PHYSICAL REVIEW B VOLUME 37, NUMBER 14 15 MAY 1988-I

Brief Reports

Brief Reports are short papers which report on completed research which, while meeting the usual **Physical Review** *standards of scientific quality, does not warrant a regular article. (Addenda to papers previously published in the* **Physical Review** *by the same authors are included in Brief Reports.) A Brief Report may be no longer than 3½ printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Adsorption of potassium on the ideal Si(111) surface

Inder P. Batra and S. Ciraci*
IBM Research Division, Almaden Research Center, Mail Stop K33/801, 650 Harry Road, San Jose, California 95120-6099

(Received 4 September 1987)

We present the results of self-consistent pseudopotential total-energy and charge-density calculations for the potassium-covered ideal Si(111) surface. It is found that K adsorbed on the π-bonded Si(111)-(2$\times$1) surface is less stable by $\sim$0.3 eV as compared to adsorption on the ideal surface, suggesting that the π-bonded surface is metastable upon K adsorption. The overlayer binding energy is estimated to be $\sim$3.4 eV. However, at monolayer coverage of the metal, the bonding is found to be ionic on both the ideal and π-bonded reconstructed surfaces. No evidence for the overlayer metallization is detected at such coverages, presumably due to the presence of active dangling bonds and strong ionic bonding.

In a recent paper[1] some interesting properties of the π-bonding Si(111)-(2$\times$1) surface[2] upon potassium adsorption were reported. Based on the experimental evidence,[3] the adsorption of K on the π-bonded Si reconstructed surface only was considered theoretically. From the total-energy minimization, the equilibrium position of the adsorbate was reported to be at 2.8 a.u. above the center of the tilted hexagon (formed from the surface and subsurface Si atoms) leading to an average K-Si interatomic distance of $\sim$5 a.u. It was also found[1] that the forces acting on Si atoms were rather small for each position of the potassium atom approaching the equilibrium position from a large height. It was thus concluded that the π-bonded chain structure of surface silicon atoms may be distorted slightly, but basically remains stable upon adsorption. The charge distribution and electronic structure corresponding to the equilibrium configuration indicated that the valence electrons of the adsorbed alkali-metal atoms are donated to the empty π^* band leading to an ionic bonding. As a result, it was found that at low coverage ($\Theta < 1$) the surface, and at high coverage ($\Theta > 1$) the bulk substrate, become metallic.

A significant aspect of the K/Si system, which has not been dealt with theoretically before, is the absolute stability of the π-bonded structure since no total-energy calculations have been reported for K adsorption on ideal Si(111). It is also important to investigate the nature, strength of bonding, and metallization when a potassium atom is adsorbed on the ideal Si(111) surface. In this work we present new results for the K adsorption on the ideal Si(111) surface. Then by comparing these with previous experimental and theoretical results, the stability issue is explored in greater depth. Also in the light of our present calculations, we discuss some earlier conductivity measurements on an etched Si(111) surface as a function of Cs coverage.

We have carried out total-energy and charge-density calculations for K adsorption on the ideal Si(111) surface by using the self-consistent-field (SCF) pseudopotential method[4,5] within the local-density-functional formalism. To compare our results directly with those obtained for adsorption on the π-bonded reconstructed surface, the parameters of the calculations (i.e., the type of the ionic pseudopotentials, exchange-correlation potential, expansion of the Bloch states in terms of $\simeq$1000 plane waves, etc.) are taken to be the same as in the previous study.[6] To treat the coverage of one K atom per two surface Si atoms ($\Theta = 1$) we consider an ideal (2$\times$1) unit cell including 12 Si, one K, and two H atoms to saturate the dangling bonds on the back surface. This corresponds to a potassium coverage of $N_K \simeq 4\times10^{14}$ cm^{-2}. The adsorbed atoms were placed above the center of the hexagons (formed by three surface and three subsurface Si atoms in the ideal configuration) at a vertical height of 2.6 a.u. above the Si surface. The smallest K-Si distance is thus 4.9 a.u. This configuration is chosen to make direct comparison with the total energy[1] of the π-bonded surface. Also, this adsorption site is a low-charge-density region (hole site) of the ideal Si(111) surface and is consistent with studies[1,7-9] on Si(100)-(2$\times$1) and Si(111)-(2$\times$1) surfaces. In the present adsorption structure corresponding to $\Theta = 1$, potassium atoms are arranged on the chains along the [1$\bar{1}$0] direction, the interchain distance being 12.56 a.u. (see Fig. 1). However, the nearest-

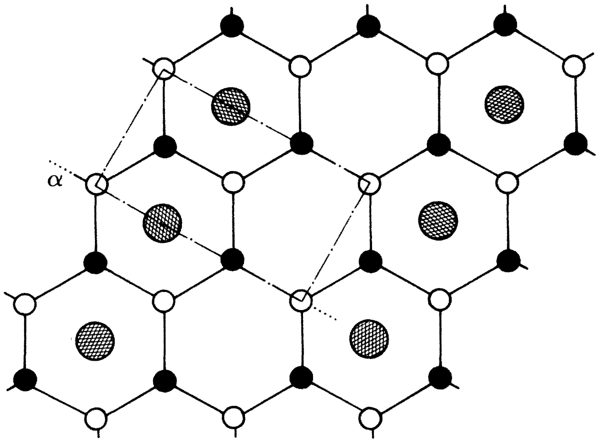

FIG. 1. Top view describing the atomic structure of the potassium adsorbed on the ideal Si(111) surface. Potassium and surface and subsurface Si atoms are shown by large shaded, small solid, and small open circles, respectively. The unit cell (twice the primitive cell) used in our calculations is delineated by dash-dotted lines. α denotes the vertical plane, in which charge-density contour plots are shown.

neighbor distance in the chain is only 7.25 a.u., which is smaller than the nearest-neighbor distance in the bulk metal (~8.7 a.u.). The K-K separation is thus small enough to allow a strong interaction among potassium atoms on the same chain.

A significant result of our calculation is that the total energy of the adsorption structure described in Fig. 1 [K on the ideal Si(111) surface] is ~0.3 eV lower than that found[1] for the π-bonded surface. This suggests that the π-bonded reconstruction is unstable relative to the ideal structure upon K adsorption at $\Theta=1$. On the other hand, the force[1] and electronic structure calculations[1,9] have proposed that the chain structure is maintained upon K adsorption. Although there are no ultraviolet photoemission spectroscopy (UPS) results available for K/Si, the adsorption of Cs on Si has been studied[3] using synchrotron radiation. It is reasonable to use Cs/Si results to gain some qualitative insight. The UPS experiment for Cs on Si(111)-(2×1) reports that the Si surface state located near the Fermi level is shifted to higher binding energy up to Cs coverage to ~0.5 monolayer (ML). (It should be noted that 0.5 ML corresponds to $\Theta=1$ in our notation.) From difference-energy curves Tochihara *et al.*[3] deduced a new peak near the Fermi level which was attributed to Cs 6*s* electrons. The origin of the new peak has been challenged by Soukiassian[10] using the argument that the cross section for alkali-metal *s* electrons is quite low for high UV photon energies. Consequently, the new peak may have its origin in the π* band of Si(111)-(2×1). Thus the above experimental results, i.e., shifting of the surface-state band to higher binding energies, the development of a new peak just below the Fermi level, and the pinning of the Fermi level for $\Theta>1$, all appear to be consistent with the adsorption of K on the π-bonded reconstructed surface. These features are difficult to explain by K adsorption on the ideal Si(111) surface since the ideal surface has a metallic and nearly dispersionless surface-state band.

The energetics, on the other hand, show that K adsorbed on the ideal Si(111) surface has definitely lower energy (by ~0.3 eV) than the K/Si(111)-(2×1) π-bonded system. This naturally leads to the conclusion that the K adsorbed on the π-bonded Si(111)-(2×1) is a local minimum on the Born-Oppenheimer surface. The barrier to cross over to the ideal topology, however, is not known. But in the absence of the adsorbate, the barrier[11] to go from the ideal surface to the π-bonded topology is reported to be only ~0.03 eV per surface atom. The calculation of the corresponding barrier in the presence of K requires the optimization of a large number of structural parameters and hence is not feasible. It is therefore desirable to explore the transition from the metastable to stable structure experimentally.

In order to reliably calculate the binding energy of the K overlayer, ΔQ (heat of formation), on the ideal Si(111) surface we proceeded along two independent directions. In one case, we performed total-energy calculations using the (1×1) cell for the ideal Si(111) surface with and without the K overlayer. In our notation this corresponds to $\Theta=2$. For this coverage, we are able to check the sensitivity of our results to the calculational parameters. For $\Theta=1$, the unit cell is too large to permit many test calculations. The back surface, as usual, was saturated with H atoms. Our results are summarized in Table I. The binding energy of the overlayer is defined as the difference in the following total energies:

$$\Delta Q = E_{\mathrm{Si}} + E_{\mathrm{K}} - E_{\mathrm{K/Si}} ,$$

keeping in mind that the enthalpy of formation is defined with the opposite sign. An important point to note from Table I is that, although the absolute values of the total energies for clean and K-covered surfaces have changed by ~3.5 eV upon increasing the number of plane waves by 226, ΔQ has changed by only <0.1 eV. Thus we conclude that the K overlayer at $\Theta=2$ is bound to the surface by ~3.1 eV. (The corresponding value reported[12] for the Na overlayer is ~2.1 eV and is lower, as expected.) The absolute binding energy (not the overlayer binding energy) at $\Theta=1$ on the π-bonded Si(111)-(2×1) surface is known[1] to be higher by ~0.3 eV than that of

TABLE I. Total energies $E_{\mathrm{K/Si}}$ for K adsorbed on the ideal Si(111)-(1×1) at $\Theta=2$ calculated for two different kinetic energy cutoffs leading to a total of 751 and 525 plane waves (PW's) in the wave-function expansion set at Γ. Values are also given for the clean Si(111), E_{Si}, as well as the isolated K overlayer, E_{K}. The heat of formation of the K overlayer is ΔQ. The clean and K-covered Si(111) had their back surfaces passivated with H.

Energy (Ry)	751 PW's	525 PW's
$E_{\mathrm{K/Si}}$	−48.969	−48.711
E_{Si}	−48.356	−48.104
E_{K}	−0.381	−0.380
ΔQ	0.232	0.227
ΔQ (eV)	3.16	3.09

$\Theta=2$. This is primarily due to the larger K-K distance (and thus reduced repulsion energy) at $\Theta=1$ as compared to $\Theta=2$. Thus a similar change may be expected on the ideal Si(111) surface, and hence we deduce that at $\Theta=1$ the K overlayer is bound to the ideal Si(111) surface by ~ 3.4 eV.

The second way to arrive at the value of ΔQ is from

$$\Delta Q-\Delta Q^{\pi}=(E_{\mathrm{Si}}^{I}-E_{\mathrm{Si}}^{\pi})+(E_{\mathrm{K/Si}}^{\pi}-E_{\mathrm{K/Si}}^{I}) ,$$

where the superscripts denote the state of the substrate, ideal (I) or π reconstructed (π). The terms within the first parentheses on the right-hand side correspond simply to the energy lowering due to the (2×1) π-bonded reconstruction, which is known[2,11] to be ~ 0.6 eV. The difference of terms within the second set of parentheses on the right-hand side is calculated by us here and is ~ 0.3 eV. An important conclusion arrived at is that for $\Theta=1$, the binding energy per K atom is ~ 0.9 eV higher on the ideal as compared to the π-bonded Si(111) surface. Recalling[1] that $\Delta Q^{\pi}=2.8$ eV, the (absolute) binding energy $\Delta Q \simeq 3.7$ eV at $\Theta=1$. Thus the two methods lead to rather similar values indicative of a strong ionic bond. The two values differ somewhat because of cohesion in the isolated K overlayer which is excluded to get the absolute binding energy of the K atom. In practice, one may not observe such a high value of the binding energy on the ideal surface (having a narrow surface-state band) due to the large (~ 1 eV) intra-atomic Coulombic repulsion[13] U. On the π-bonded surface, the dangling-bond bands are broad and U can be effectively screened out. Therefore our calculated value for the binding energy is more nearly correct for this surface. Thus the difference in binding energies for a K overlayer on the ideal and π-reconstructed surfaces is likely to be smaller than our estimate. This raises the possibility that the metastable π reconstruction upon K adsorption may be observable. High values of the binding energies also suggest that the overlayer metallization is energetically less favorable as compared to the ionic bond formation.

The nature of the K—Si bond is found to be quite similar on the ideal as well as the reconstructed Si(111) surface. The contour plots of the total valence charge density in Fig. 2 depict the ionic bonding at the surface region (no charge is seen around the adsorbed K atom). The ionic bond is also supported by the strong reduction in work function (~ 2.6 eV) found in our calculation, which is in reasonable agreement[14] with recent experiment (~ 3.2 eV). Up to the coverage studied, our calculations do not show the formation of a one-dimensional (1D) metallic band over the potassium atoms. This is illustrated by examining state charge densities. Figure 3

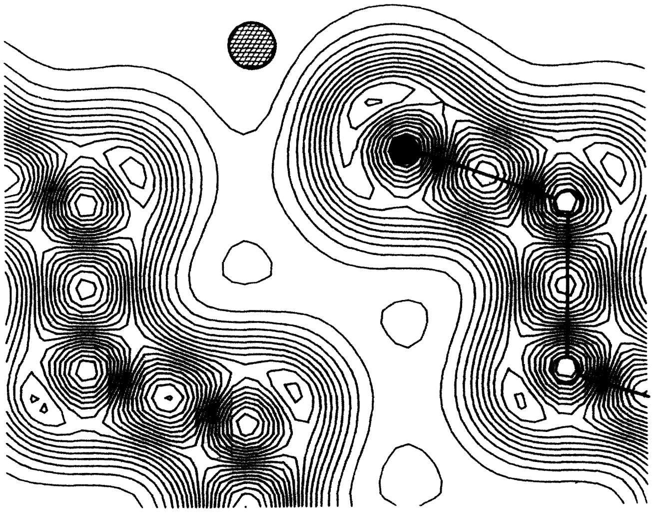

FIG. 2. Contour plots of the total charge density in the vertical plane α passing through the longer edge of the unit cell. The positions of the atoms in this plane are indicated according to the labeling of Fig. 1. The contour spacings are 0.0045 a.u.

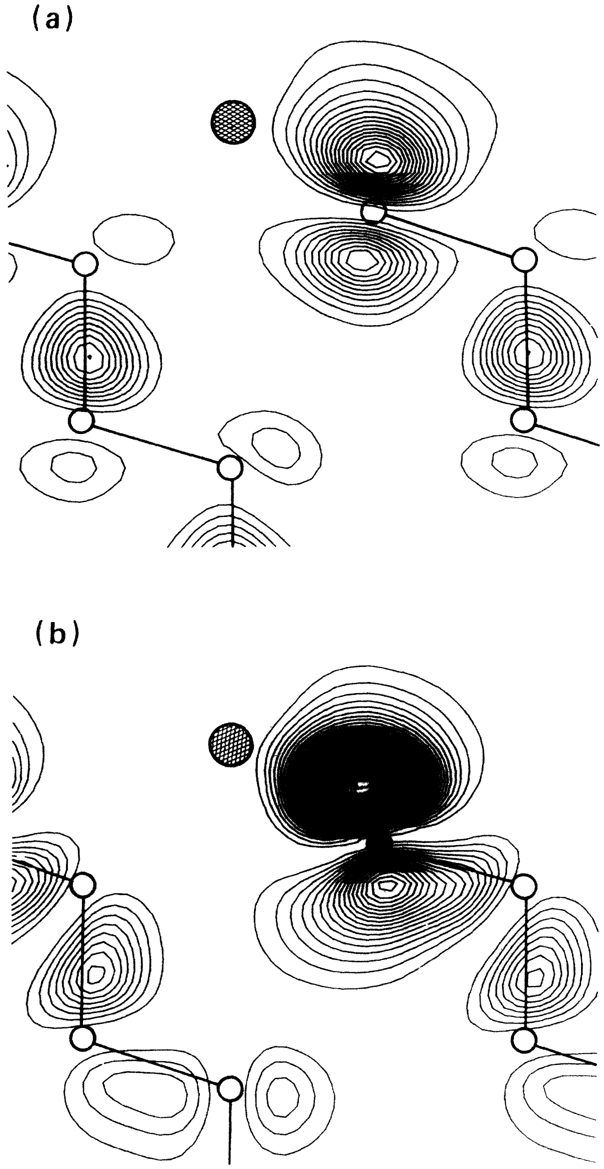

FIG. 3. Contour plots of the charge density of the states in the half-filled band lying in the band gap. (a) State with $\mathbf{k}=(0,0,0)$ and (b) state with $\mathbf{k}=(0,0.43,0)$ a.u.$^{-1}$. Contour spacings are 0.0006 a.u.

shows the charge distribution of the states from the half-filled band in the gap region. It is well known that the ideal Si(111) surface has a half-filled dangling-bond surface-state band S_1 in the band gap. When the same surface is treated by a larger unit cell, say an ideal (2×1) unit cell, as we have done in this study, S_1 is folded into two bands, which are degenerate at certain directions of the surface Brillouin zone. The adsorption of potassium may induce either new, half-filled band—indicating the overlayer metallization—or cause the upper folded dangling-bond band to be half filled—corresponding to the donation of the valence electrons of the overlayer to the surface states. The contour plots of the states at Γ, and J points of the surface Brillouin zone[1] clearly show that they are dangling-bond states, confirming the latter possibility. This conclusion is confirmed by the calculations of Northrup,[12] who has predicted an ionic bonding for sodium adsorbed on the ideal Si(111) surface. Thus our calculations show no evidence of the overlayer metallization.

We now briefly discuss important conductivity measurements on an etched Si(111) surface with adsorbed Cs which have been reported[15] up to $N_{\mathrm{Cs}}=1\times10^{13}$ cm^{-2}. The observation of a minimum in electron concentration versus temperature at a fixed high ($>3.5\times10^{12}$ cm^{-2}) coverage has been explained in terms of a two-band model. The two-band model used consists of two-dimensional subbands in an inversion layer and a donorlike Cs impurity band. Our results are in conformity with the formation of two-dimensional subbands[16] since we find an ionic type of bonding and a strong reduction in work function upon alkali adsorption up to even beyond the coverages used in the experiment.[15] The high electric field so generated[17] leads to strong band bending. This can cause the bottom of the conduction band to come near the Fermi level and hence an n-type inversion layer can be produced on a p-type material. The subbands are usually associated with such an inversion layer and appear naturally in our SCF calculations. However, due to the small slab thickness the subbands may be incompletely developed. The formation of an alkali-metal impurity band, however, is not found in our calculation even up to 4×10^{14} cm^{-2} coverage. It is difficult for us to envisage the emergence of impurity bands at an order-of-magnitude lower coverage. Certainly, the presence of the dangling-bond states in our system prevents the formation of the overlayer metallic band. If these surface states are somehow passivated in the experiment[15] then an impurity band can develop at lower coverages. The suppression of the overlayer metallization in the presence of surface states has been found earlier.[7,8]

In summary, the total-energy and charge-density calculations lead to the following conclusions for K on an ideal Si(111) surface at $\Theta=1$. (i) The alkali atom is adsorbed by donating the valence electrons to the active, but empty dangling-bond surface states. (ii) Despite the relatively short nearest-neighbor distance of K atoms arranged on chains, a metallic bond leading to a 1D metal does not occur.[18] The substrate surface, which is metallic when it is clean, continues to be metallic at $\Theta=1$. However, it may become insulating at high coverages. (iii) Since the total energy of the K/Si(111) system is found to be lower than that of the K on π-bonded Si(111)-(2×1) system, the latter is only a metastable structure. The transition from the metastable to stable structure may be an interesting phenomenon to observe experimentally.

We thank Dr. R. M. Martin and Dr. F. Stern for discussions regarding the metastability of the K/Si(111) system. We are grateful to Dr. F. Stern for bringing Ref. 15 to our attention.

---

*Permanent address: Department of Physics, Bilkent University, Ankara, Turkey.

[1] S. Ciraci and I. P. Batra, Phys. Rev. Lett. **58**, 1982 (1987).

[2] K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981); **49**, 223 (1982).

[3] H. Tochihara, M. Kubota, M. Miyao, and Y. Murata, Surf. Sci. **158**, 497 (1985); Jpn. J. Appl. Phys. **23**, L271 (1984).

[4] M. Schluter, J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B **12**, 4200 (1975).

[5] I. P. Batra and S. Ciraci, Phys. Rev. B **33**, 4312 (1985).

[6] Further details of calculations, labeling of the (2×1) surface Brillouin zone, and other relevant references can be found in Ref. 1. For the sake of comparison with the results in Ref. 1 we denote the coverage of one K atom per two surface Si atoms as $\Theta=1$, which is one K atom per (2×1) surface unit cell.

[7] S. Ciraci and I. P. Batra, Phys. Rev. Lett. **56**, 877 (1986).

[8] I. P. Batra, J. M. Nicholls, and B. Reihl, J. Vac. Sci. Technol. A **5**, 898 (1987); I. P. Batra, Prog. Surf. Sci. (to be published).

[9] H. Ishida, K. Terakura, and M. Tsukada, Solid State Commun. **59**, 365 (1986).

[10] P. Soukiassian, Surf. Sci. **172**, L507 (1986); also see Y. Enta, T. Kinoshita, S. Suzuki, and S. Kono, Phys. Rev. B **36**, 9801 (1987).

[11] J. E. Northrup and M. L. Cohen, Phys. Rev. Lett. **49**, 1349 (1982); Physica B + C **117&118B**, 774 (1983).

[12] J. E. Northrup, J. Vac. Sci. Technol. A **4**, 1404 (1986).

[13] J. Hubbard, Proc. R. Soc. London, Ser. A **243**, 336 (1957); R. Del Sole and D. J. Chadi, Phys. Rev. B **24**, 7431 (1981); C. B. Duke and W. K. Ford, Surf. Sci. **111**, L165 (1981).

[14] E. M. Oellig and R. Miranda, Surf. Sci. **117**, L947 (1986).

[15] Y. Kawaguchi and S. Kawaji, Surf. Sci. **58**, 33 (1976).

[16] F. Stern and W. E. Howard, Phys. Rev. **163**, 816 (1967).

[17] F. G. Allen and G. W. Gobeli, Phys. Rev. **144**, 558 (1966).

[18] T. Aruga, H. Tochihara, and Y. Murata, Phys. Rev. Lett. **33**, 372 (1984).