

Surface metallization of silicon by potassium adsorption on Si(001)-(2×1)

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We present the detailed results of self-consistent and geometry-optimized total-energy, band-structure, and charge-density calculations for a potassium-covered Si(001)-(2×1) surface, and for an unsupported potassium monolayer. We found that the (2×1) reconstruction and the dimer bonds of the Si surface continue to be stable after the adsorption of alkali-metal atoms. At the monolayer coverage the charge from the adsorbed potassium atoms is transferred into the empty, antibonding dangling-bond surface states, resulting in the metallization of the Si(001) substrate surface. The bonding between the overlayer and the substrate surface is ionic, and the Fermi level is pinned by the partially filled silicon surface states. Our theory for the metallization and the surface collective excitations is different from previous ones developed for an alkali-metal overlayer on a metal substrate which suggest that the system undergoes a Mott transition, and can successfully account for recent experimental observations. The presence of the active dangling-bond states prevents the alkali-metal monolayer from metallization, and thus provides the crucial difference between metal and semiconductor substrates.

I. INTRODUCTION

Generation of desired electronic properties by metal deposition on the semiconductor surfaces has been exploited¹⁻⁵ in a number of technical applications in the area of microelectronics and electronic devices. Because of their rectifying properties, metal-semiconductor junctions, and particularly the mechanism of the Fermi-level pinning and the formation of the Schottky barrier, have been extensively investigated.⁶⁻¹⁵ Metal-induced gap states,^{7,8} which propagate in the thick metal film, but become evanescent in the semiconductor, have been proposed as the states responsible for the pinning of the Fermi level. Recent experiments, however, have come to different conclusions, revealing the fact that the Fermi level can be pinned and thus the Schottky barrier is formed even at submonolayer coverage.⁹⁻¹¹ Different kinds of states, such as intrinsic surface states, defect states,¹¹ and chemisorption bond states,^{13,14} have been postulated for the pinning mechanism at submonolayer coverage. Batra and Ciraci¹³ suggested coverage-dependent effects after studying a prototype, lattice-matched metal-semiconductor interface¹² [i.e., Al on a Ge(001) surface] from submonolayer to multilayer coverages. At submonolayer coverage they found that the chemisorption bond states and Al-atom states dominate the energy spectrum near the band-gap region, and are responsible for the pinning of the Fermi level. Above the monolayer coverage they showed, however, that owing to the interaction among deposited Al atoms the overlayer changes into a (quasi-) two-dimensional (2D) metal characterized by a (modulated) ladder-type density of states.^{13,14} Concomitantly, the metallic overlayer relaxes outwards away from the semiconductor surface,

and the metal-semiconductor bonds are delocalized.

For those semiconductors which have active surface states the metallization of the overlayer must compete with the formation of metal-semiconductor bonds.¹⁵ In fact, depending on the relative value of the metallic cohesive energy and the metal-substrate interaction energy the overlayer metallization may be suppressed altogether. In this respect, the adsorption of alkali-metal atoms on metal and semiconductor surfaces is rather special, and presents very interesting conceptual ideas about bonding, metallization, and collective excitations.

Alkali-metal atoms are usually characterized by a single electron of large atomic radius. In the metallic state, the structure is open, and the charge density is featureless and low as compared to other divalent and trivalent close-packed metals.¹⁶ In band-structure language the conduction band can be described by a nearly-free-electron picture. From the surface-science point of view alkali-metal adsorption is important because of its work-function lowering effect,¹⁷ which provides several technological applications.

Interesting coverage-dependent features of alkali-metal adsorption on metal surfaces have appeared from the work of Mac Rae *et al.*¹⁸ At the initial stage of cesium adsorption on the W(001) surface, the work function Φ decreases rapidly, and Cs atoms form a (2×2) structure with a Cs-Cs nearest-neighbor distance significantly smaller than that in the Cs metal. Further Cs deposition (above the monolayer coverage) yields a close-packed hexagonal Cs layer with a nearest-neighbor distance comparable to that of the bulk metal. At this coverage the work function passes through a minimum, and a loss peak grows in intensity. Subsequent studies have shown that these coverage-dependent features are common to

other alkali-metal-covered metal surfaces.^{19,20}

Recent work by Tochiwara²¹ has attracted much attention to the adsorption of alkali-metal atoms on semiconductor surfaces. His experimental observations on the potassium-covered Si(001) surface suggested that alkali-metal atoms on semiconductor surfaces lead to practically the same features as observed on transition metals. The maximum coverage obtained is one monolayer [$\Theta=1$, i.e., one K atom per (2×1) surface unit cell] showing a clear (2×1) low-energy electron-diffraction (LEED) pattern but with a different intensity as compared to the clean surface. The work function decreases rapidly at submonolayer coverage ($\Theta \ll 1$), and later, concomitant with the onset of an electron-energy loss peak at 2 eV, it decreases slowly without passing through a minimum. As for alkali-metal adsorption on metal surfaces,¹⁸ these observations were interpreted to imply a metal-insulator (Mott) transition. It was proposed that up to $\Theta=0.5$, K atoms donate their 4s valence electrons to the substrate and become ionic as evidenced by a higher core excitation energy and lower work function. Continued deposition of alkali-metal atoms causes the interatomic distance of the potassium atoms to decrease. Beyond a threshold adatom density the smaller K-K distance allows the formation of metallic bands which, in turn, results in a retransfer of charge to the alkali-metal overlayer. Accordingly, the growing intensity of the peak in the electron-energy-loss spectra (EELS) with increasing Θ was attributed to a collective excitation of the metallic electrons of the overlayer. Data for the Cs-covered Si(001) surface²² were interpreted in a similar fashion.

Aruga, Tochiwara, and Murata²³ carried out detailed analysis of the plasmon loss by the use of angle-resolved EELS and obtained an anisotropic and positive dispersion in contrast to the plasmon dispersion of an alkali-metal overlayer on a metal surface. In view of the interband and intraband (zero-sound) plasmon modes calculated^{24,25} for a simple model, these q-dependent loss peaks were attributed to the 1D plasmons associated with the K chains on the surface.

The experimental data on the alkali-metal-covered Si(111) surface are unfortunately not as abundant as for the Si(001)- (2×1) surface. However, the ultraviolet photoemission spectrum (UPS) taken from the Cs-covered Si(111)- (2×1) surface²⁶ has been interpreted to imply the metallization of the alkali-metal overlayer beyond the adatom coverage of $\Theta=1$.

In this paper we present a detailed study of the K-covered Si(001)- (2×1) surface at $\Theta=1$, which is based on first-principles total-energy, electronic-structure, and force calculations. Some of our results were briefly reported earlier.²⁷ The objective here is to elucidate the interaction of an alkali metal with the reconstructed Si surfaces, and to place emphasis on the metallization by contrasting it with that encountered in other metal overlayers. Our theory for the metallization of the alkali-metal overlayer and the character of collective excitations is at variance with previous suggestions, and can successfully account for the experimental findings. It is also quite different from the metallization of divalent

and trivalent metal overlayers adsorbed on semiconductor surfaces. Our results indicate that the metallic character attributed to the alkali-metal monolayer is, in fact, the metallization of the reconstructed Si surface. Moreover, our work introduces a metal-semiconductor interface, wherein the pinning of the Fermi level at $\Theta=1$ is almost totally determined by the intrinsic surface states.

The organization of this paper is as follows. In the next section the model and the details of the self-consistent-field (SCF) calculations are described. In Sec. III the optimization of the atomic geometry for the K+Si(001) system, yielding an equilibrium structure with a large ionic binding energy, is explained. Section IV is devoted to discussion of the calculated electronic structure, such as the energy band structure of the unsupported K monolayer, the clean and K-covered Si(001) surfaces, and the work function. In Sec. V the analysis of the SCF charge density is presented. In Sec. VI our results are compared with the experimental and theoretical studies, and our interpretation is presented. In addition, a brief discussion of the surface collective excitations relevant to the system at hand is given. Finally, our conclusions are stated in Sec. VII.

II. METHOD OF CALCULATIONS

We performed SCF-pseudopotential calculations²⁸ within the framework of the local-density functional theory applied in momentum space.²⁹ We used nonlocal, norm-conserving ionic pseudopotentials given by Bachelet *et al.*³⁰ These ionic pseudopotentials were generated by using Ceperley-Alder exchange-correlation potential.³¹ For the sake of compatibility, we carried out calculations by using the same exchange-correlation potential with a parametrized form of Perdew and Zunger.³² The calculations were done for an unsupported K monolayer, and for a clean, and a K-covered Si(001) surface using a repeating slab geometry. The vacuum spacing between slabs was taken to be 14 a.u. The silicon substrate with the (001)- (2×1) reconstructed surface is simulated by a slab consisting of eight atomic layers (i.e., 16 Si atoms in the slab unit cell). The top surface is either clean or covered by alkali-metal atoms, but the bottom surface is always saturated by hydrogen atoms. For the positions of the Si atoms we used the optimized reconstruction geometry with a symmetric dimer bond model proposed by Abraham and Batra.³³ That the symmetric dimer bond is favorable relative to the asymmetric dimer bond was first suggested by Pandey,³⁴ and subsequently was observed³⁵ by scanning-tunneling microscopy.

Electronic states were represented by ~ 550 plane waves. During the self-consistency iterations the charge density was sampled at 15 k points placed uniformly in the surface Brillouin zone (BZ). This parameter set, though sufficiently large, may not provide absolutely converged results. However, we believe that the degree of convergence to be achieved should be compatible with the accuracy required in the calculation of a particular property. For example, a small energy difference between the symmetric and asymmetric dimer bond recon-

struction certainly requires a much larger basis set, whereas the gain of energy from the dimer bond formation in a (2×1) reconstruction is rather large (~ 1.5 eV), and thus the overall properties of the Si(001)- (2×1) surface can be dealt with by a relatively small basis set.^{33,36}

As will be seen in the following section the binding energies resulting in these calculations are sufficiently large, and thus can be handled with reasonable accuracy by using a basis set consisting of about 550 plane waves and a charge density sampled at 15 k points. Since the surface bands and the *s* band of the unsupported K monolayer are smooth, and are also devoid of band crossings near the Fermi level, the coarse BZ sampling may lead to an error of $\sim \pm 0.03$ eV in the calculated total energies. This error is further reduced by using a thermally broadened Fermi-Dirac distribution function. As an independent test for the convergence the width of the valence band of an eight-layer Si slab was close to the value for bulk Si calculated with a basis set of 250 plane waves, which corresponds to a kinetic energy cutoff, $|\mathbf{k} + \mathbf{G}|^2 = 12$ Ry. We have repeated calculations of structure optimization with a larger kinetic energy cutoff and with a thinner [i.e., five-layer Si(001)- (2×1)] slab, and observed that the values, in particular the equilibrium configuration and the binding energy, are not seriously affected. Moreover, for critical geometries (i.e., the equilibrium structure proposed here and the structure in which the Si-K internuclear distance $d_{(\text{Si-K})}$ is obtained from the sum of the atomic radii of Si and K) we used a large basis set consisting of ~ 1000 plane waves to calculate total energies.

III. EQUILIBRIUM STRUCTURE AND BINDING ENERGY

To find the equilibrium structure and the position of the adsorbed potassium layer we carried out an extensive geometry optimization within the (2×1) unit cell. In view of the LEED data exhibiting a clear (2×1) pattern^{21,23,37} (1×1) reconstruction was not considered. By positioning a potassium atom above the dimer bond, along the dangling bond, and above the hollow site with varying heights (*h*) from the surface, we investigated several adsorption sites. For each atomic configuration (corresponding to the different location and height of the K atom) the total energies were calculated with a self-consistency tolerance of 10^{-5} Ry (root-mean-square deviation), assuring a reasonable level of self-consistency. Among these atomic configurations, our calculations yielded the lowest total energy for the K atom located at the center of the sixfold hollow site, between two parallel dimer bonds, and 2.4 a.u. above the surface. This leads to an internuclear distance of the substrate silicon and the adsorbed potassium, $d_{(\text{Si-K})} = 4.9$ a.u. The equilibrium structure as illustrated in Fig. 1 indicates that the adsorbed K atoms form a chain along the $[110]$ direction with an interchain distance of $2a\sqrt{2}$ (*a* being the lattice parameter of Si). Because of this atomic configuration the K overlayer (and K monolayer) is denoted as the K chain in the text. Along the chain each K atom has two nearest neighbors with an internuclear distance of 7.26

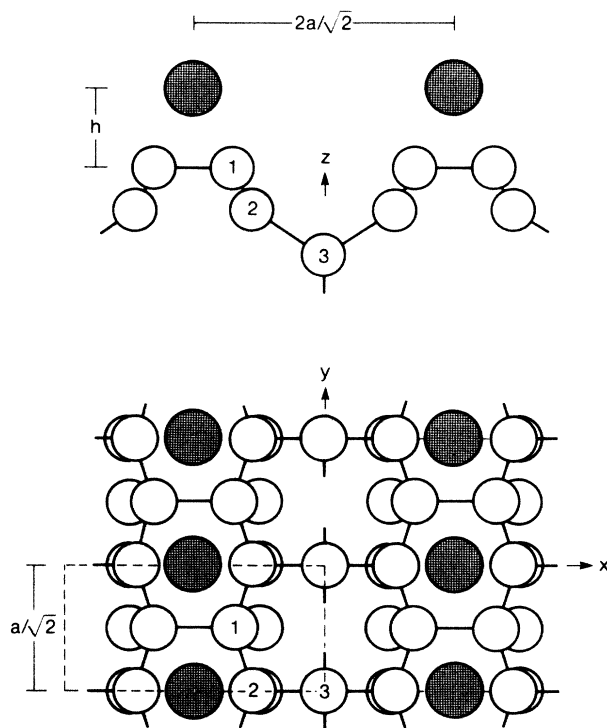


FIG. 1. Side and top views of the equilibrium structure of the potassium-covered Si(001)- (2×1) surface. Shaded large and empty small circles denote K and Si atoms, respectively. Numerals in the circles indicate the atomic layers. $a = 10.26$ a.u., h (or z) = 2.4 a.u.

a.u. Based on the LEED data the formation of chain structure from the K overlayer was previously proposed.²³

We found that K located above Si as if it saturates the dangling bonds is energetically unfavorable relative to the optimized equilibrium structure. This implies that K behaves differently as compared to other atoms (such as H), which form strong (covalent) chemisorption bonds with the surface Si atoms.³⁸

The stability of the clean, reconstructed surface upon adsorption is usually a critical point to be taken into account. In the present system the dimer bond is a strong bond (almost as strong as the bulk Si—Si bond). As far as the adsorption site of K is concerned, one does not expect any bond breaking, or any other significant rearrangement of surface atoms upon K adsorption. However, since the atomic structure of the substrate was fixed during the geometry optimization of the adsorption, the stability of the Si(001)- (2×1) surface has to be investigated to assure that this is indeed the case. We examined the stability of the (2×1) reconstruction geometry by calculating the interatomic forces³⁹ in the presence of the K overlayer. We found the forces acting on the Si atoms were small. This suggests that the displacement of Si atoms is insignificant, and the substrate surface is stable after the adsorption of potassium at $\Theta = 1$.

Having determined the equilibrium structure we next calculate the binding energy. This is done in three steps.

We first calculate the total energy of the unsupported K monolayer. Secondly, we calculate the total energy of the clean Si substrate. For the sake of a consistent comparison of the total energies the parameters of calculations in Sec. II are kept fixed. The binding energy of the K monolayer to the Si surface is found to be 2.4 eV per K atom. By adding the cohesive energy of the K monolayer we obtain the binding energy of a potassium atom to the Si(001)-(2×1) surface to be ~3 eV. To provide an analysis of the stability, we calculate also the total energy of the bulk K by varying the cubic lattice parameter. The energetics of the K+Si(001)-(2×1) system and bulk potassium with respect to the unsupported, metallic K chain in registry with the K adsorbed on Si(001)-(2×1) surface are presented in Fig. 2.

Recently, Kendelewicz *et al.*⁴⁰ based on surface-extended x-ray-absorption fine-structure (SEXAFS) results, estimated that the internuclear distance of the surface silicon and the adsorbed potassium, $d_{(\text{Si-K})}$ is 5.9 a.u. ($3.14 \pm 0.1 \text{ \AA}$). This particular structure was considered in our earlier geometry optimization²⁷ and was found to be energetically unfavorable. We have since repeated the calculations for these two structures (i.e., $d_{(\text{Si-K})}=4.9$ and 5.9 a.u.) with a much larger basis set (~1000 plane waves). Our pseudopotential calculations find the structure derived from SEXAFS data has ~44 mRy higher energy (less stable). This is even 6 mRy higher than that calculated by using ~550 plane waves. The significant point to note, however, is that the SEXAFS-derived structure with $d_{(\text{Si-K})}=5.9$ a.u. still has

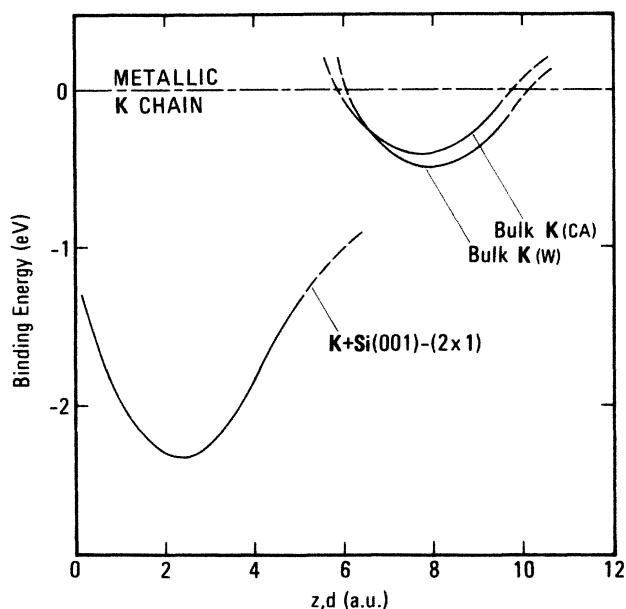


FIG. 2. Calculated binding energies of K+Si(001)-(2×1) and the bulk K relative to the unsupported, metallic K chain in registry with the K-adsorbed Si(001)-(2×1). W and CA denote Wigner and Ceperley-Alder exchange-correlation potentials used in the calculations, z the height of the adsorbed K above the surface, and d the nearest-neighbor distance in the bcc lattice of the bulk potassium.

a high binding energy (~2.5 eV). It is not too surprising since the local-density approximation underestimates the structural parameters related to K. For example, calculations⁴¹ with a Hedin-Lundquist exchange-correlation potential⁴² provide excellent prediction for the binding energy of the bulk potassium, but underestimate the cubic lattice constant by ~0.6 a.u. Calculated structural parameters are strongly dependent on the treatment of the exchange-correlation potential. The values obtained for the cubic lattice constant by using the Wigner⁴³ and Ceperley-Alder³¹ exchange-correlation potentials are 9.2 and 8.9 a.u., respectively. Owing to the low charge density between Si and K atoms (and also perhaps due to the ionic pseudopotential used here) our calculations may underestimate the value of $d_{(\text{Si-K})}$. Nevertheless, as will be shown in Sec. VI, the nature of the interaction between K and the Si surface is unaltered even for $d_{(\text{Si-K})}$ derived from SEXAFS. Also, the binding energies and the character of the interaction between K and the Si surface are in agreement with the independent Hartree-Fock calculations.⁴⁴

Another possibility one considers is that SEXAFS measurements may correspond to a different adsorption site. In view of the fact that K adsorbs in the low-charge-density regions,⁴⁵ we have examined also the second hollow site, i.e., K positioned above the third-layer Si, between two dimer bonds in Fig. 1. This configuration leads to a value of $d_{(\text{Si-K})}$ which is close to that estimated from SEXAFS,⁴⁰ and may also be the location where K atoms are adsorbed at $\Theta > 1$. This adsorption site is, however, less stable according to our calculations. In Table I the total energies of these structures are compared.

High binding energy obviously indicates that a strong interaction takes place between the K overlayer and the Si surface. The calculated binding energy is three times larger than the binding energy of the bulk metal, and also five times larger than that of the metallic K chain. It is also seen that the unsupported, metallic K chain is unstable relative to the bulk K. However, owing to this strong interaction both the metallic K chain (or monolayer) and the bulk K become unstable relative to the K adsorbed on the Si surface at $\Theta=1$. We now examine the nature of this interaction, and determine the effect of the Si surface, which makes the metallic state of the K chain unstable.

TABLE I. Comparison of total energies calculated for three adsorption structures. $E_T^{(0)}$, the total energy of the equilibrium structure we found with $d_{(\text{Si-K})}=4.9$ a.u. and $h=2.4$ a.u.; $E_T^{(1)}$, same adsorption site but $h=4.2$ a.u. and $d_{(\text{Si-K})}=5.9$ a.u. as proposed in Ref. 40; $E_T^{(2)}$, the hole site above the Si atom in the third layer and $d_{(\text{Si-K})}=6.2$ a.u. The reference of energy is taken to be $E_T^{(2)}$. Calculations are performed using ~550 plane waves.

$E_T^{(0)}$ (mRy)	$E_T^{(1)}$ (mRy)	$E_T^{(2)}$ (mRy)
-56	-18	0

IV. ELECTRONIC STRUCTURE

The character of the interaction underlying the large binding energy is clarified by a study of the electronic structure. The energy band structure of the unsupported K monolayer with the same 2D lattice registry as the K overlayer is shown in Fig. 3(a). The lowest band is formed from the 4s-valence orbital, and thus has an s symmetry. The dispersion of this band is large along the chain direction ($\parallel k_y$) but small in the directions perpendicular to the chain ($\parallel k_x$), so that the ratio of the effective masses $m_x^*/m_y^* \approx 6$. This implies that the alkali-metal overlayer would display a 1D metallic character if it underwent a metal-insulator transition. However, as we shall see later, this does not happen. The dimensionality of the upper p -like bands is not as obvious as of the lowest s -like band.

The energy bands of the K-covered Si are shown in Fig. 3(b). It is seen that upon adsorption the metallic bands of the K monolayer are almost totally discarded, and perhaps are merged in the conduction band of the substrate. Two bands in the gap, labeled D_1 and D_2 , originate from the dangling bonds of the reconstructed Si(001) surface. In Fig. 3(c) we have schematically traced the origin of these two bands. Dangling orbitals (rabbit ears) of a Si atom interact with those of the adjacent Si atom to give a fully occupied σ dimer bond and a completely empty σ^* band in addition to $\pi(D_1)$ and $\pi^*(D_2)$ bands in the region of E_F . Earlier it was proposed that owing to the asymmetry⁴⁶ of the dimer bond, the D_1 and D_2 bands split, causing the clean reconstructed surface to have an insulating character. It was later shown³⁴ that the energy difference between the symmetric and asymmetric dimer bonds is too small for this to occur, and upon adsorption the dimer bond is symmetrized leading to a slight overlap of the surface-state bands.³⁸ Therefore the overlap of the bands in the gap arises mainly from the polarization effects of the adsorbed potassium. The Fermi level passes through the D_2 band, which is normally empty when the Si surface is free of adsorbates. It appears that the valence 4s electrons of the K overlayer are accommodated by D_2 (which becomes partially occupied) leading to the metallization of the surface.

Surface states or resonances in the conduction band are shown only in the energy region where the interband plasmon dispersion is measured.²³ These states are accessible by the excited electrons in the EELS experiment, which samples mainly the surface region, and are likely to be responsible for collective and individual excitations. The resonance state R (which originates from σ^*) hybridizes with different bulk conduction-band states along the [100] direction. At the center of the surface BZ the R state is located 1.9 eV above the filled D_1 band. The individual excitation energy inferred from the energies of the D_1 and R states is in fair agreement with the observed EELS peak.^{21,47} The local and total density of states in Fig. 4 shows the surface character of D_1 and D_2 states. The backbonding and dimer-bond states can be identified in the valence band, indicating that the effect of the adsorbed alkali-metal layer on the surface

states is insignificant. The calculated work function of the K-covered surface is found to be 2.3 eV lower than the work function of the clean surface. This value is in fair agreement with the observed lowering of the work function upon the K adsorption.²¹

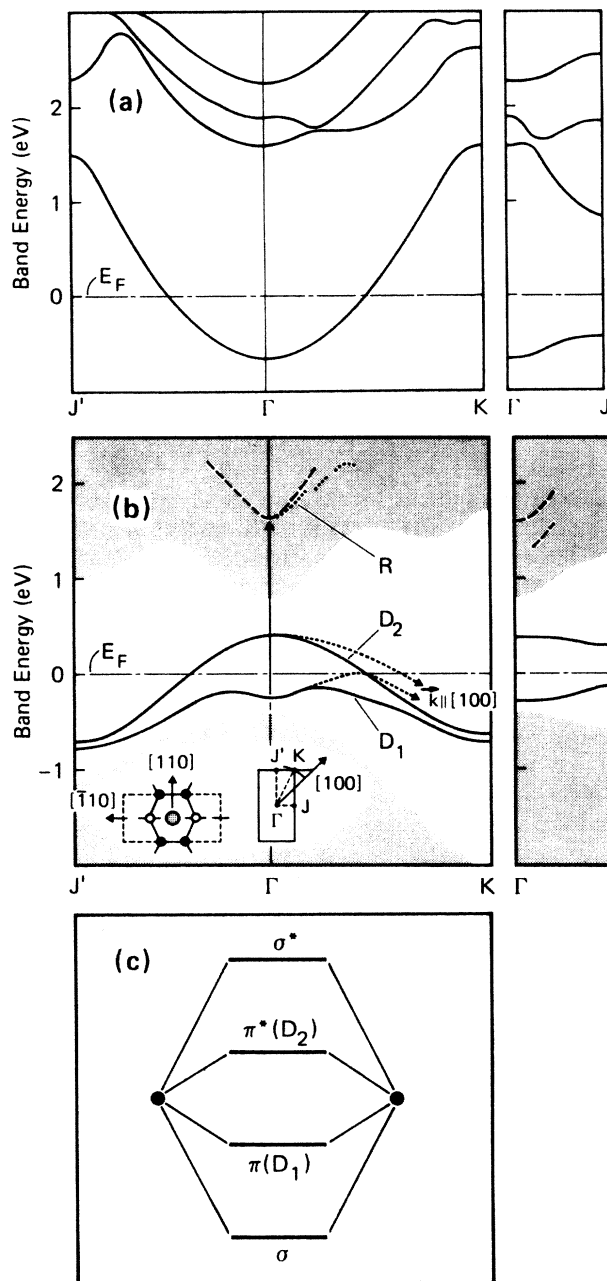


FIG. 3. Calculated energy-band structures: (a) unsupported K monolayer (or K chain) with the same 2D lattice registry as the K overlayer, (b) K+Si(001)-(2 \times 1) surface with $d_{(\text{Si-K})}=4.9$ a.u. For (c), see text. Surface states for $k_{\parallel}[100]$ are shown by dotted lines. Surface Brillouin zone and the surface atomic configuration are shown by the inset. Large shaded, small solid, and small open circles describe K and first- and second-layer Si atoms, respectively.

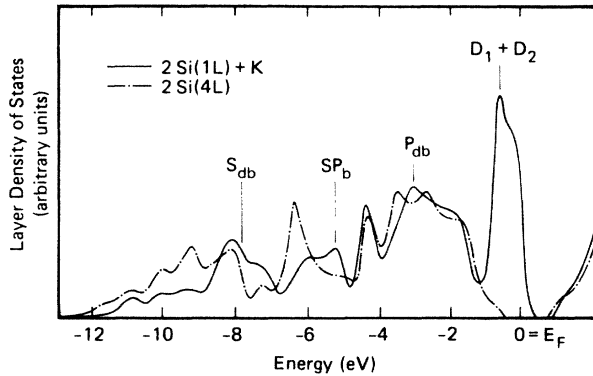


FIG. 4. Layer density of states calculated at the surface (1L) and at the fourth layer (4L) of the K-covered Si(001)-(2 \times 1) slab. P_{db} and S_{db} are p - and s -like dimer bond states. SP_b is an ($s+p$)-like backbonding state (see Ref. 38). D_1 and D_2 are dangling-bond surface states.

V. CHARGE DENSITY ANALYSIS

The origin and the localization of three states D_1 , D_2 , and R , which are relevant for the surface metallization, and the excitation spectrum are deduced from analysis of the state charge distribution. In Fig. 5 the contours of charge densities of D_1 and D_2 for the clean Si(001)-(2 \times 1) surface show clearly their dangling-bond origin. The resonance state R in the conduction band has a surface localization and an antibonding character. Figure 6 illustrates the same states after the adsorption of potassium. It is seen that except for slight polarization and changes in the value of charge maxima the dangling-bond character of D_1 and D_2 is unaltered. However, no charge accumulation is observed in the proximity of the potassium atom; this would be suggestive of the significant contribution of the alkali-metal atoms, or the retransfer of charge upon the metallization of the overlayer. The changes in the character of the empty resonance state owing to the contribution of the K atom are, on the other hand, observable [see Fig. 6(c)]. While the density between the surface and the subsurface layers recedes, the vacuum region above the alkali-metal overlayer gains some charge. The contour plots of R in Fig. 6(c) give an impression about the formation of the charge density of a state having some origin from the overlayer. Note that the clean surface has also a resonance state about 2 eV above the Fermi level. This state prevails in the presence of the overlayer, except that its energy shifts slightly.

The contour plots of the total (valence) charge density in a horizontal plane 2.4 a.u. above the surface (which corresponds to the plane of the overlayer with the equilibrium $d_{(Si-K)} = 4.9$ a.u. found in our study) are shown in Fig. 7 for the clean and K-covered surfaces. Their shape with two maxima, and their location with respect to the surface Si atoms, indicate that the charge density above the surface is peculiar to the substrate surface. The characteristic shape of the contours prevails even

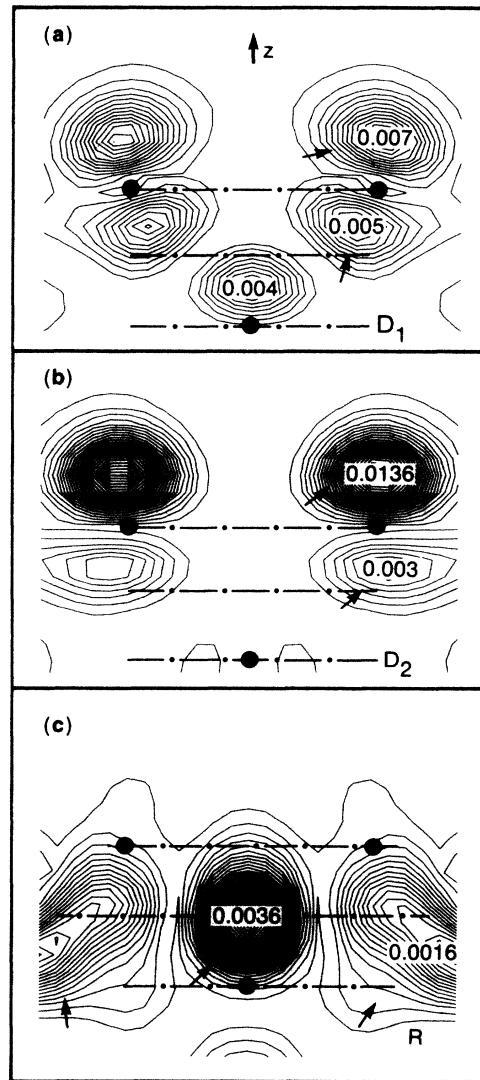


FIG. 5. Charge-density contour plots of D_1 , D_2 , and R calculated for the clean Si(001)-(2 \times 1) surface at $k=0$; (0.108 a.u.⁻¹) in a vertical plane described in Fig. 6. The atomic (001) planes of Si substrate are shown by dash-dotted lines. Charge density increases in the direction of small arrows. Contour spacings are (a) 5×10^{-4} , (b) 5×10^{-4} , and (c) 10^{-4} a.u.

far above the overlayer. The charge density of the unsupported K monolayer, which is indicative of how the charge with s symmetry would be distributed upon the metallization of the overlayer, is distinctively different and has a single maximum (see Fig. 8). A similar comparison can be made in Fig. 9, where the charge-density contour plots in a vertical plane passing through the dimer bond are shown. The pronounced effect of the adsorption is the increase of the density of contours around surface silicon atoms, but again no charge is seen above the alkali-metal overlayer.

A pictorial manifestation of the fact that the partially filled gap states are only the antibonding dangling-bond states is exhibited in Fig. 10. The vertical plane chosen passes through the potassium and its two nearest-

neighbor surface Si atoms. Figure 10(a) shows the charge density for the clean Si(001)-(2×1) surface, $\rho\{\text{Si}\}$. The corresponding contours in the presence of the K overlayer, $\rho\{\text{K+Si}\}$, are seen in Fig. 10(b). As in previous plots there is no obvious dramatic change in the shape of the contours, but notably absent is any directional bond between K and the nearest Si atoms or any metallic charge distribution above the overlayer. The density of the contours increases in the case of the K overlayer in going from the surface into the vacuum with a general accumulation of charge in the dangling-bond region. A crucial result emerges upon examining the difference plot, $\rho\{\text{K+Si}\} - \rho\{\text{Si}\}$, in Fig. 10(c). Owing to the core repulsion the charge is actually depleted from the region around the K atom and instead it has accumulated around the surface Si atoms. The shape of

the accumulated charge is reminiscent of the dangling-bond surface state D_2 in Fig. 6(b).

This analysis of the charge density demonstrates that the adsorption of the alkali-metal atom does not lead to any new state in the gap, but the 4s valence electron has simply gone into filling the empty dangling-bond surface state.

VI. DISCUSSIONS

The total energy and force calculation in Sec. III yielding an equilibrium structure, in which the adsorbed potassium atom was located at the center of the hollow site between two dimer bonds. As depicted by Fig. 10, the total charge has the lowest density, where the K atom is located. According to the equilibrium structure found in this study each potassium has four nearest-neighbor silicons, the K-Si internuclear distance being

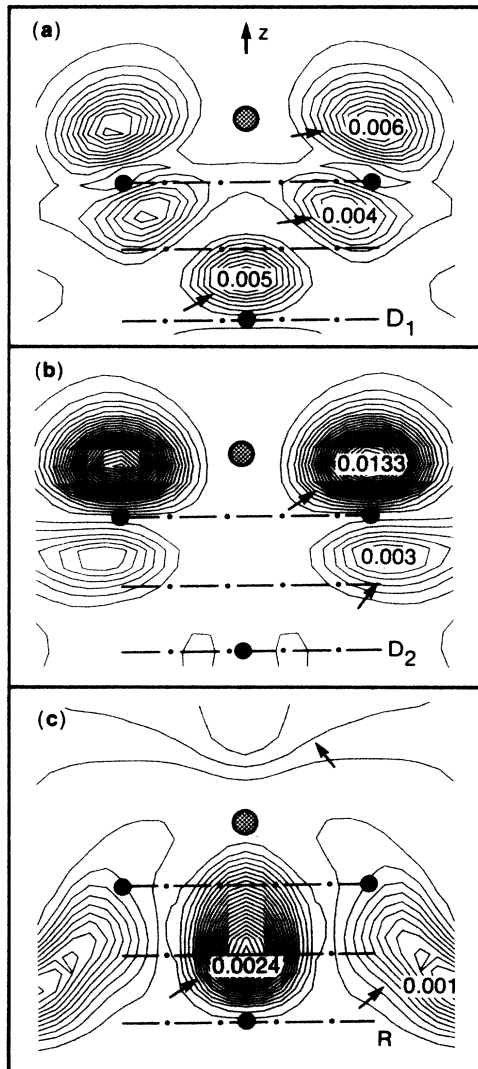


FIG. 6. Charge-density contour plots of D_1 , D_2 , and R calculated for the K-covered Si(001)-(2×1) surface at $\mathbf{k}=(0; 0.108 \text{ a.u.}^{-1})$ in a vertical plane passing through K and two nearest surface Si atoms. $d_{(\text{Si-K})}=4.9 \text{ a.u.}$ and contour spacings are 5×10^{-4} for (a) and (b), and 10^{-4} for (c) in a.u.

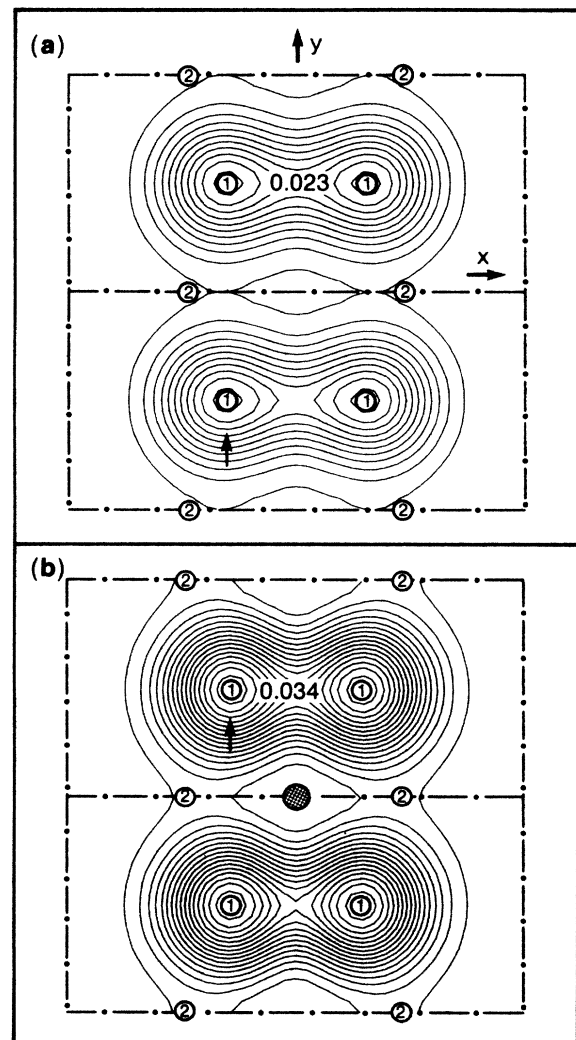


FIG. 7. Contour plots of the total charge density in an horizontal plane 2.4 a.u. above the Si surface. $x\parallel[110]$; $y\parallel[110]$, and $z\parallel[001]$. The surface unit cell is delineated by dash-dotted lines. Contour spacings are 0.002 a.u.

4.9 a.u. On the other hand, the nearest K-K distance in the overlayer chain is 7.26 a.u., which is 1.4 a.u. smaller than the nearest-neighbor distance of bulk potassium in the metallic state. The shorter distance is consistent with K being ionic on the surface. Note that Cs atoms adsorbed on W(001) surface were observed to have the Cs-Cs distance smaller than that in the bulk metallic state.¹⁸ In view of the rapid decrease of the work function an ionic state was attributed to the Cs overlayer in the initial stage of adsorption.

The cohesive energy of potassium in the bulk metallic state is known to be ~ 1 eV. We calculated the cohesive energy of the unsupported K monolayer with the same lattice registry as the K overlayer to be 0.6 eV per atom. The calculated binding energy of the adsorbed K atom

was rather large (3 eV) and is comparable with the cohesive energy in the ionic KCl crystal. This simple analysis based on energetic considerations suggests that the binding is ionic and the metallization of the adsorbed K overlayer does not take place. Otherwise, the metallization would cause the alkali-metal atoms overlayer to relax from the surface by regaining their charge, so that they would lose 3 eV per atom but gain only 0.6 eV through metallic cohesion.

Our results obtained from the calculations of the electronic structure and SCF charge density corroborate our conclusion that the binding is ionic. It becomes clear that the adsorption of the alkali-metal atom does not lead to any significant changes in the states of the clean surface. The bonding and antibonding dangling-bond bands persist with slight modifications in their dispersions. No genuine K states suggestive of the overlayer metallization appear near the Fermi level. A sizable effect of the K atom was seen only in the conduction band.

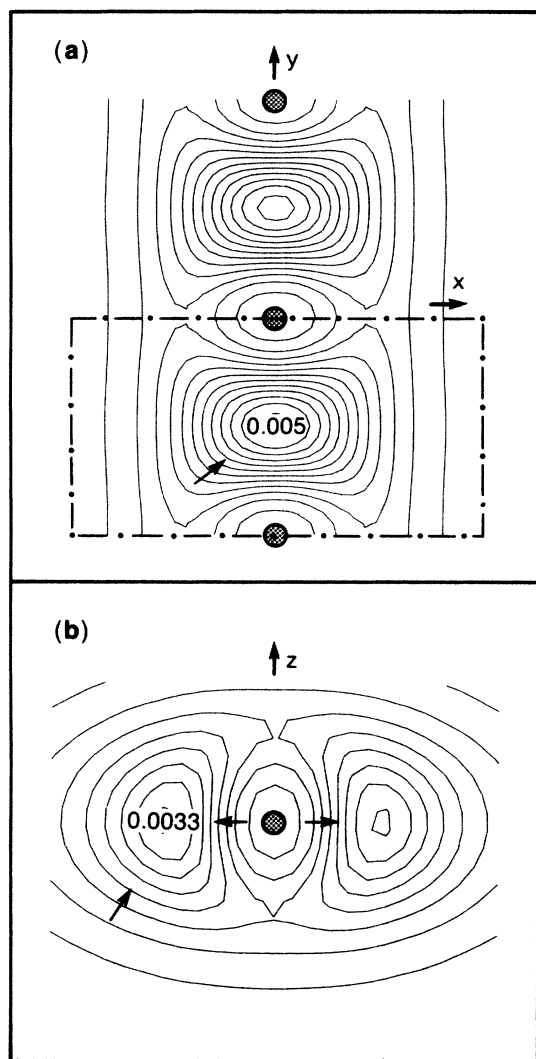


FIG. 8. Contour plots of the charge density calculated for the unsupported K chain (monolayer) with the 2D lattice registry of the K-covered Si surface. The unit cell is shown by dash-dotted lines of the (a) horizontal and (b) vertical plane as in Fig. 6. Contour spacings are 4×10^{-4} a.u.

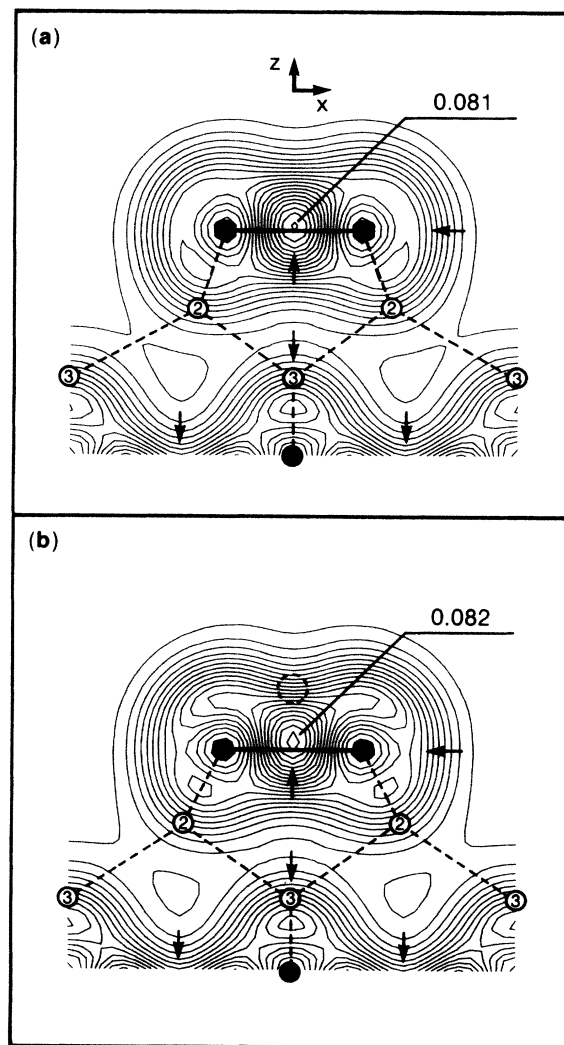


FIG. 9. Contour plots of the total charge density in a vertical plane passing through the dimer bond: (a) clean surface and (b) K-covered surface. Contour spacings are 0.004 a.u.

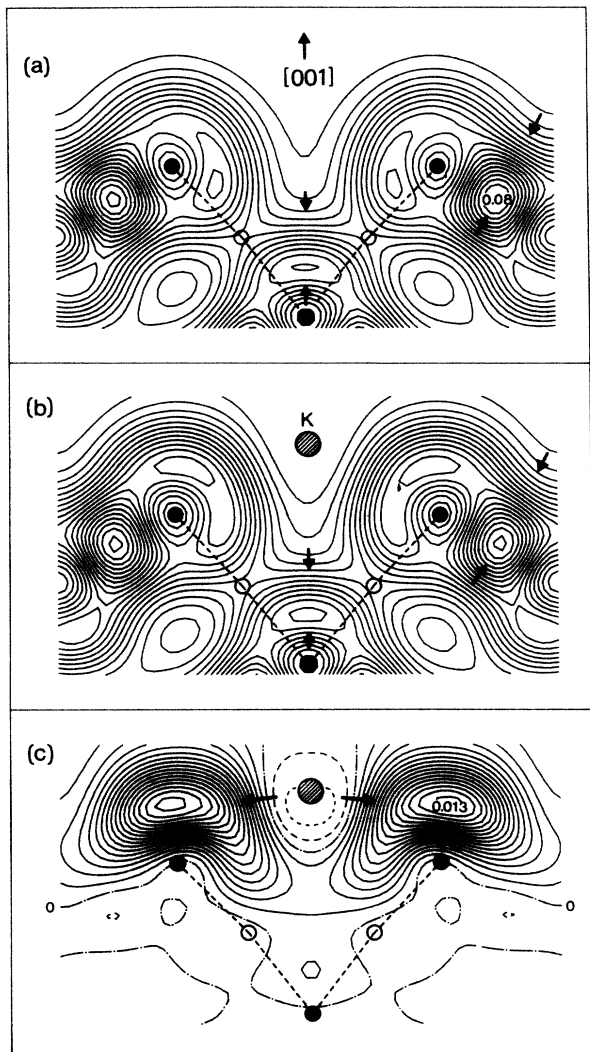


FIG. 10. Contour plots of the total density in a vertical plane passing through K and two nearest surface Si atoms (the same plane as in Figs. 5 and 6): (a) clean Si(001)-(2 \times 1); (b) K + Si(001)-(2 \times 1) with $d_{(\text{Si-K})} = 4.9$ a.u. (c) Difference plot of (a) and (b) showing regions of charge depletion (dashed lines) and charge accumulation (solid lines). Uncharged-density contours are shown by dash-dotted curves. Atoms in the plane and atoms projected onto the plane are shown by solid and open circles, respectively. The contour spacings are 0.004 in (a) and (b), and 8×10^{-4} a.u. in (c).

In order to explore the character of the empty bands, the K-covered Si(001)-(2 \times 1) surface has been recently studied by using angle-resolved inverse-photoemission spectroscopy.⁴⁸ At normal incidence two surface-sensitive features 0.25 and 2.8 eV above the Fermi level are identified, which are quenched upon exposing the surface to oxygen. The energy locations of these features coincide with the calculated empty surface states D_2 and R . The lower surface feature exhibits very little dispersion around Γ and then fades away. This is

consistent with the fact that the calculated D_2 band dips below the Fermi level and becomes occupied.⁴⁸ The upward dispersion at larger k along the [100] direction, however, is not accounted for in the calculations. The observed feature in the conduction band disperses upwards along the [100] direction, and could agree well with the R band.

These results indicate that the valence electrons of the K atoms are donated to fill the empty surface states leading to the metallization of the Si surface. In contrast, alkali-metal atoms adsorbed on transition-metal surfaces regain their charge at saturation coverage, and become metallized. This is shown by the variation of the work function, which passes through a minimum, and increases towards a saturation value corresponding to the work function of the alkali metal. Here the presence of the active dangling-bond states provides the crucial difference between a metal and a semiconductor surface at monolayer coverage. In the present system the metal-insulator transition takes place through the metallization of the semiconductor surface, but not through a Mott-type transition. Stated differently, metallic bands do not form on the K monolayer adsorbed on the Si(001) surface.

The attractive Coulomb interaction between the positively charged core and the surrounding electron density of the dangling bonds is responsible for the strong binding. Such an interpretation is also supported by the total-energy calculations. In the course of structure optimization, the valence electrons of K were already transferred to the surface even at a large distance ($h = 5.1$ a.u.). As h decreases, the Coulomb energy predominates over other components of the total energy, and pulls the ion to the equilibrium position. Strong ion-ion repulsion (represented by the ionic pseudopotential), however, prevents it from entering into the substrate.

Since the adsorbed alkali-metal atom donates its valence electron to the Si surface band, and eventually becomes positively charged, the $3p$ -core shift and the decrease of the work function are easily understandable. The rapid decrease of work function at $\Theta \ll 1$ may imply a relatively larger adatom-surface distance at the initial stage of coverage. As the coverage increases more charge builds up on the surface and, consequently, higher attractive forces act on the adatom to pull it closer to the surface. Toward saturation coverage, the adatom-surface distance becomes smaller and results in an effective core screening. The local density of states above a horizontal plane bisecting the first and second Si layers yields 8.9 electrons per surface unit cell (slightly fewer than nine electrons). In this region the surface electrons can provide a screening of the K core potential comparable to that of the bulk metal. This picture is consistent with the decrease of the work function at a lower rate near saturation coverage. At this point we comment upon recent experimental work by Oelling and Miranda,⁴⁹ revealing for the first time the multilayer coverage of K on the Si(001) surface. In contrast to previous data,²¹ they observed that the work function also passes through a minimum at $\Theta = 1$. Upon further K

deposition Φ saturates 0.4 eV above the minimum value. By using the Helmholtz expression they estimated a dipole length of ~ 1 a.u. for the case of complete charge transfer from K to dangling-bond states. Their experimental results can be interpreted to provide additional support for our predictions. The observation of $\Phi(\Theta)$ beyond $\Theta=1$ is certainly possible, but that range of coverage has not been examined in our calculations. However, the lack of a minimum in the work-function change, $\Delta\Phi(\Theta)$ for $0 < \Theta < 1$ confirms the absence of overlayer metallization even when the K chain has been fully formed. As the coverage increases beyond $\Theta=1$, where K either adsorbs at a different site or forms a new layer, $\Phi(\Theta)$ undergoes a change as expected. Finally, as is clear from the charge distributions shown in Figs. 6 and 10, the average dipole length should be smaller than our calculated equilibrium height, as is in fact obtained by them. This is due to the sizable protrusion of the dangling bond towards the vacuum, in which the valence charge of K is accommodated. It should also be noted that the change in work function cannot be related in a simple way to the degree of ionicity because of the effects of polarization.⁵⁰ In our calculations a rigorous account of the charge distribution led to $\Delta\Phi$ in fair agreement with the experimental value.²¹ There is apparently some confusion about the change of h with coverage. It has been shown by us earlier¹³ that with increasing Θ , h increases, provided that there is overlayer metallization. In the present work, up to $\Theta=1$ only, the overlayer was not metallized up to that coverage, and hence there is no increase in h .

So far we have established the type of the binding and the origin of the metallization. In view of these findings let us turn to a brief discussion of the excitation spectrum.²³ Electron-energy-loss spectra (EELS) show a peak with the energy position depending on the K coverage.²¹ At low coverage a broad and weak loss peak at 4 eV could not be identified clearly because of the strong bulk transitions. However, the intensity of the energy-loss peak increases sharply for $\Theta > 0.6$, and is stabilized in energy near 2 eV. Tochiyama²¹ attributed this loss peak to the excitation of the plasmon of the overlayer. Subsequently, a positive dispersion (starting from 1.7 eV at $q=0$ and dispersing upwards along $q\parallel[100]$ and $q\parallel[110]$ directions) was observed by angle-resolved EELS.²³

The collective excitations of 2D metals have been, in the past, investigated extensively.⁵¹⁻⁵⁸ Introducing the so-called box model, News⁵³ was able to formulate the dispersion relations of 2D metals from a 2D degenerate electron gas. For small momentum, he found the intraband plasmon dispersion as $\omega_{ac} \propto q$ and the interband plasmon dispersion as $\omega_{op} \propto (1-q)$. According to his findings, ω_{op} first disperses downwards at small q and passes through a shallow minimum and thereafter increases with increasing q . This behavior of the interband dispersion was confirmed experimentally from work on the K overlayer on Ni(001) surface.¹⁹ Based on this dispersion relation, which is not in agreement with the observed dispersion, and in view of the structural model of the K overlayer on a Si(001) surface, Aruga

*et al.*²³ attempted to deduce the dimensionality of the overlayer. Using the parallel-rod model and also the Wannier representation based on the surface band structure, Tsukada *et al.*^{24,25} calculated the dispersion of the K overlayer.

The observed plasmon dispersion²³ should deviate from the dispersion relations based on the 2D degenerate electron gas⁵³ for the following reasons: First, as illustrated in Fig. 11 the surface charge density is reminiscent of a rod, which originates from the Si surface states, but not from the metallization of the overlayer. Secondly, as revealed from the self-consistent-field microscopic theory of the surface plasmons,^{55,58} the form of the initial- and final-state wave functions plays a decisive role in determining the dispersion of the collective excitations. The initial- and the final-state wave functions in Fig. 6 do not display any free-electron-like separable

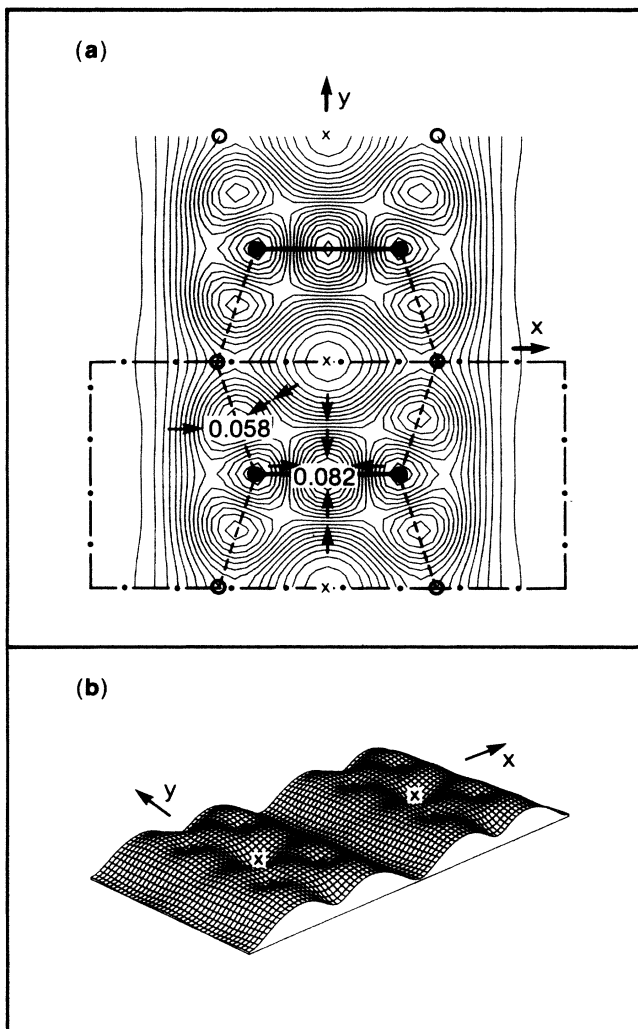


FIG. 11. (a) Contours of the total charge density of the K-covered Si(001)-(2 \times 1) surface in the Si surface plane with contour spacings of 0.004 a.u. Surface and subsurface Si atoms are shown by solid and open circles. Solid and dashed lines denote the dimer and back bonds. The (x,y) position of the adsorbed K atom is indicated by x . (b) The surface plot of (a).

components. Therefore, one cannot attribute a literally 1D character (i.e., states are confined in two dimensions, but have a free-electron-like behavior in the third dimension) to the charge density arising from the D_2 band. In principle, the Fourier transform of the overlap matrix has to be incorporated. Since the dimer bond and the backbonding states are localized in the proximity of the surface,³⁸ they are easily sampled by EELS. Moreover, the energies of these states occur near the gap. Consequently, these states should also be taken into account in the initial states of the polarization operator. The logarithmic singularities of the polarization operator correspond to single-particle (individual) excitations. The single-particle excitation from D_1 or D_2 to R is expected to have a significant contribution to the loss peak at about 2 eV. As noted earlier, an EELS peak at 1.7 eV was observed⁴⁷ even for the clean Si(001)-(2×1) surface, and was assigned to an individual excitation from D_1 to an unknown surface resonance in the conduction band.³⁸ Such a surface resonance (labeled R) is found in the present study in nearly the correct energy position, and is found to persist in the presence of the K overlayer. Since the overlayer has not metallized because of the presence of active dangling bonds, the origin of the EELS peak can reasonably be sought in single-particle excitations.

In summary, the type of bonding proposed in this work is based on the considerably high binding energy of potassium, the electronic structure, and an extensive charge-density analysis of the K + Si(100)-(2×1) system. The consensus is that the bonding is ionic for $\Theta \ll 1$, and as $\Theta \rightarrow 1$ the surface becomes metallic. The controversy lies in, however, what is metallized (the Si surface or the K overlayer), and what is the character of the bonding. Theories claiming the metallization of the K overlayer are based mainly on the formation of a 1D metallic chain of alkali-metal atoms having a nearest-neighbor distance smaller than that of the bulk.^{21–26,40} Such a metallization is conceivable for metal substrates, and the gain of energy would not be larger than 1 eV. However, owing to the active, empty dangling-bond states, the energy of metallization cannot balance the large binding energy of ~ 3 eV, and hence the bonding continues to be ionic even at $\Theta = 1$. As becomes clear from the above discussion the present assignment for the bonding is consistent with the experimental data,⁴⁸ and is also in compliance with the electronegativity considerations. Recalling the electronegativity of Si [$\chi(\text{Si}) = 1.8$] and the electronegativity of K [$\chi(\text{K}) = 0.8$] one infers that Si is twice as likely to capture charge than K. Our arguments about the bonding are supported by similar SCF calculations by Northrup,⁵⁹ who has predicted an ionic bonding for sodium adsorbed on the ideal Si(111) surface. Beyond the local-density approximation, Hartree-Fock calculations⁴⁴ indicate also a large binding energy and transfer of charge from K to Si.

Other theoretical results^{25,60} proposing the metallization of the overlayer either lack the total-energy minimization, or are based on inadequate interpretation of experimental data. Previously Ishida *et al.*²⁵ calculated the band structure of the KSi_8H_4 thin film by using an

LCAO- $X\alpha$ method. They did not carry out the total-energy calculations to find the equilibrium structure, but estimated the K-Si distance from the atomic radii to be 6.65 a.u. It is apparent that the K-Si distance they used in their calculations is much larger than what we found by SCF total-energy minimization. Their LCAO- $X\alpha$ calculations resulted in a fundamental energy gap of 3 eV (which is much larger than the experimental energy gap) and three surface bands with dominant K contribution. Based on a Mulliken's population analysis, which yielded +0.13 charge on the adsorbed K atom, they concluded that the overlayer was metallized. These re-

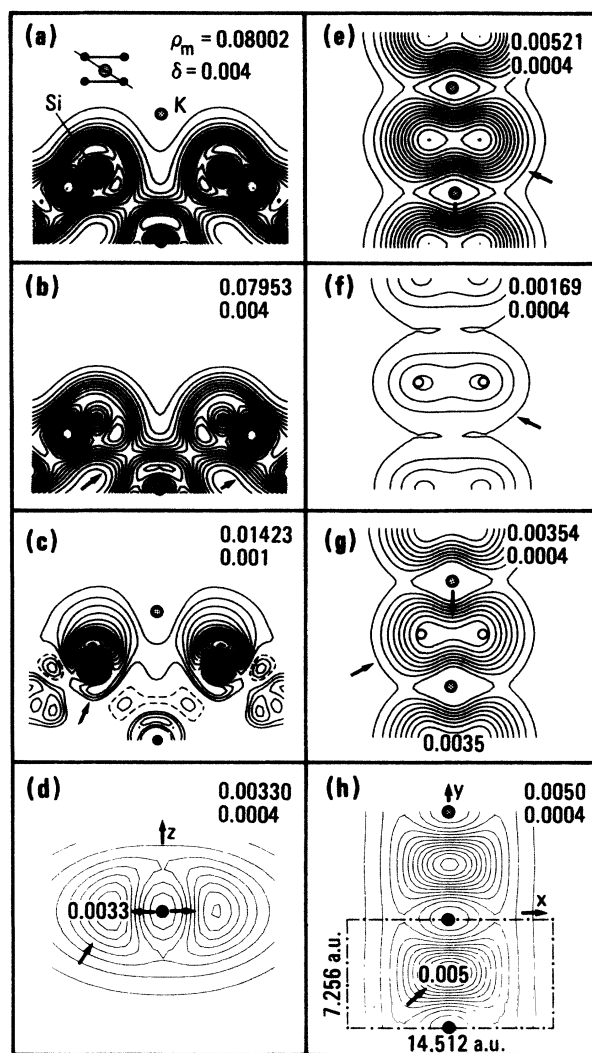


FIG. 12. Contours of the total charge density. First column is in a vertical plane passing through K and two nearest surface Si shown in the inset. (a) K + Si(001)-(2×1) with $d_{(\text{Si-K})} = 5.9$ a.u. (3.14 Å); (b) clean Si(001)-(2×1) surface; (c) difference plot of (a) and (b); (d) unsupported, metallic K chain in registry with K on Si surface. Second column [(e)–(h) in the same order as the first column] is in the plane of the K overlayer 4.2 a.u. above the surface Si. ρ_m is the maximum value of charge, and δ is the contour spacing. Dash-dotted curves show the regions of charge depletion.

sults are at variance with our findings. Kasowski and Tsai⁶⁰ carried out pseudofunction calculations within the local-density approximation, and concluded that K does not form an ionic bond with Si. They also find a $d_{(\text{Si-K})}$ value larger than ours. They compared their model with the UPS spectrum obtained from the Cs+Si(111)-(2×1) system. That the electronic structure of K+Si(111)-(2×1) is different from that of K+Si(001)-(2×1) and is coverage dependent, has been demonstrated⁴⁵ recently. Their arguments based on the EELS peak observed at ~2 eV are not conclusive, because the clean Si surface exhibits an EELS peak in the same energy region.⁴⁷ These experiments do not provide any direct support for their model calculations. Using an arbitrary charge partitioning they assign the high charge density of the clean Si surface to K. Consequently, they find charge transfer from Si to *less electronegative* K.

More recently, angle-resolved photoelectron spectroscopy by Enta *et al.*⁶¹ rules out previous band models, and verifies our theory of the surface metallization. By going to higher K coverage, they have observed that the metallic surface becomes insulating at $\Theta=2$, because the surface-state band D_2 becomes fully occupied.

Conclusions about the nature of bonding based on SEXAFS work⁴⁰ measuring $d_{(\text{Si-K})}$ are not definite. According to a criterion set by Citrin,⁶² the interatomic distance measured by SEXAFS is a perfect candidate for ionic bonding. We believe that one cannot draw definite conclusions about the nature of the bond simply by looking at the bond length. Since the local-density approximation underestimates the structural parameters of K, and thus calculated values for $d_{(\text{Si-K})}$ depend on the form of the exchange-correlation potential, the important issue is the nature of the bonding. The point to emphasize is that the bonding is ionic even for the value of $d_{(\text{Si-K})}$

deduced from SEXAFS. To this end we show the SCF charge distribution for $d_{(\text{Si-K})}=5.9$ a.u. (3.14 Å). Plots of the valence charge-density difference, i.e., $\rho\{\text{K+Si}\}-\rho\{\text{Si}\}$, in Fig. 12 unambiguously show that the origin of the surface metallization is the dangling bond and not the metallic chain. As a result, the bond is ionic at our $d_{(\text{Si-K})}$, as well as at the large $d_{(\text{Si-K})}$ derived from SEXAFS.

VII. CONCLUSIONS

The alkali-metal-Si(001) surface system at monolayer coverage presents remarkable features in the adsorption phenomena, as well as in the electronic structures of surfaces. It appears that the alkali-metal atoms, which normally form simple metals, lead to ionic bonding when they are adsorbed on the Si(001) surface. The substrate with a superlattice gap changes into a metallic state. Although the surface charge density displays a 1D-like character, the observed EELS dispersion cannot be associated with the metallization of the adsorbed K chains. As far as the pinning of the Fermi level is concerned, the K overlayer on the Si(001) surface is a unique system among metal-semiconductor interfaces investigated so far. The Fermi level of the present system is pinned completely by the surface states as proposed by Bardeen,⁶ but not by chemisorption states or metal-induced states. With these results the interaction of potassium with the Si surface and the character of the normal modes of charge-density fluctuations will be elucidated, leading to significant revisions in the previous understanding. The multilayer coverage, on the other hand, seems to remain as a challenging problem both experimentally and theoretically.

¹R. H. Williams, *Contemp. Phys.* **23**, 329 (1982).

²L. J. Brillson, *Surf. Sci. Rep.* **2**, 123 (1982).

³M. Schlüter, *Thin Solid Films* **93**, 3 (1982).

⁴A. Kahn, *Surf. Sci. Rep.* **3**, 193 (1982).

⁵G. W. Rubloff, in *Festkörperprobleme (Advances in Physics)*, edited by J. Treusch (Pergamon, Vieweg, 1983), Vol. XXII, p. 179.

⁶J. Bardeen, *Phys. Rev.* **71**, 717 (1947).

⁷V. Heine, *Phys. Rev.* **138**, A1689 (1965).

⁸S. G. Louie and M. L. Cohen, *Phys. Rev. Lett.* **35**, 866 (1975); *Phys. Rev. B* **13**, 2461 (1976).

⁹J. E. Rowe, S. B. Christman, and G. Margaritondo, *Phys. Rev. Lett.* **35**, 1471 (1975).

¹⁰G. Margaritondo, J. E. Rowe, and S. B. Christman, *Phys. Rev. B* **14**, 5396 (1976).

¹¹W. E. Spicer, I. Lindau, P. Skeath, C. Y. Su, and P. Chye, *Phys. Rev. Lett.* **44**, 420 (1980); *J. Vac. Sci. Technol.* **17**, 1019 (1980).

¹²I. P. Batra, *J. Vac. Sci. Technol. B* **1**, 558 (1983); I. P. Batra and F. Herman, *J. Vac. Sci. Technol. A* **1**, 1080 (1983).

¹³I. P. Batra and S. Ciraci, *Phys. Rev. B* **29**, 6419 (1984); *J. Vac. Sci. Technol. B* **3**, 427 (1984); *Phys. Rev. B* **33**, 4312 (1986).

¹⁴S. Ciraci and I. P. Batra, *Phys. Rev. B* **33**, 4294 (1986).

¹⁵A. Zunger, *Phys. Rev. B* **24**, 4372 (1981).

¹⁶N. D. Lang, *Phys. Rev. B* **4**, 4234 (1971).

¹⁷E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, *Phys. Rev. B* **24**, 864 (1981).

¹⁸A. U. MacRae, K. Muller, J. J. Lander, J. Morrison, and J. C. Phillips, *Phys. Rev. Lett.* **22**, 1048 (1969). The two-layer model, proposed in this work for explaining the minimum in $\Delta\Phi$, has been challenged on other grounds by J. L. Fehts, T. J. Lee, B. J. Hopkins, and R. E. Stickney, *Surf. Sci.* **21**, 197 (1970); and J. P. Muscat and I. P. Batra, *Phys. Rev. B* **34**, 2889 (1986).

¹⁹U. Jostell, *Surf. Sci.* **82**, 333 (1979).

²⁰S. A. Lindgren and L. Wallden, *Phys. Rev. B* **22**, 5967 (1980).

²¹H. Tochiwara, *Surf. Sci.* **126**, 523 (1983).

²²H. Tochiwara and Y. Murata, *J. Phys. Soc. Jpn.* **51**, 2920 (1982).

²³T. Aruga, H. Tochiwara, and Y. Murata, *Phys. Rev. Lett.* **33**, 372 (1984).

²⁴M. Tsukada, H. Ishida, and N. Shima, *Phys. Rev. Lett.* **53**, 376 (1984); H. Ishida, N. Shima, and M. Tsukada, *Phys. Rev. B* **32**, 6236 (1985).

²⁵H. Ishida, N. Shima, and M. Tsukada, *Surf. Sci.* **158**, 438

- (1985).
- ²⁶H. Tochihara, M. Kubota, M. Miyao, and Y. Murata, *Surf. Sci.* **158**, 497 (1985).
- ²⁷S. Ciraci and I. P. Batra, *Phys. Rev. Lett.* **56**, 877 (1986).
- ²⁸M. Schluter, J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, *Phys. Rev. B* **12**, 4200 (1975).
- ²⁹J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12**, 4409 (1979); M. T. Yin and M. L. Cohen, *Phys. Rev. Lett.* **45**, 1004 (1980).
- ³⁰C. B. Bachelet, D. R. Hamann, and M. Schlüter, *Phys. Rev. B* **26**, 419 (1982).
- ³¹D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- ³²J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ³³F. F. Abraham and I. P. Batra, *Surf. Sci. Lett.* **163**, L572 (1985). The asymmetric dimer bond was proposed by D. J. Chadi, *Phys. Rev. Lett.* **43**, 34 (1979).
- ³⁴K. C. Pandey, in *Proceedings of the Seventeenth International Conference on the Physics of Semiconductors*, edited by D. J. Chadi and W. A. Harrison (Springer-Verlag, New York, 1985), p. 55.
- ³⁵R. M. Tromp, R. J. Hamers, and J. E. Demuth, *Phys. Rev. Lett.* **55**, 1303 (1985).
- ³⁶M. T. Yin and M. L. Cohen, *Phys. Rev. B* **24**, 2303 (1981).
- ³⁷J. D. Levine, *Surf. Sci.* **34**, 901 (1973).
- ³⁸S. Ciraci, R. Butz, E. M. Oelling, and H. Wagner, *Phys. Rev. B* **30**, 711 (1984). Many references related to the clean, reconstructed Si(001) surface can be found in this reference.
- ³⁹For the method and related references see I. P. Batra, S. Ciraci, G. P. Srivastava, J. S. Nelson, and C. Y. Fong, *Phys. Rev. B* **34**, 8246 (1986).
- ⁴⁰T. Kendelewicz, P. Soukiassian, R. S. List, J. C. Woicik, P. Pianetta, I. Lindau, and W. E. Spicer (unpublished).
- ⁴¹V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).
- ⁴²L. Hedin and B. I. Lundquist, *J. Phys. C* **4**, 2064 (1971).
- ⁴³For an extensive discussion see D. Pines, *Elementary Excitations in Solids* (Benjamin, New York, 1964), p. 156.
- ⁴⁴I. P. Batra and P. S. Bagus, *J. Vac. Sci. Technol.* (to be published).
- ⁴⁵S. Ciraci and I. P. Batra, *Phys. Rev. Lett.* **58**, 1982 (1987).
- ⁴⁶F. J. Himpsel and D. E. Eastman, *J. Vac. Sci. Technol.* **16**, 1297 (1979); D. J. Chadi, *ibid.* **16**, 1297 (1979).
- ⁴⁷J. E. Rowe and H. Ibach, *Phys. Rev. Lett.* **32**, 451 (1976).
- ⁴⁸I. P. Batra, J. M. Nicholls, and B. Reihl, *J. Vac. Sci. Technol. A* **5**, 898 (1987).
- ⁴⁹E. M. Oelling and R. Miranda, *Surf. Sci.* **177**, L947 (1986). In this work the coverage was defined as the atomic ratio between K and surface Si. Consequently, $\Theta=0.5$ in this work corresponds to $\Theta=1$ here.
- ⁵⁰L. G. Pettersson and P. S. Bagus, *Phys. Rev. Lett.* **56**, 500 (1986); I. P. Batra, *Prog. Surf. Sci.* (to be published).
- ⁵¹F. Stern, *Phys. Rev. Lett.* **18**, 546 (1967).
- ⁵²J. N. Gadzuk, *Phys. Rev. B* **1**, 1267 (1970).
- ⁵³D. M. Newns, *Phys. Rev. B* **1**, 3304 (1970); *Phys. Lett.* **38A**, 341 (1972).
- ⁵⁴S. Anderson and U. Jostell, *Solid State Commun.* **13**, 833 (1973).
- ⁵⁵M. Nakayama, *J. Phys. Soc. Jpn.* **39**, 265 (1975).
- ⁵⁶H. Froitzheim, H. Ibach, and D. L. Mills, *Phys. Rev. B* **1**, 4980 (1975).
- ⁵⁷For a review of the subject, see T. Ando, A. B. Fowler, and F. Stern, *Rev. Mod. Phys.* **54**, 437 (1982).
- ⁵⁸M. Nakayama, T. Kato, and K. Ohtomi, *Solid State Commun.* **50**, 409 (1984).
- ⁵⁹J. E. Northrup, *J. Vac. Sci. Technol. A* **4**, 1404 (1986).
- ⁶⁰R. V. Kasowski and M.-H. Tsai, *Bull. Am. Phys. Soc.* **32**, 865 (1987).
- ⁶¹Y. Enta, T. Kinoshita, S. Suzuki, and S. Kono, *Phys. Rev. B* **36**, 9801 (1987).
- ⁶²P. H. Citrin, *Surf. Sci.* **184**, 109 (1987).

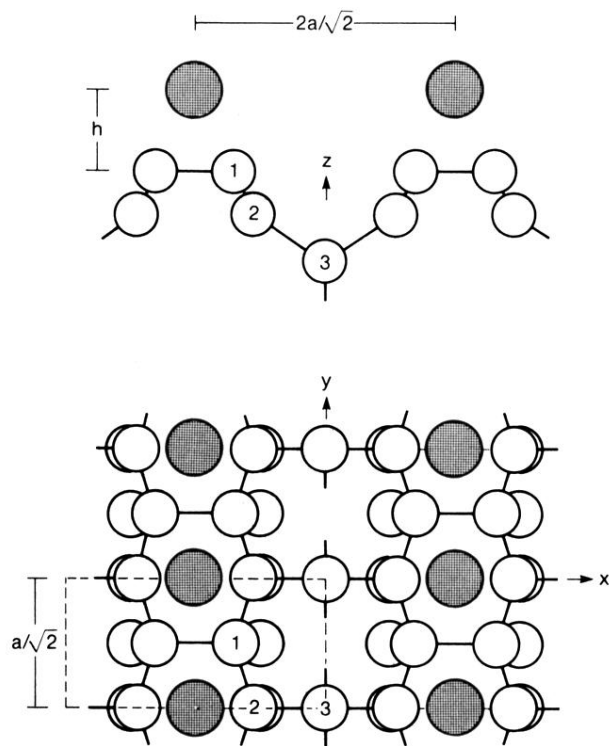


FIG. 1. Side and top views of the equilibrium structure of the potassium-covered Si(001)-(2 \times 1) surface. Shaded large and empty small circles denote K and Si atoms, respectively. Numerals in the circles indicate the atomic layers. $a = 10.26$ a.u., h (or z) = 2.4 a.u.

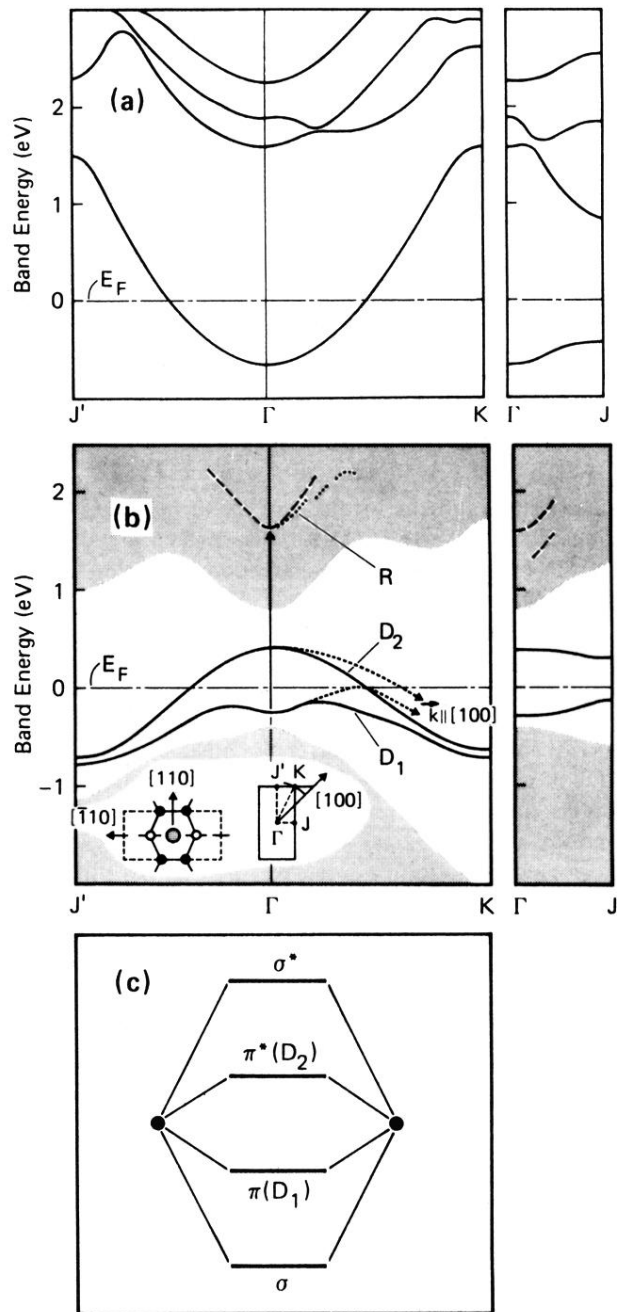


FIG. 3. Calculated energy-band structures: (a) unsupported K monolayer (or K chain) with the same 2D lattice registry as the K overlayer, (b) $K+Si(001)-(2 \times 1)$ surface with $d_{(Si-K)}=4.9$ a.u. For (c), see text. Surface states for $\mathbf{k}||[100]$ are shown by dotted lines. Surface Brillouin zone and the surface atomic configuration are shown by the inset. Large shaded, small solid, and small open circles describe K and first- and second-layer Si atoms, respectively.