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Chemisorption bonding, site preference, and chain formation at the K/Si(001)2 × 1 interface

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A variety of possible chemisorption models has been investigated for the K/Si(001)2 × 1 interface by use of the local-density formalism and the discrete variational method to carry out self-consistent total-energy calculations with Hedin and Lundqvist exchange correlation. Cluster models with up to 89 atoms are adopted to simulate various chemisorption sites. Electronic structures, charge distributions, and bonding characteristics are studied and discussed. The binding energy and relative stability are determined with a total-energy approach. It turns out that the most stable site predicted—the cave site—has been ignored previously in both theoretical calculations and experimental analyses. However, it is the site towards which dangling bonds of the two nearest surface Si atoms are directed and looks to be a reasonable feature for chemisorption. The resulting K—Si bond length (3.22 Å) is in good agreement with the latest surface extended x-ray-absorption fine-structure experimental value. A charge of about $0.5e$ per K atom is transferred from the K atom to the surface, indicating that a mixed type of bonding occurs. Moreover, for monolayer adsorption, a potassium chain formed on the surface tends to undergo a small zigzag Peierls-like deformation to form a lower-energy state.

I. INTRODUCTION

The possibility of forming conducing chains of alkali-metal atoms on the dimerized surface of Si(001)2 × 1 is considered to be one of the most interesting subjects in surface physics today.[1–8] In particular, while much effort has been devoted the K adsorbed system—both theoretically[1–3] and experimentally[5–7] some results are still significantly controversial and have raised challenging questions regarding our fundamental understanding of the nature of metal-semiconductor bonding, possible metallization, etc. The main disagreement centers on whether the adsorbates form (i) a conducting chain on the dimerized Si(001)2 × 1 surface or (ii) a nonconducting ionic chain in which case the Si surface gains charge from potassium atoms and changes into a metallic state. Thus, Ciraci and Batra[1] found a strong K—Si bond length of only 2.59 Å, and complete charge transfer from K to the substrate with metallization of the substrate which involves an ionic type of bonding between the overlayer and the substrate. Instead, Shima and Tsukada[2] found the charge transferred from the K atom to the surface Si dimer to be only about $0.1e$. In contrast to Ciraci and Batra, Ishida *et al.* concluded that the K—Si bond length is 3.52 Å and recently Tsai and Kasowski[3] calculated it to be 3.32 Å, which is consistent with Pauling bond lengths and metallic bonding. From extensive photoemission experiments,[5] a model was proposed which claims that at monolayer coverage, the alkali metal is not perturbed by the substrate and forms a metallic chain on the surface.

It is further important to note that these totally different features are obtained in these theoretical calculations even though they use almost the same starting models: All use the same "pedestal" site proposed by Levine[4] for Cs/Si(001)2 × 1, in which the adsorbed atoms sit on the fourfold sites between two parallel Si dimers (cf. Fig. 1) and form into chains on the ridges of the Si dimers.

Experimentally, it is known that the deposition of potassium on the Si(001)2 × 1 surface does not change the low-energy electron diffraction (LEED) pattern[5] but only brings some redistribution of the intensities of the Si(001)2 × 1 reconstruction. It is now recognized that the identification of the exact geometry of potassium on the Si surface may not be easy to perform experimentally. Thus, for example, a recent photoelectron-diffraction study[6] of Si(001)2 × 1 K suggested the existence of a potassium double layer. The results of their kinematical calculations for the generally assumed one-dimensional (pedestal site) K-chain model do not reproduce the experimental curves, however, and differ significantly when angle-tilted values are compared.[6] This also implies that the pedestal site chemisorption may not be appropriate for this system.

In this paper, we investigate a variety of possible chemisorption sites using the total-energy local-density formalism as applied to cluster models with up to 89 atoms. The most stable site turns out to be the cave site. Evi-

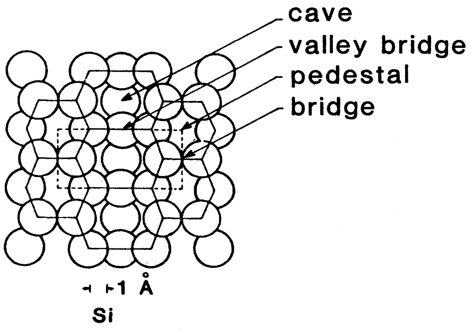


FIG. 1. Model of the reconstructed Si(001) surface (taken from Ref. 4, with two additional sites indicated).

dence is presented for a zigzag Peierls-like distortion[8] to occur on the K chain. The K—Si bond length (3.22 Å) is in good agreement with the latest surface extended x-ray-adsorption fine-structure (SEXAFS) value (3.14±0.10 Å) in disagreement with the results of Ciraci and Batra. A sizable charge transfer from the K to the Si substrate is predicted which indicates a mixed bonding character for the interface and weakened one-dimensional conductivity for the K atoms and some metallization of the Si substrate.

The material which follows is organized in five sections. The method and the models used are described briefly in Sec. II. In Sec. III, the calculations on different sized pedestal chains are given, as is a discussion on the convergence and applicability of the cluster models used. Cave site chemisorption is discussed in Sec. IV which also includes a comparison among several possible K chemisorption sites on this surface. In Sec. V, the results obtained for K on a cave chain are presented and discussed; these include the total-energy curve, the bonding, charge distribution and density of states, and a consideration of the Peierls distortion of the chains. Section VI presents some conclusions.

II. THE METHOD AND THE MODELS

As far as we know, the exact geometry of this chemisorbed surface has yet to be determined experimentally. Therefore a variety of adsorption structures need to be studied theoretically using a total-energy approach to find the optimized one. Quite clearly, cluster models provide a flexible approach for dealing with this problem. Now, the Si(001) surface is quite anisotropic especially after dimerization of the surface Si atoms. This reconstruction of the Si(001) surface was studied by Chadi[9] and by Ihm *et al.*[10] From a comparison of the calculated density of states with photoemission they concluded that the asymmetric dimer is preferred over the symmetric one for the clean surface. For the case of K/Si(001)2×1, however, we agree with the argument of Ishida *et al.*[2] that due to charge transfer the mechanism which stabilizes the asymmetric dimer (compared to the symmetric one) for the clean Si(001) surface might not be applicable to the potassium covered surface. Hence, in the following calculations, the symmetric dimerized Si(001)2×1 surface is adopted.

As expected from the reconstruction of the clean surface, K chains are generally assumed to be formed with monolayer coverage of K (i.e., one K per two Si atoms). Now, the distance between two adjacent K atoms on the same chain is 3.84 Å and that between two adjacent chains is 7.68 Å; these distances are the lattice constants of the reconstructed surface. Assuming that the interaction between K and the surface is mainly short ranged and that the interaction between K atoms on different chains is weak, we modeled the chemisorption system with chain models containing up to 89 atoms. The dangling bonds of the Si atoms which point towards the bulk region on the boundary of the clusters are all saturated by hydrogen atoms. Since it is known that the bond strength does not differ much between Si—H and Si—Si, this kind of saturation is considered reasonable for Si and so is widely used in both cluster and slab calculations for Si.

For the pedestal chain, we use three layers of Si atoms with K atoms above and H atoms below and on the sides. Each K atom has four nearest surface atoms (two dimers), two second layer Si atoms, and a third layer atom right below it as neighbors. For cave chains, one more Si layer is needed, because the Si atom on the fourth layer is now at the bottom of a bowl over which the potassium atom sits. The specific structures of the clusters will be described below along with the calculations.

The self-consistent local-density total-energy formalism[11] is used for the cluster models chosen. Hedin and Lundqvist[12] exchange-correlation terms are adopted in the potential, and a new approach[13] based on the discrete variational method[14]—as manifested in the DMOL program—is used in which the matrix elements of the Hamiltonian and overlap (and therefore the wave functions and charge densities) are all given by numerical values on a set of sample points. The wave function of the cluster is expanded variationally in symmetrized atomic basis functions which are generated self-consistently in numerical form. A frozen-core approximation is used for the Si 1*s*-2*p* and the K 1*s*-3*p* shells. Hamiltonian and overlap matrix elements are calculated by numerical integration in three dimensions using a grid of up 41 749 points. The self-consistent multicenter-multipolar representation of the charge density is used in each iteration.

Finally, we should note—as is well known—that excellent bond lengths can be obtained by using the local-density approximation. Now, while dissociation energies may be overestimated, the comparative values of binding energies, which are important for determining the geometry, provide meaningful results.

III. PEDESTAL CHAIN AND SINGLE PEDESTAL SITE CHEMISORPTION

It is generally assumed that a one-dimensional array of alkali-metal atoms is formed on the ridge of Si dimers for K chemisorption on the Si(001)2×1 surface. As stated earlier, this pedestal model, first proposed by Levine[4] in studying the Cs/Si(100) interface, was used in previous

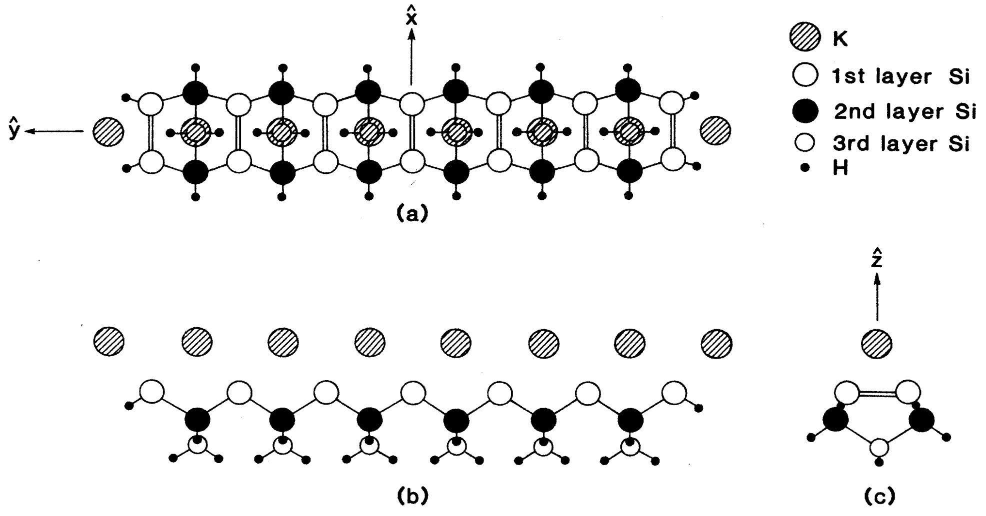


FIG. 2. Cluster model of a pedestal chain, $K_8Si_{32}H_{28}$: (a) top view, (b) side view, and (c) end view. Note that there is no relation between the size of the circles and real atomic sizes; they are depicted as different only for clarity.

theoretical calculations[1-3] for K/Si(100). In this section, we present several calculations with different sized clusters for this assumed model. Then a zigzag shift is allowed for the K atoms on the chain. The total-energy curve is calculated with respect to the magnitude of shift, which results finally in the instability of this pedestal chain. Further evidence for this instability is obtained from both the total-energy study of a single pedestal site (in the latter part of this section) and a comparison of chemisorption energies among several possible sites (in the next section).

Four different clusters are adopted for this pedestal chain model. They are $K_3Si_7H_8$, $K_6Si_{22}H_{20}$, $K_8Si_{32}H_{28}$, and $K_6Si_{32}H_{28}$. The structures are basically the same, and that for $K_8Si_{32}H_{28}$ is illustrated in Fig. 2. For monolayer deposition, the proportion of K atoms to surface Si atoms is 1:2. Now, clusters with C_{2v} symmetry for the pedestal site do not satisfy this proportion. Thus, the first three clusters mentioned have one K atom too many, while the fourth has one Si dimer too many. Actually, the third and the fourth have the same substrate, but the two terminal K atoms are taken away from the former to form the latter cluster. The smallest cluster, $K_3Si_7H_8$, is only a single pedestal site model but with more K atoms.

As a first step, we checked to see the effect of the two terminals of this finite cluster on the results. Fortunately, we find that the bonding between the K atoms and the surface dimers does not differ much for all these four clusters. Calculations of the change of total energy with respect to the vertical distance between K atoms and the surface were carried out. A minimum in the total-energy curve is obtained for all four cases. (Three of these are shown in Fig. 3.) The resulting K—Si bond lengths have converged quite well, even with the smallest cluster; they are 3.19, 3.23, 3.21, and 3.21 Å, respectively. This actually implies that the interaction between the potassium atom and the dimerized Si surface is mainly short ranged in nature, and cluster models, suitable chosen, are quite sufficient to study the bonding properties of this system. The resulting bond length, which differs drastically from the results of Ciraci and Batra,[1] is in very good agreement with the observed value of 3.14±0.10 Å. The K occupation number for the third and the fourth cluster is 0.39e and 0.35e, respectively; on the average, a charge transfer of about 0.63e occurs from one potassium atom to the substrate.

At first sight, it seems that one should be satisfied with the calculated results, since it is a chemisorption struc-

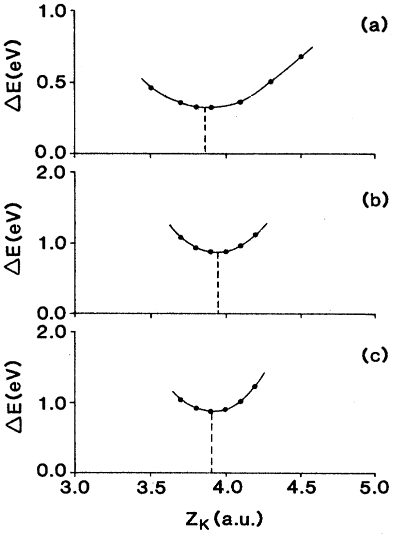


FIG. 3. Calculated total-energy curves for different sized pedestal chain clusters as a function of the vertical distance between K atoms and the undimerized surface: (a) $K_3Si_7H_8$, (b) $K_6Si_{22}H_{20}$, and (c) $K_8Si_{32}H_{28}$.

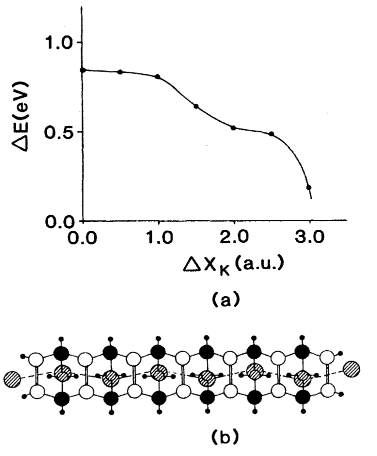
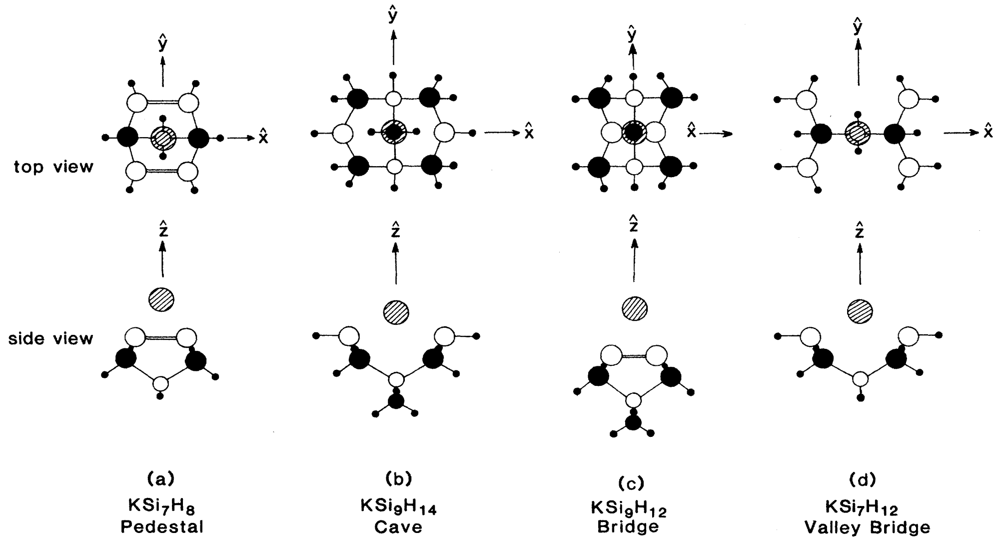


FIG. 4. (a) The total energy vs lateral shift, Δx (with vertical height fixed). (b) The model of K atoms with a lateral shift and forming a zigzag chain on the ridge of the Si(001) surface.

ture that can be explained by the LEED pattern and the bond length agrees so well with the results of surface extended x-ray-absorption fine-structure spectroscopy (SEXAFS) study of the K/Si(100) interface. However, it is well-known that a Peierls' lattice distortion occurs on a monoatomic chain with one delocalized electron per atom. This distortion doubles the size of the unit cell, introduces a gap at the Fermi energy, and thereby results in the reduction of the total energy. It can be shown that in a simple weak-binding approximation, the decrease in electron energy always outweighs the increase in lattice energy, and distortion occurs. If the band is not half-filled,[15] and for a Fermi energy given by say, $k_F = \pi/\nu a$ (where a is the undistorted lattice constant), an atomic distortion repeating every νth atom will again cause a gap and reduce the total energy. Thus, a Peierls' distortion should always occur in the free linear chain.

In our case, the potassium chain is not a free atomic chain, as it is confined to a certain extent on the Si surface. Whether it will undergo a distortion depends on both the Peierls' mechanism and the binding between the K atoms and the surface. To study this feature of the interface system, the $K_8Si_{32}H_{28}$ cluster is used with C_2 symmetry. A displacement in the $\hat{x}$ direction (parallel to the dimers) is given to each K atom to make a zigzag chain (i.e., the shifts are along opposite directions for nearest-neighbor K atoms), as shown in Fig. 4(b). The resulting total-energy curve versus the magnitude of shift is given in Fig. 4(a). It is obvious that the system is unstable with respect to a zigzag displacement. Moreover, the monotonic decrease in total energy with increase of K atom displacement exists even up to a value of 3.0 a.u.—namely, the edge of the cluster. This tendency leads us to suspect that whether or not there is a Peierls distortion, certain properties of the surface itself exist that cause chemisorption on the pedestal site to be unstable.

As a next step, a simple pedestal cluster, KSi_7H_8 [cf. Fig. 5(a)] was adopted which may allow us to simulate the case of very low coverage and since the interaction between K atoms is neglected, no Peierls' mechanism can exist. The σ_v symmetry used for this cluster allows the K atom to be displaced along the $\hat{x}$ and $\hat{y}$ axes as well as along the $\hat{z}$ direction. The total-energy curves are shown in Fig. 6; there is a minimum with respect to the $\hat{z}$ axis, indicating an "optimum" stable position along the $\hat{z}$ axis. The other two total-energy curves are computed in a plane parallel to the surface containing this optimum position, one along the $\hat{x}$ axis (parallel to the dimer) and the other along the $\hat{y}$ axis (perpendicular to this dimer). Clearly, the energy curve along the $\hat{y}$ direction [Fig. 6(b)] has a minimum for zero displacement. The total energy decreases slowly with displacement along the $\hat{x}$ direction [Fig. 6(c)] and is quite flat at small displacements. (Note



(a) KSi_7H_8 Pedestal

(b) KSi_9H_{14} Cave

(c) KSi_9H_{12} Bridge

(d) KSi_7H_{12} Valley Bridge

FIG. 5. Cluster models: (a) a single pedestal site cluster, KSi_7H_8, (b) single cave-site cluster, KSi_9H_{14}, (c) single bridge-site cluster, KSi_9H_{12}, and (d) single valley bridge site, KSi_7H_{12}.

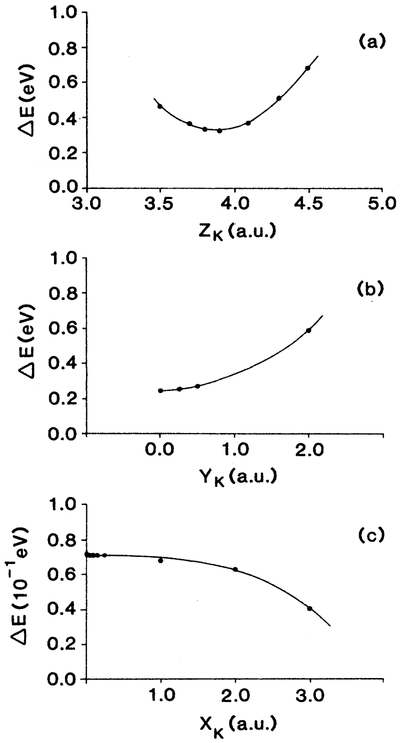


FIG. 6. Total energy for single pedestal site chemisorption as a function of (a) vertical distance between K atom and the undimerized surface, (b) the shift along $\hat{y}$ axis, towards the bridge site (with z coordinate fixed at its optimum value), (c) the shift along the $\hat{x}$ axis, parallel to the surface dimer (with z coordinate fixed at its optimum value).

that the coordinates of the K atom are all taken on a plane parallel to the surface whose height is taken as that of the original pedestal site. If they were optimized along the $\hat{z}$ direction, the corresponding energies would be even lower.) These total-energy curves agree with the results of the calculation for a zigzag shift reported above. Clearly, instead of being an optimum chemisorption site, the pedestal site behaves as a saddle point. Thus, it is energetically unstable for displacement along the $\hat{x}$ axis, parallel to the dimer. In the next section, we report on calculations for other possible chemisorption sites on this surface, and comparisons will be made.

IV. COMPARISON OF CHEMISORPTION ENERGY FOR DIFFERENT SITES

A. The cave site

Historically, the pedestal site for the K/Si(100) interface was first proposed by Levine[4] for the Cs/Si(100)2×1 surface. He arrived at this conclusion by arguing that Cs^+, of diameter 3.38 Å, cannot fit into the caves having an aperture of 2.98 Å on the dimerized Si(100) surface (Fig. 1). Now, since K^+, of diameter 2.66 Å, is smaller than the cave aperture and hence such an argument is not valid, we turn now to the study of K chemisorption on the cave site. Note that an attractive feature of the cave site is that the dangling bonds of the dimerized Si surface atoms actually point towards the area over the cave. It thus appears to be more plausible for the surface Si atoms to form bonds with the potassium atoms in these regions.

A KSi_9H_{14} cluster is used [cf. Fig. 5(b)] to model the chemisorption on the cave site at very low coverage when interactions between adsorbate atoms can be neglected. The total energy versus distance between the K atom and the surface is computed, in which K is moved along the $\hat{z}$ axis perpendicular to the surface and through the middle of the cave. The result is shown in Fig. 7(a). There is a minimum in the energy which corresponds to a K—Si bond length of 3.22 Å; this is again in good agreement with our earlier results for the pedestal site and with the experimental value of 3.14±0.10 Å. Note that since the K—Si bond lengths are almost the same for the pedestal and the cave site, and since both sites are consistent with the LEED results, the determination of the bond length is by itself not able to decide between the pedestal and the cave sites. (Later on we will show that this discrimination may be done by comparing the chemisorption energies obtained for the different sites.)

In order to compare binding energies for K adsorption on these sites, a clean Si(001) surface cluster is calculated along with the chemisorption cluster for each case. The calculated difference between the total energies of the KSi_9H_{14} [cf. Fig. 5(b)] and Si_9H_{14} clusters gives the chemisorption energy on the case site to be 3.7 eV. In the case of the pedestal site, the corresponding clusters are KSi_7H_8 and Si_7H_8, and the resulting chemisorption energy is 3.0 eV, namely, 0.7 eV less binding than calculated for the cave.

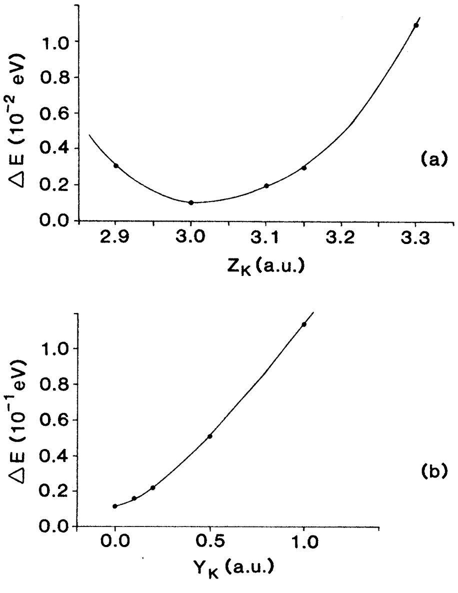


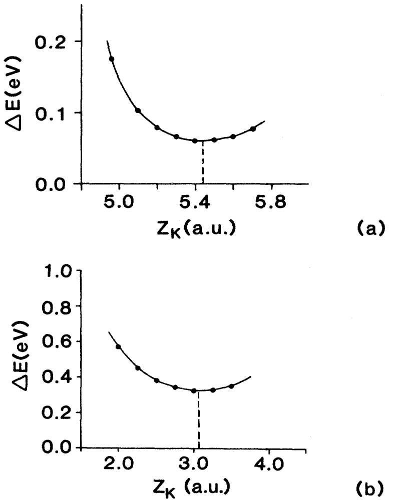
FIG. 7. Total energy for cave-site chemisorption as a function of (a) the vertical distance between the K atom and the undimerized surface, and (b) the shift along the $\hat{y}$ axis, towards the valley bridge site [with vertical height fixed at the optimum distance obtained from (a)].

B. The bridge site

The bridge site (cf. Fig. 1) is studied with a cluster KSi_9H_{12} [Fig. 5(c)] where the K atom sits right above the midpoint of a surface Si dimer. The total energy versus vertical distance between K and the surface is shown in Fig. 8(a). Interestingly, the resulting chemisorption energy is almost the same as the pedestal case, i.e., only slightly less stable (by 0.05 eV). The corresponding bond length is found to be 3.11 Å.

C. The valley bridge site

Another possible site to be considered is the valley bridge site (cf. Fig. 1) because the most recent photoelectron-diffraction study of the K/Si(001)2×1 interface[6] was interpreted in terms of a sawtooth double-layer model. In this model, in addition to the generally assumed pedestal chains, there is another type of chain with K atoms aligned right next to (but lying lower than) those on the pedestal site and their vertical (sawtooth) separation if 1.1 ± 0.1 Å. That is the valley bridge site. This is a rather unusual site for simple chemisorption, since the distance between the K atom and the nearest surface Si atoms is larger than that between the K atom and the nearest second layer Si atoms. A single valley bridge-site chemisorption was studied with a KSi_7H_{12} cluster [cf. Fig. 5(d)] and its corresponding clean surface, Si_7H_{12}. There is a minimum in the calculated total-energy curve [cf. Fig. 8(b)] versus vertical distance between the K atom and the surface. The calculated chemisorption energy is 3.4 eV, so it is less binding than the cave site, but more stable than the pedestal site. The bond length between K and the first layer Si atom is 3.76 Å, and that with the second layer Si is 3.54 Å. This chemisorption site is ruled out from being a preferred site since it is less binding than the cave site and the bond length does not agree well with the experimental value.[7]



(a)

(b)

FIG. 8. Total energy as a function of the vertical distance between the K atom and the undimerized surface for (a) bridge-site and (b) valley bridge-site chemisorption.

D. Further cave-site displacements

To make sure that the cave-site chemisorption represents a minimum energy structure, we also performed calculations for the simple cave cluster, KSi_9H_{14}, with σ_v symmetry as in the case of the pedestal site, and allowed the K atom to move away from the center of the cluster towards the valley bridge site in a plane parallel to the surface and passing through the optimum position along $\hat{z}$. The total-energy curve in Fig. 7(b) shows that the large increase in total energy is again in agreement with the relative chemisorption energies of the cave site and the valley bridge site, and confirms that the cave site is actually the optimum chemisorption site. Hence the cave site is stable and has the lowest binding energy of the four sites considered.

V. K CHAIN STRUCTURE ON CAVE SITES AND ITS PEIERLS DISTORTION

In the preceding section, single chemisorption sites were investigated which describe only the situation for very low coverage. Now in order to study K chain structure on cave sites, a cave chain cluster, $K_6Si_{39}H_{44}$, with four layers of Si, saturated below and on the sides with hydrogen atoms (cf. Fig. 9), is adopted. In this case, 12 surface Si atoms and six K atoms, so the stoichiometry is correct for monolayer coverage. Here too, the total energy was calculated versus vertical distance between K atoms and the surface. The result is shown in Fig. 10. The optimum position is again found to correspond to a K—Si bond length of 3.22 Å. There is a charge transfer of 0.53e from each K atom to the substrate, so the binding is again seen to be neither simple covalent nor simple ionic. (The effect—if any—of this charge transfer on core level shifts cannot be assessed at this time because we have used a frozen-core approximation in order to make the calculations on these large systems tractable.)

In order to further investigate the nature of the bonding, we plot in Fig. 11 the calculated valence charge density. It can be seen from this figure that the charge densities around the central and outer K atoms in the chain do not differ very much, implying that the end effects of the finite K chain may not be a problem in studying the bonding properties of the K/Si(001)2×1 interface. As a result of charge transfer from K atoms to the surface, only a low-density distribution ($\sim 10^{-4}-10^{-3}$ electrons/a.u.^{3}) is found around the K atoms. The charge distribution does exhibit a denser mapping between the K atom and surface Si atom, but no obvious simple covalent bonding can be seen. This result agrees with the previous argument that a mixed type of bonding exists in this case.

The calculated density of states for the $K_6Si_{39}H_{44}$ cluster is shown in Fig. 12. Since only a finite cluster is used, clearly the value of the valence band width and the (larger) gap of the Si(001) surface cannot be compared with the results of band calculations. Qualitatively, as in

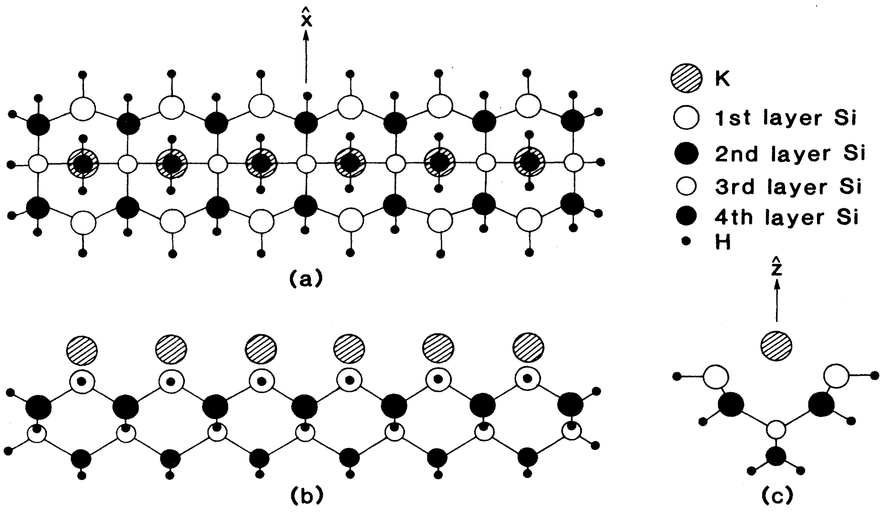


FIG. 9. A chain cluster model, $K_6Si_{39}H_{44}$, for cave-site chemisorption of K/Si(001)2×1, (a) top view, (b) side view, and (c) end view.

the energy-band results, a group of states (labeled E for the clean surface in Fig. 12) exist within the gap which are half-filled. These are the well-known remaining dangling-bond states of the 2×1 Si(001). For the K/Si(001) interface the states labeled E' in Fig. 12 are $\frac{3}{4}$ filled. An analysis of the wave functions of these gap states indicates that they are chemisorption states composed mainly from the K s orbitals and the p_z,s orbitals of the surface Si dimers. This result shows that the potassium chain on the cave sites exhibits metallic behavior along the channel direction. Therefore, it is not unreasonable to say that a one-dimensional-like metallic array does exist on the Si(001) surface which interacts with the surface and that there is significant charge transfer between them which induces a metallization of the Si surface.

Again, one of the interesting features of this one-dimensional chain to be examined is a possible Peierls distortion. In the present case, there are complications, as mentioned in Sec. III, since the occupation number per potassium is no longer an integer. Thus, the atomic distortion may not repeat every other atom, and also the electronic structure of the surface will certainly affect the deformation, if it exists. In addition, we need to keep in mind that since we are using a finite chain with only six potassium atoms, it will not be possible to obtain a detailed deformation structure, should this be demanded from this model. However, it is reasonable to believe that qualitative results on whether or not there is a Peierls deformation can be obtained from the calculation of total energies.

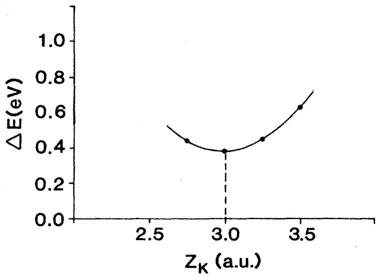


FIG. 10. Total energy for cave chain chemisorption as a function of the vertical distance between K atoms and the undimerized surface.

The $K_6Si_{39}H_{44}$ cluster is again considered with C_2 symmetry. A plane passing through the K atoms at the optimum height and parallel to the surface is taken, on which the K atoms are allowed to shift. A zigzag lateral shift is assigned to the K atoms—as shown in Fig. 13(a). A very smooth total-energy curve is obtained [cf. Fig. 14(a)]. The minimum appears at 0.075 a.u. (0.040 Å) for Δx for the K atoms and indicates that, unlike the pedestal chain studied in Sec. III, a zigzag displacement for the potassium chain on the cave sites is a more stable configuration. The K—Si bond length for the chain (3.22 Å) is now 3.25 and 3.19 Å after the shift, which implies a distortion of about 2%. The straight chain is not the lowest energy structure; the Peierls' mechanism is operative, but due to the interaction between the chain and the surface, that mechanism is moderated considerably.

For comparison, a free K chain of six K atoms (sited along the $\hat{y}$ axis) was calculated with the K—K bond length chosen to be that for K on the Si(001) surface, i.e., 3.84 Å. A zigzag displacement along the $\pm\hat{x}$ direction (adjacent K atoms move in opposite direction) was found to lower the total energy. The optimized zigzag displacement is found to be large (0.69 Å—almost 17 times larger than when confined on the Si(001) surface—and to result in a K—K bond length of 4.08 Å. (It is interesting to note that if the internuclear separation of the free linear K chain is optimized first, a value of 4.05 Å is found for the K—K bond length. Allowing for a Peierls distortion then results in a zigzag of 0.32 Å which optimizes the total energy and results in a bond length of 4.10 Å.)

Another possible distortion tendency for the K chain is dimerization along the chain. Since there are only six atoms in this cluster, only the tendency can be (crudely) tested. In the first test, the two inner K atoms [1 and 2 in Fig. 13(b)] are contracted towards the origin by an amount Δy, atoms 3 and 4 are expanded by Δy, while atoms 5 and 6 are kept stationary. Thus, we have a short K—K bond in the middle, connected with two long bonds, and two half-shortened bonds outside. The potential curve obtained with respect to Δy shows that no minimum occurs. The second test is to have a long K—K bond in the middle (atoms 1 and 2 expanded), connected with two short bonds, and with two half-stretched bonds outside (atoms 3 and 4 contracted). The potential curve is given in Fig. 14(b), with a minimum energy for $\Delta y = 0.03$ a.u. (0.016 Å), which implies a dimerization of 1.7%. Thus, it can be seen that while we cannot study the dimerization accurately with such a small cluster, the tendency towards dimerization is obviously obtained, and even the magnitude of the dimerization looks quite reasonable.

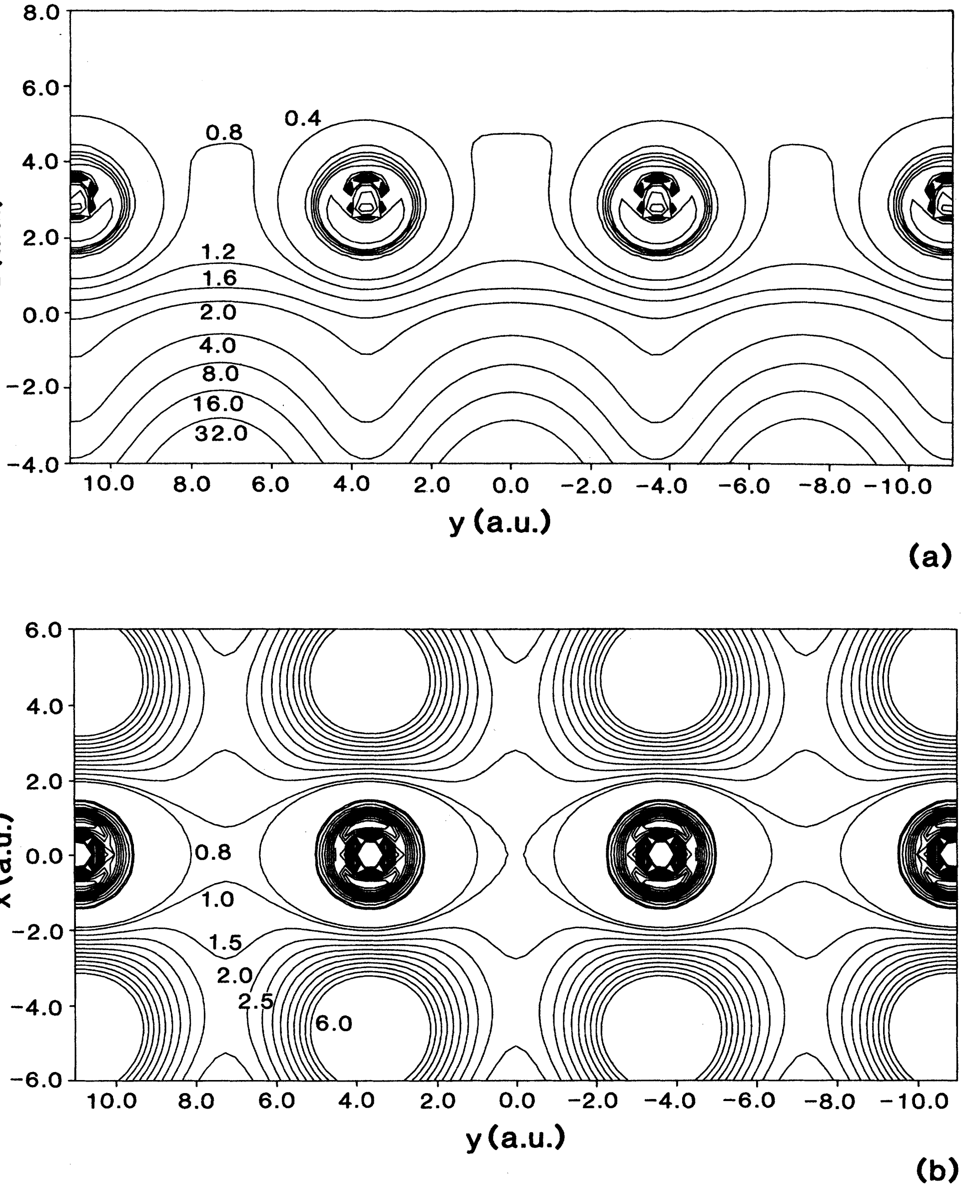


FIG. 11. The contour plots of charge density [in units of 10^{-3} electrons/(a.u.)^3)] for a $K_6Si_{39}H_{44}$ cluster: (a) in vertical *yz* plane which passes through the K atoms and perpendicular to the surface; (b) in a horizontal plane, parallel to the surface and 0.2 a.u. below the K atoms.

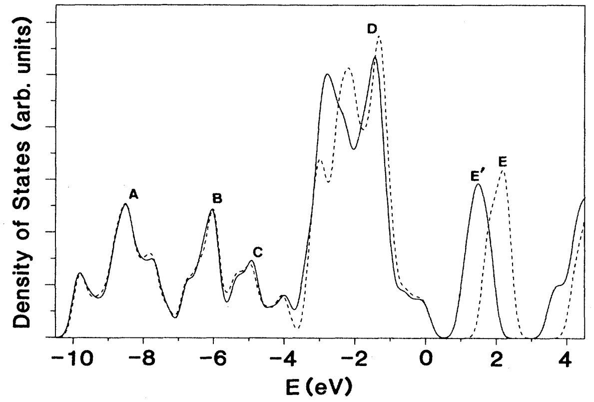


FIG. 12. The solid line shows the total density of states for $K_6Si_{39}H_{44}$, and the dotted line shows the density of states for a clean surface $Si_{39}H_{44}$.

Finally, we need to discuss the LEED pattern. One would ask, since the K atoms undergo a distortion on the surface, why the LEED pattern is unchanged. Actually one may notice that the shift is only 0.04 Å on the plane; such a very small displacement may not be observed by LEED unless it is carefully performed at higher energies.

VI. SUMMARY AND CONCLUSIONS

Four different chemisorption sites for K/Si(001)2×1 were studied with self-consistent total-energy cluster calculations. The sixfold cave site was found to be the most stable site, with a K—Si bond length of 3.22 Å which is in good agreement with the most recent experimental value. Since this is actually the position where the dangling bonds of the two nearest surface Si atoms point, it looks more reasonable to have the adsorbate fall in this position.

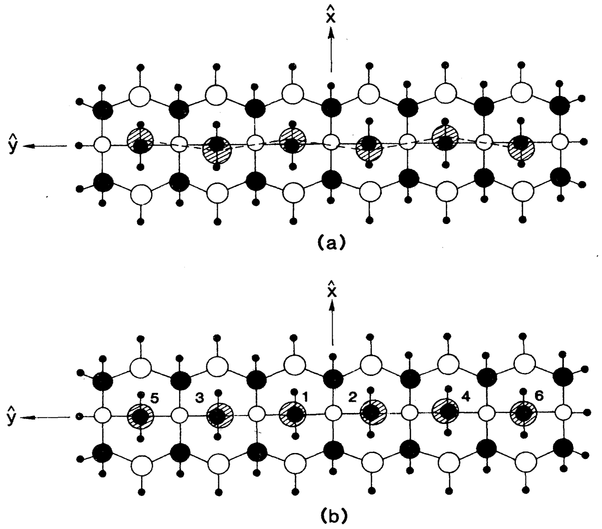


FIG. 13. This model describes the distortion of an adsorbate chain: (a) a zigzag distortion, and (b) a linear dimerization with the middle K—K bond stretched.

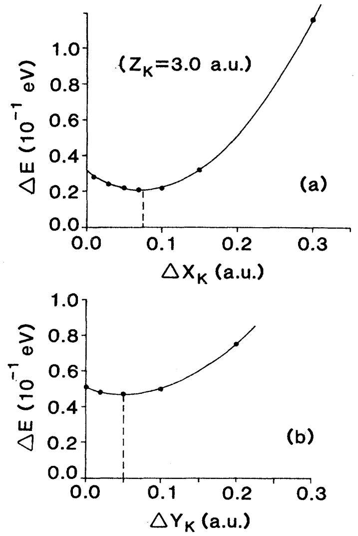


FIG. 14. Total energy as a function of the amount of distortion as in Fig. 13: (a) zigzag distortion and (b) linear dimerization.

All the three other sites—pedestal, bridge, and valley bridge—are found to be less binding. Among these the former two give similar bond lengths to that of the cave site. We also found that for different sized clusters of the pedestal chain, the K—Si bond lengths of this quasioptimum position give almost the same values as that obtained for the cave chain. This may indicate that the bonding between K and Si is predominantly short ranged in nature. For the valley bridge site, in which K is closer to the second layer Si than to the first layer Si, the resulting bond length is much larger than the observed value. The pedestal site is found to be unstable with respect to a lateral shift. It is actually a saddle point on the energy curve.

For cave chain chemisorption, a charge transfer of 0.53e is found from the K atom to the surface, so the bonding is not simply ionic or covalent, but is instead of a mixed type. The K chain, which channels its way through two ridges of charged surface dimers, may result in the metallization of the Si(001) substrate in addition to its own weakened one-dimensional conducting behavior.

It was interesting also to determine whether the chain formed on the cave sites is linear or zigzag. And if it is zigzag, why doesn't the LEED pattern change? The total-energy curve computed for a cave chain cluster shows that the middle of the cave, with the vertical distance optimized, is actually not the point of lowest binding energy. A lateral zigzag shift was found to lower the total energy. However, due to the interaction between the chain and the surface, this effect is compensated considerably from that expected from a free chain and only a very small zigzag shift (0.04 Å) is found to occur. The small magnitude of the zigzag obtained corresponds to a K—Si bond length difference of only 2%. Such a small shift may not be easily observed by LEED.

By contrast, our studies of the zigzag chain model on the pedestal site was especially instructive. We were puzzled at first to find that the binding energy increased with amount of zigzag displacement (cf. Fig. 4) indicating an unstable situation. As a result a more careful study was carried out for a single chemisorption on the pedestal site. We found that the optimum site obtained along the $\hat{z}$ axis (perpendicular to the surface) is a saddle point with respect to motion of the potassium atom along the $\hat{x}$ axis (perpendicular to the chain and parallel to the dimers). Along the $\hat{y}$ axis, the pedestal site corresponds to a minimum in the total energy, which implies that the bridge site right over a dimer may not be a good site either. Thus the total energy versus displacement along the x axis and the above mentioned zigzag instability reveal that the pedestal site is not a likely chemisorption model for the K/Si(001)2×1 interface.

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