NaSi$_7$H$_8$	−30.966 44	−31.303 19	−31.362 58	−31.380 27
NaSi$_7$H$_8$ [a]	−30.953 65	−31.297 26	−31.356 67	−31.373 11
NaSi$_7$H$_{12}$	−33.174 79	−33.528 15	−33.601 59	−33.622 18
NaSi$_8$(2, 4, 2)	−29.885 14	−30.376 31	−30.346 45	−30.372 46
NaSi$_8$(4, 2, 2)	−29.820 29	−30.206 21	−30.232 61	−30.256 88
NaSi$_9$H$_{12}$	−40.861 92	−41.289 64	−41.370 25	−41.393 37
NaSi$_9$H$_{14}$	−41.953 45	−42.399 08	−42.485 71	−42.508 83
NaSi$_9$H$_{14}$ [b]	−41.953 44	−42.399 07	−42.485 71	−42.508 83

[a] Na across the dimer bond.
[b] Na at the middle of the cave.

Table 4. Chemisorption energies (eV) of NaSiH clusters.

Cluster	SCF E_c	MP2 E_c	MP3 E_c	MP4 E_c
NaSi$_7$	1.98	2.05	1.98	2.04
NaSi$_7$ [a]	1.61	2.31	2.17	2.10
NaSi$_7$H$_8$	0.02	−0.24	−0.25	−0.22
NaSi$_7$H$_8$ [a]	−0.33	−0.41	−0.41	−0.42
NaSi$_7$H$_{12}$	−0.02	0.26	0.24	0.25
NaSi$_8$(2, 4, 2)	1.38	0.06	0.68	0.42
NaSi$_8$(4, 2, 2)	0.83	1.72	1.41	1.46
NaSi$_9$H$_{12}$	1.42	1.14	1.14	1.15
NaSi$_9$H$_{14}$	0.37	0.49	0.44	0.42
NaSi$_9$H$_{14}$ [b]	0.37	0.49	0.44	0.42

[a] Na across the dimer bond.
[b] Na at the middle of the cave.

For the pedestal site, two approach positions were investigated: Na at the centre between the two surface dimers for a 0.5 ML coverage and across the dimer bond. The optimum adsorption position for Na between the dimers is 4.54 au above the surface-layer Si atoms with an average Na–Si bond of 3.26 Å and a chemisorption energy of −0.22 eV for the Na–Si$_7$H$_8$ cluster. Adsorption at this approach position for this cluster is thus not binding. For the same approach position for the Na–Si$_7$ cluster, the optimum position of Na is 4.60 au above the Si surface with a bond of 3.42 Å and a chemisorption energy of 2.04 eV. Na adsorption across the dimer bond for the Si$_7$H$_8$ cluster with an optimum NaSi bond length of 3.03 Å is not binding (negative chemisorption energies), as can be seen from table 4. Adsorption for this approach position on Si$_7$, on the other hand, is a very energetically favourable adsorption site with a chemisorption energy of 2.10 eV. The optimum Na–Si bond length of 3.02 Å is identical with that of Na–Si$_7$H$_8$.

At the valley bridge site (Na–Si$_7$H$_{12}$), Na adsorbs between the surface asymmetric dimers at an optimum height of 3.68 au above the surface-layer silicon atoms with an average Na–Si bond length of 3.40 Å. The chemisorption energy E_c at the SCF level is not binding (−0.02 eV), but is binding with E_c of 0.25 eV when electron correlation effects are accounted for in the calculation. In our previous study of Li

atom chemisorption [47], this site was the least binding (lowest E_c).

Adsorption at the bridge site modelled with $Na-Si_9H_{12}$ resulted in a chemisorption energy of 1.15 eV with an optimum Na–Si bond length of 3.09 Å. For the $Na-Si_8(2, 4, 2)$ cluster modelling the bridge site, with the adatom above a surface dimer, an almost identical Na–Si bond length of 3.08 Å was obtained with a chemisorption energy of 0.42 eV. It should be noted that the chemisorption energies for the two bridge-model clusters are higher at the SCF level than at the MP4 level.

For the cave site ($Na-Si_9H_{14}$), adsorptions between the symmetric surface dimer and at the middle of the cave gave almost identical results: an Na–Si bond length of 3.32 Å and chemisorption energy of 0.42 eV. We obtained basically the same result for $LiSi_9H_{14}$. For the $Na-Si_8(4, 2, 2)$ cluster, the optimum Na–Si bond length is 3.36 Å and the chemisorption energy of 0.83 eV at the SCF level is less binding than that of the bridge models. However, when electron correlation effects are included, this site becomes more binding with a chemisorption energy of 1.46 eV than the bridge site model.

The above results suggest that for the adsorption sites modelled with the hydrogen-bonded silicon clusters, the bridge site is favoured energetically. For the bare silicon clusters, however, the pedestal (hollow) site is found to be most favourable. If one considers simultaneous adsorption, pedestal followed by cave sites seem to be most favourable. This is in agreement with the recent studies of Kobayashi *et al* [22] and Zhang *et al* [48].

5. Bonding and charge density

The valence charge densities of the clean silicon surface and the sodium-adsorbed surface (energetically favoured sites) are shown in figure 3. The charge-density contours for the Si_7 clean surface are shown in the vertical xz and yz planes perpendicular to the surface. The contours for this surface in the same planes are shown next after the adsorption of Na. It can be seen that there are no significant changes in the Si surface on the adsorption of sodium. Also, while the charge density around Na has a comparatively low-density distribution, clearly, the Na charge density is not depleted. This is because there is only a partial charge transfer, Δq, of $0.52e$ and $0.43e$ for sodium atoms adsorbing between the surface dimers and across a surface dimer bond, respectively. Contour plots of $Si_8(4, 2, 2)$ and $NaSi_8$ also do not show any remarkable difference from that of the clean surface; the shapes of the contours remain similar. In particular, the Na charge density is not depleted. The charge transfer from Na to the Si substrate in this case is $0.53e$. The same pictures emerge from Si_9H_{12} and $NaSi_9H_{12}$. The Na adatom is not completely ionized on adsorption to the silicon surface.

An analysis of the wavefunction coefficients shows that the highest occupied molecular orbital and the lowest occupied molecular orbital (HOMO–LUMO) states of the surface layer atoms of the Si_7 cluster before Na adsorption consist principally of p (p_y and p_z) states. On the adsorption of Na, the Si HOMO–LUMO states remain the p states (p_y and p_x) and the Na states are basically s and p. Also, the HOMO states are pushed up slightly in energy ($\Delta E = 0.42$ eV). For $Si_8(4, 2, 2)$, the HOMO–LUMO states for Si surface atoms are mainly p_x and p_z. For the adsorbed surface ($NaSi_8$), the Si states remain p (p_x and p_y) and the Na states are s and p. Almost the same situation is obtained for Si_9H_{12} and $NaSi_9H_{12}$: p_y and p_z for

Total density of si7. x–z plane.

Total density of si7. y–z plane.

Total density of nasi7. x–z plane.

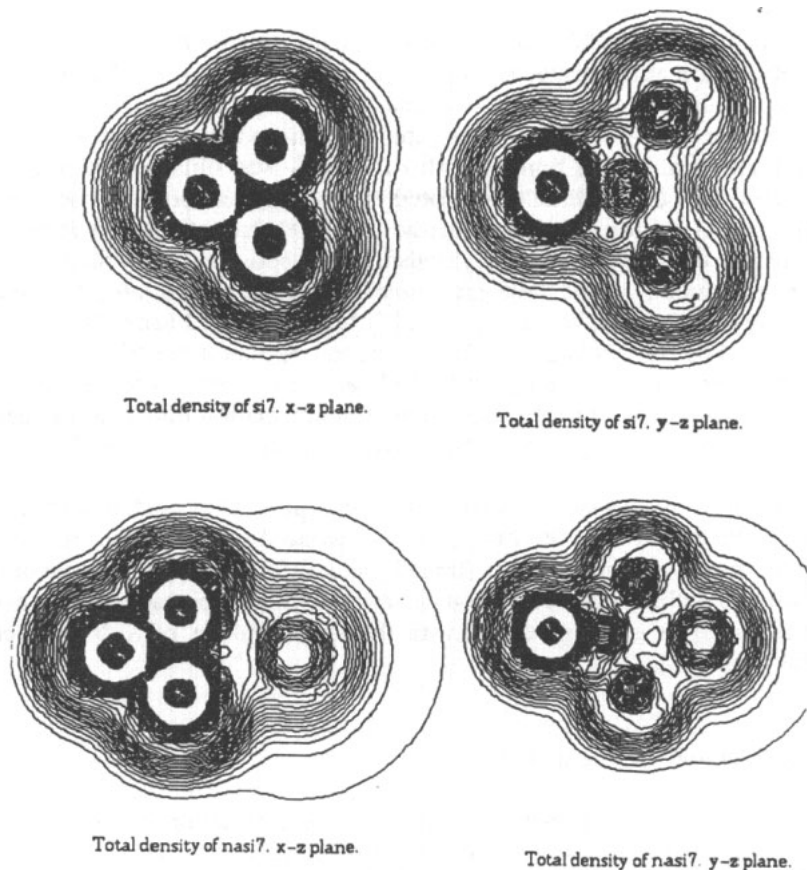Total density of nasi7. y–z plane.

Figure 3. Total densities of Si_7 and $NaSi_7$ systems.

surface Si atoms of the clean surface while for the Na-adsorbed surfaces, Si atoms are mostly p_y and Na atoms are mostly s and p_y in character. The upward shift in energy of the HOMO states on Na adsorption does imply that an interface electronic state is induced by the alkali metal atom. This is in partial agreement with the photo emission spectroscopy of Soukiassian *et al* [19].

6. Summary and conclusions

We have investigated the adsorption of Na atom at different possible sites on/near a silicon surface. An Na atom adsorbing across a dimer bond for a 0.5 ML coverage at the pedestal site modelled with the $NaSi_7(4,2,1)$ cluster is found to be the most energetically favoured adsorption site. The results of the Na atom adsorption on this site at the same approach position modelled with $NaSi_7H_8$ give an almost identical NaSi bond length of 3.03 Å as for Na–Si_7 (3.02 Å). However, Na adsorption on Si_7H_8 across a dimer results in negative chemisorption energy values and is not binding, in sharp contrast to the favourable adsorption of $NaSi_7$. Obviously Na adsorption on the hydrogen-bonded silicon cluster Si_7H_8, where each of the four surface Si atoms has a singly occupied dangling bond (with the other dangling bond paired) [2, 41],

does not give exactly the same bonding as Na adsorption on the bare Si_7 cluster with unoccupied surface dangling bonds.

Previously proposed preferred adsorption sites have been based on results of calculations at the SCF level. Our results for the chemisorption energies for all the NaSi systems, specifically $NaSi_7H_8$, $NaSi_7H_{12}$, $NaSi_8(2, 4, 2)$ and $NaSi_8(4, 2, 2)$, as shown in table 4, indicate that the effects of electron correlation are very important for proper identification of preferred adsorption sites. For example, if one considers $NaSi_8(2, 4, 2)$ and $NaSi_8(4, 2, 2)$, calculation at the SCF level only would result in the bridge site having a higher chemisorption energy than the cave. However, when the effects of electron correlation are included, the cave site becomes more binding than the bridge, and thus is a preferred site next to the pedestal.

An analysis of the Mulliken population shows that the amount of charge transfer from the Na atom to the silicon atoms ranges from $0.39e$ for $NaSi_9H_{12}$ to $0.52e$ and $0.53e$ for the $NaSi_7$ and $NaSi_8(4, 2, 2)$, respectively. Since the alkali metal atom is thus not completely ionized, and since the Na HOMO–LUMO states are still partially occupied, the bonding between the Na atom and the silicon surface atoms is not purely covalent or ionic but mixed.

Acknowledgments

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