Stabilities of adsorption sites and charge transfers at the K/Si(001) surface

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Various adsorption models of a K atom on the Si(001) surface including the top-site model, and the charge transfer between K and Si have been exhaustively investigated using accurate *ab initio* self-consistent unrestricted Hartree-Fock total-energy calculations with the Hay-Wadt effective core potentials. Several cluster models of bare and hydrogen-bonded silicon atoms used to simulate the different possible adsorption sites on the Si(001) surface have been examined. The structural relaxation of the substrate on adsorption of K atoms has been accounted for by optimizing all the atomic positions of the adsorbed and substrate atoms. Also, the effects of electron correlation have been included by invoking the concepts of fourth-order many-body perturbation theory and these are found to be crucial in determining the preferred adsorption sites. Population analyses up to the many-body perturbation theory at the second level of all the models studied consistently show that the charge transferred from the K atom to Si lies between $0.12e$ and $0.40e$. This charge transfer combined with the values of the K-Si bond lengths obtained in our calculations tend to suggest a polarized covalent bonding for the K/Si(001) system.

There probably is no other surface that has been so extensively studied both theoretically and experimentally in the last decade as the alkali-metal-adsorbed silicon surface, especially the K-adsorbed Si(001) surface.[1] The chief motivations for these studies are the potential technological applications such as uses in negative electron affinity devices and catalytic effects of alkali metals (AM) adsorbed on semiconductor surfaces.[2] Also, the AM/semiconductor interfaces, of which the K-adsorbed Si(001) surface is a prototype, present good physical models for the study of phenomena such as bonding characteristics, chemisorption, and possible metallization. Since the proposal by Ciraci and Batra[3] of the metallization of Si(001)-2×1 surface by alkali metals, there has been an explosive increase in research activity on this subject. Despite these numerous studies, there are still areas of controversy. For example, there is no agreement on the preferred chemisorption sites, the nature of the chemical bonding at the AM/Si(001)-2×1 interface, and the extent of the overlayer coverage. The possible adsorption models presently are the (pedestal) hollow (H) site, the bridge (B) site, and the cave (C) site. Levine[4] had proposed the H site in his study of Cs on Si(001). Ciraci and Batra,[5] using self-consistent total-energy pseudopotential calculations, found the H site to be preferred and a K-Si bond length of 2.59 Å. Abukawa and Kono,[6] using an analysis of x-ray photoelectron diffraction, proposed a K double layer where K atoms adsorb on H/C sites simultaneously. Batra, upon optimization of H/B and H/C models,[7,8] found both structure to have identical energies. Ling, Freeman, and Delley,[9] using cluster models of hydrogen-bonded silicon atoms and applying self-consistent total-energy calculation in the density-functional formalism, found the C site to be most stable for K adsorption. Ramirez, based on a slab calculation using a self-consistent-field–Hartree-Fock (SCF-HF) scheme with intermediate neglect of differential overlap,[10] also found the C site to be favored. However, the K-Si bond lengths in these studies differ, 3.22 and 2.65 Å, re-

spectively. A surface-extended x-ray-absorption fine-structure spectroscopy study that is not site dependent found a K-Si bondlength of 3.14 Å.[11] Recently, based on a scanning-tunnel-microscopy (STM) study at low coverages [~0.02 monolayers (ML)], a top-site model[12] has been proposed. In this geometry, the K adatom adsorbs on top of one of the dimer-forming silicon atoms and tends to stablize the asymmetric (buckled) dimerization.

Another area of disagreement is the nature of the K-Si surface bonding. Various results have suggested that the bonding is covalent,[11,13] ionic,[3,5,10] and mixed.[9] There is also no consensus with regard to the nature of the K overlayer and of the K-adsorbed Si(001) surface.[3,5,13–16] Alternate theoretical models and/or approaches are thus clearly needed to study more critically the nature of the K overlayer on a Si(001)2×1 surface and, in this paper, we consider K-Si interaction from a different point of view.

Previous theoretical calculations have all used pseudopotential total energy employing the slab geometry and hydrogen-bonded silicon clusters within the density-functional-theory formalism and have, as mentioned before, arrived at differing results regarding the preferred adsorption sites and the type of bonding. We employ here cluster models (both bare and hydrogen-bonded silicon atom clusters) to simulate the silicon surface and carry out accurate *ab initio* unrestricted Hartree-Fock (SCF) theory calculations and study the effects of electron correlations by invoking the concepts of many-body perturbation theory at the second-, third-, and fourth-order ($MP2$, $MP3$, and $MP4$) levels.[17]

In particular, we have used bare silicon clusters[18] $Si_7(4,2,1)$, $Si_8(2,4,2)$, and $Si_8(4,2,2)$ modeling the pedestal (H), bridge (B), and cave (C) sites, respectively, which have been derived from the structural models of the top Si surface layers around an adsorption site in a slab geometry.[7] Thus, our H, B, and C sites conform with the notations of Batra[7] and the earlier literature. However, our B- and C-site notations are not the same as

those of Zhang, Chan, and Ho[19] and some other recent works in the literature. Also, a modified Yin-Cohen asymmetric structural model[20] is adapted as a cluster in order to investigate the top-site adsorption model. The hydrogen-bonded silicon clusters $Si_7(4,2,1)H_8$, $Si_9(2,5,2)H_{12}$, and $Si_9(2,5,2)H_{14}$ had earlier been considered for the possible chemisorption sites (H, B, or C) of K.[9] All the above cluster geometries were fully optimized by self-consistent energy minimization with the use of analytical gradient techniques, a significant improvement over the fixed symmetric dimer model. In this way, we carry out K-atom adsorption on symmetric and asymmetric reconstructed Si(001) surfaces, since it is known that a distribution of both symmetric and asymmetric dimer configurations occur on the Si(001) surface.[21,22] Pseudopotentials used in most local-density-approximation studies are ionic[7,8] and these may affect the results of the K-Si interactions. Here, Hay-Wadt effective core potentials,[23] known to provide very good agreement with all electron results[24] and double-ζ 3-21G basis sets,[25] were used and all computations were done on a Cray Y-MP computer using the GAMESS (Ref. 26) and GAUSSIAN-88 (Ref. 27) programs. In order to include the effects of electron correlation, many-body perturbation theory up to the fourth order was applied. Population analyses have been done at both the SCF and the $MP2$ levels of computation for more accuracy.

The total energies for the different clusters are given in Table I. The adsorption of a K atom on each of these optimized clusters, shown in Fig. 1, is investigated and the total energies as a function of the vertical height above the surface Si atoms have been calculated. The optimum
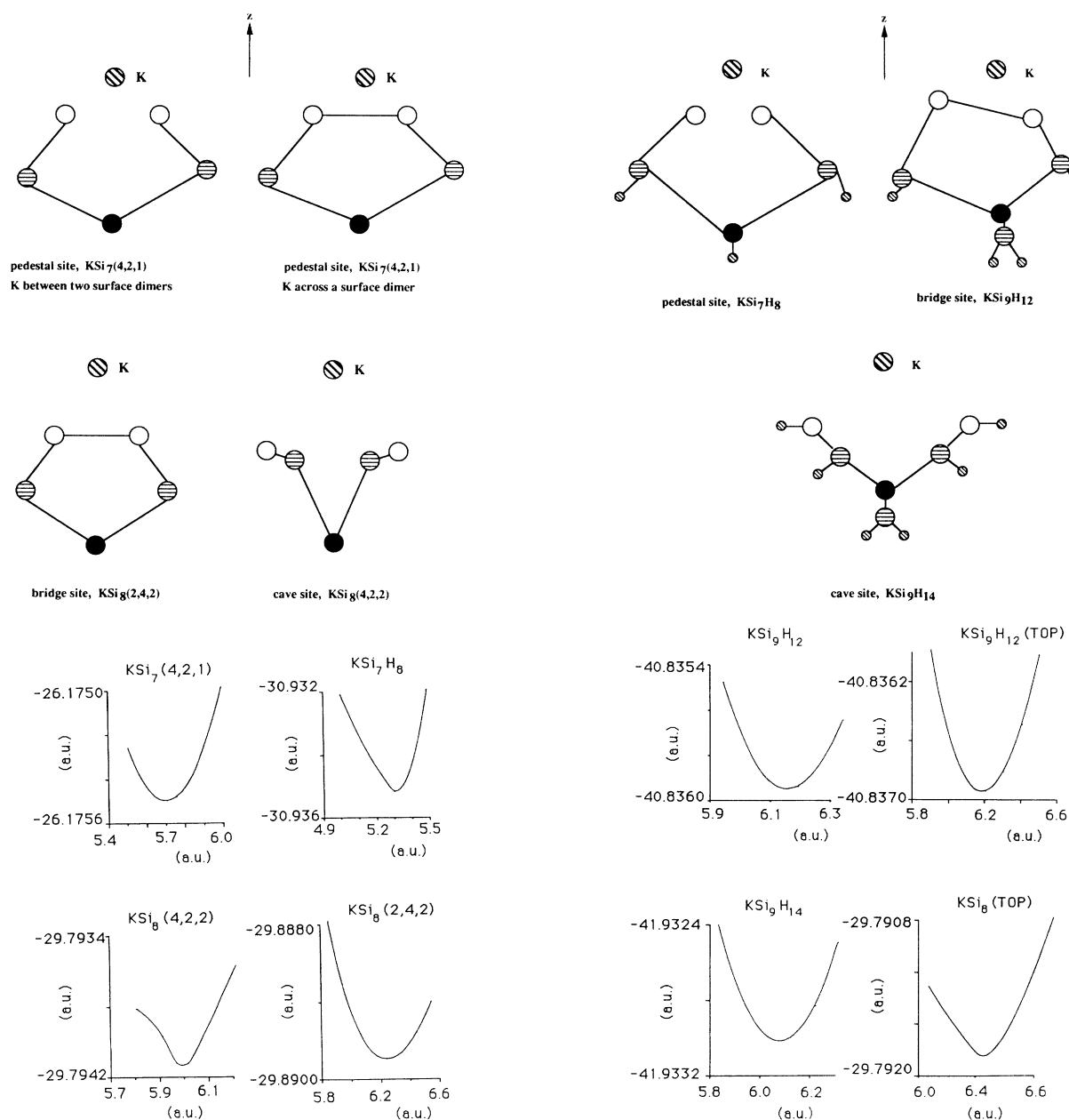

FIG. 1. Chemisorption sites.

K vertical height was then used to calculate the fourth-order perturbation-theory energy eigenvalues and shown in Table II and the chemisorption energies are shown in Table III.

We consider first the K adsorption on bare Si clusters. Table III shows that at the SCF level, the chemisorption energy of 2.45 eV for adsorption on the B site is higher than those at the H and C sites. The K-Si bond length of 3.51 Å obtained for this site is in agreement with the previously accepted value of 3.52 Å.[28,29] However, on inclusion of correlation effects, the H and C sites become more binding (higher values of chemisorption energies) with the H site more favored. Thus, for K adsorption on the bare silicon clusters, the pedestal H site modeled with a $KSi_7(4,2,1)$ cluster is most energetically favored, with adsorption on the bridge site least favored.

The variation of the total energies of the K-Si clusters as the K atom is displaced (keeping the optimum vertical height fixed) along the x and y axes parallel and perpendicular, respectively, to the surface dimers is also investigated. It is found that the total energy for the KSi_7 cluster decreased by about 0.82 eV for shifts along the x axis up to 2.0 bohrs, and increased by about 0.14 eV for shifts of 3.50 bohrs along the y axis. Thus, K adsorption on this site is slightly unstable with respect to displacement along the x axis. This result of the relative instability of the H site is in agreement with an earlier cluster calculation of Ling, Freeman, and Delley.[9] It is also in agreement with that of Batra,[30] which states that the Δx distortion of the H sites is energetically unfavorable. For $KSi_8(4,2,2)$, the total energies decreased by about 0.40 eV for shifts up to 3.0 bohrs along both x and y axes, indicating instability for displacement along both axes. Thus, we find the H site to be more stable than the C site. On the other hand, for $KSi_8(2,4,2)$, the total energies increased for shifts along both x and y axes. These energy increases are uniform and are about 0.13 and 0.07 eV for $\Delta x \sim 2.0$ bohrs and $\Delta y \sim 2.50$ bohrs, respectively. These increases in total energies for displacement along these axes would tend to suggest that the B site is a stable one. However, as we pointed out above, the inclusion of electron correlation effects shows this site to be least favored energetically of the three KSi clusters. The chemisorption energies at the $MP4$ level for the B, C, and H sites are 1.06, 1.75, and 2.22 eV, respectively.

The preferred adsorption site is further investigated by considering the possible changes in the substrate geometry that may be induced by the adsorbate. An is-

TABLE I. Total energies (a.u.) of Si and SiH clusters.

Cluster	SCF	MP2	MP3	MP4
Si7(4,2,1)	−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[a]	−29.560 10	−29.960 97	−29.983 48	−30.014 90
$Si_8(2,4,2)$	−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

[a]Yin-Cohen model as modified by Batra.

TABLE II. Total energies (a.u.) of K-Si and K-SiH clusters.

Cluster	SCF	MP2	MP3	MP4
KSi_7	−26.175 51	−26.493 73	−26.520 57	−26.539 51
KSi_7[a]	−26.189 97	−26.495 79	−26.525 60	−26.544 80
KSi_7H_8	−30.935 22	−31.264 38	−31.323 43	−31.341 19
KSi_8[b]	−29.785 93	−30.201 84	−30.217 83	−30.249 25
KSi_8[c]	−29.780 01	−30.201 33	−30.216 08	−30.247 33
$KSi_8(2,4,2)$[a]	−29.868 86	−30.400 47	−30.346 02	−30.382 74
$KSi_8(2,4,2)$	−29.889 80	−30.351 22	−30.331 83	−30.361 18
$KSi_8(4,2,2)$	−29.822 99	−30.180 64	−30.211 54	−30.233 13
KSi_9H_{12}	−40.835 95	−41.260 70	−41.341 10	−41.364 13
KSi_9H_{12}[b]	−40.836 95	−41.260 17	−41.340 65	−41.363 69
KSi_9H_{14}	−41.933 02	−42.376 78	−42.463 53	−42.486 56

[a]Optimized substrate adatom.

[b]K on top of one of the dimer-forming Si atoms.

[c]K between a surface Si dimer. K adatom is actually above the midpoint of the surface Si dimer, which can also be interpreted as the dimer bridge adsorption position.

sue has been raised in the literature over the structural reconstructions of the Si substrate that might occur on the adsorption of the alkali metal.[31] To this end, some of the KSi clusters of substrate plus adatom were optimized. Following this substrate relaxation the chemisorption energy for the H site increased by 0.39 eV form 2.30 to 2.69 eV at the SCF level, while that for the B site decreased by 0.57 eV from 2.45 to 1.88 eV. These results are shown in Table III. Thus, the H site becomes more energetic than the B site on the inclusion of substrate relaxation even at the SCF level of computation. Hence, the trend of the results of the total energies and chemisorption energies shown in Tables II and III, respectively, for the optimized adatom plus substrate remains the same as that found on the inclusion of the effects of electron correlations. In particular, the K-Si bond lengths remain essentially unchanged. The surface layer Si-Si bond lengths tend more toward the bulk value while the interlayer Si-Si distances tend to increase slightly.

Of the hydrogen-bonded Si clusters, the KSi_9H_{12} clus-

TABLE III. Chemisorption energies (eV) of K-Si and K-SiH clusters.

Cluster	SCF	MP2	MP3	MP4	Site
$KSi_7(4,2,1)$	2.30	2.24	2.18	2.22	H
KSi_7[a]	2.69	2.29	2.32	2.35	H
KSi_7H_8	0.11	−0.36	−0.37	−0.34	H
KSi_8[b]	2.16	2.57	2.40	2.40	
KSi_8[c]	2.00	2.56	2.35	2.34	
$KSi_8(2,4,2)$[a]	1.88	1.66	1.61	1.64	B
$KSi_8(2,4,2)$	2.45	0.33	1.23	1.06	B
$KSi_8(4,2,2)$	1.85	1.97	1.78	1.75	C
KSi_9H_{12}	1.66	1.30	1.29	1.30	B
KSi_9H_{12}[b]	1.68	1.28	1.28	1.29	
KSi_9H_{14}	0.75	0.83	0.78	0.76	C

[a]Optimized substrate and adatom.

[b]K on top of one of the dimer-forming Si atoms.

[c]K between a surface Si dimer. K adatom is actually above the midpoint of the surface Si dimer, which can also be interpreted as the dimer bridge adsorption position.

ter is favored energetically with a chemisorption energy of 1.30 eV and a K-Si bond length of about 3.54 Å. A similar K-Si bond length of 3.56 Å is obtained for the KSi_7H_8 cluster with a much lower chemisorption energy that is not binding (negative values of chemisorption energy) on inclusion of correlation effects. For KSi_9H_{14}, smaller positive values of the chemisorption energy are obtained with a K-Si bond length of 3.76 Å. We had earlier obtained similar results of low chemisorption energies for Na atom adsorption on these SiH clusters. It appears that the Si_9H_{12} cluster in which the Si atoms in the lower layers are saturated by H bonding with the top surface-layer Si atoms free in an adequate model. However, for the Si_7H_8 and Si_9H_{14} clusters, each of the surface Si atoms has a singly occupied dangling bond with the other bond paired by a H atom.[29,32] These do not give the same adsorption picture as the cases of unpaired Si surface dangling bonds to which the adatom transfers charge. It is known that such surface H bonding leads to some charge-transfer effects that can bias the results.[33] Thus, in our scheme of calculations, Si_7H_8 and Si_9H_{14} clusters do not appear to be suitable for the study of the chemisorption problem for Na and K adatoms.

The top-site adsorption model proposed by STM is also investigated. For this case, the asymmetric Si_9H_{12} cluster is utilized with a K adatom on top of one of the dimer-forming Si atoms. Also, a Yin-Cohen asymmetric model as modified by Batra[20] is adopted as a cluster in order to study this top-site model. The K-Si bond lengths obtained are 3.27 Å for KSi_9H_{12} and 3.33 Å for the modified Yin-Cohen asymmetric model. The values of the chemisorption energy in both cases (Table III) are about the same as in the instances of K adsorbing on a dimer bond between two surface Si atoms when correlation

effects are included in the calculations. Similar results have been obtained for Li atom chemisorption on Si(001).[34]

Population analyses at both the SCF and $MP2$ levels show only a partial charge transfer from the K atom to the Si. The values of the transferred charge range from about $0.16e$ for $KSi_8(2,4,2)$ to $0.29e$ for $KSi_7(4,2,1)$ at the SCF level. AT the $MP2$ level, these range from $0.12e$ for KSi_9H_{14} to about $0.40e$ for KSi_7H_8. These values of charge transferred from the K atom are in agreement with the results of a tight-binding calculation that obtained values of $0.20e - 0.30e$ (Ref. 35) and show that the K adatom is not ionized completely. An earlier cluster-model calculation[29] for K-Si_7H_8 found an almost complete charge transfer from the K adatom. However, this presupposed an interaction with K^+ and it used the virtual orbitals of K^+ to represent the neutral K orbitals of a projection operator. A further analysis of the wave-function coefficients of the energetically preferred adsorption sites is also done. The highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) states of the surface-layer atoms of the bare Si clusters consist principally of the p states [p_y and p_z for $Si_7(4,2,1)$, p_x and p_z for $Si_8(4,2,2)$].[18] On K adsorption, these Si HOMO-LUMO states retain their p character and the K states are s and p_z. thus, our results seem to suggest that the nature of the chemical bonding between K and Si tends to be more of a polarized covalent type.

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