

## Novel Electronic Properties of a Potassium Overlayer on Si(001)-(2×1)

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We report self-consistent, geometry-optimized, total electronic energy calculations for a K overlayer on a Si(001)-(2×1) surface. Our theory for metallization of the overlayer and dimensionality of collective excitations is different from previous suggestions and can successfully account for the experimental findings about this system. The metal-insulator transition is proposed to have its origin in active dangling bonds and not in the conventional Mott transition. We find a strong ionic type of binding between the overlayer and the substrate.

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The experimental observations<sup>1,2</sup> on the potassium-covered Si(001) surface present fascinating conceptual ideas about bonding, metallization, and collective excitations. The maximum coverage obtained is one monolayer ( $\theta = 1$ ) showing a clear (2×1) LEED pattern but with a different intensity with respect to the clean surface. The work function decreases rapidly at  $\theta \ll 1$ , and later, concomitant with the appearance of an electron-energy-loss peak at 1.8 eV, it decreases slowly without passing through a minimum. Similar to the conclusions arrived at for the alkali-metal adsorption on metal surfaces,<sup>3</sup> these observations were interpreted to imply a metal-insulator (Mott) transition: Up to  $\theta = 0.5$ , K atoms donate their 4s electrons to the substrate and become ionic as evidenced by a higher core-excitation energy and lower work function. Beyond a certain adatom density the smaller K-K distance allows formation of metallic bands which result in a retransfer of charge to the alkali-metal overlayer. Accordingly, the increasing intensity of the peak in electron-energy-loss spectra (EELS) with  $\theta$  was attributed to a collective excitation of the overlayer. Aruga, Tochiara, and Murata<sup>2</sup> carried out a detailed analysis of this plasmon loss by use of angle-resolved EELS and found 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 for a simple model,<sup>4</sup> these  $q$ -dependent loss peaks were attributed to the 1D plasmons associated with the K chains.

In this Letter we report a novel result indicating that the metallic character attributed to the overlayer is in fact the metallization of the Si(001) surface. Consequently, the interaction and bonding between the K overlayer and the Si surface is quite different from the one previously assumed. With these results the interaction of potassium with the Si surface and the character of the normal modes of surface charge-density fluctuations will be elucidated leading to significant revisions in previous understanding. Moreover, this study introduces a metal-semiconductor system

wherein the pinning of the Fermi level, and thus the height of the Schottky barrier, are almost totally determined by the intrinsic surface states. We have arrived at these conclusions by an extensive geometry optimization using the self-consistent electronic structure and force calculations and analyzing state charge density and the dielectric response function.

The calculations were done for an unsupported K monolayer and a clean and a K-covered Si(001) surface. We used a repeating slab geometry<sup>5,6</sup> for the self-consistent field calculations within the framework of a local-density-functional theory applied in momentum space,<sup>7</sup> and nonlocal, norm-conserving pseudopotentials.<sup>8</sup> Electronic states were represented by  $\sim 550$  plane waves. During the self-consistency iterations the charge density was sampled at 15  $k$  points placed uniformly in the surface Brillouin zone. The substrate was simulated by a slab consisting of eight layers (i.e., sixteen Si atoms in a unit cell). This parameter set, though sufficiently large, may not provide an absolutely converged state. Therefore, most physical conclusions drawn below are based upon large energy differences which are not likely to be affected by such convergence considerations. Among several geometries investigated, our calculations yielded a minimum total energy and a minimum force for the K atom at the center of the sixfold hollow site, between two parallel dimer bonds and at 2.4 a.u. above the surface forming a chain along the [110] direction. This site has been previously used,<sup>2</sup> the new aspect being the shorter Si-K interatomic distance (4.9 a.u.). If we subtract the covalent radius of Si from 4.9 a.u. we obtain a radius which is close to the ionic radius of K. This reflects the type of bonding we are proposing. Another evidence for a strong K-Si binding is given by our total energies. The cohesive energy of the unsupported monolayer is calculated to be about 0.6 eV. The binding energy of the K monolayer to the substrate is about 3 eV. In contrast to previous assumptions this obviously suggests a rather strong interaction.

Figure 1 shows some important aspects of the elec-

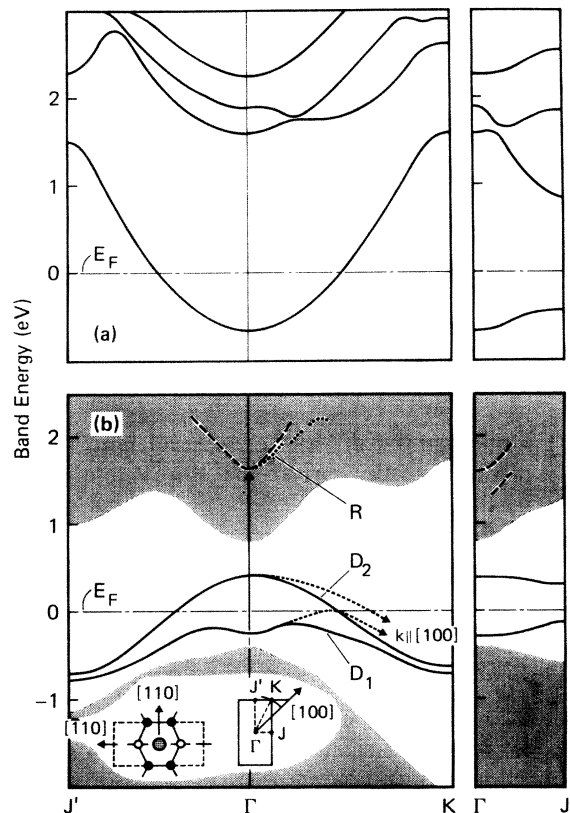


FIG. 1. Energy band structure for (a) unsupported K monolayer, (b) K overlayer on  $\text{Si}(001)-(2 \times 1)$ . Surface states for  $k \parallel [100]$  are shown by dotted lines. Shaded area indicates projected bulk Si bands. Inset: Atomic configuration shown by large shaded, small filled, and small open circles describing K and first-layer and second-layer Si atoms, respectively.

tronic structure of the K-covered  $\text{Si}(001)$  surface. The lowest band in Fig. 1(a) of the unsupported K layer has  $s$  symmetry. Smaller dispersion perpendicular to the chain implies that it has indeed 1D character. The upper  $p$ -like bands have obviously higher dimensionality. However, Fig. 1(b) conspicuously reveals that these bands are almost totally discarded upon adsorption. Two bands in the gap,  $D_1$  and  $D_2$ , arise from the dangling bonds of  $\text{Si}(001)-(2 \times 1)$ , which are modified because of overlap. The reconstructed  $\text{Si}(001)$  surface is known to be an insulator because of the superlattice gap between  $D_1$  and  $D_2$ . For K-covered  $\text{Si}(001)$  the Fermi level passes through  $D_2$ . The electrons from the K overlayer are accommodated in  $D_2$  which is then partially occupied and causes the metallization of the Si surface. Backbonding and dimer bond states are identified near the top of the valence band. Surface states in the conduction band are shown only in the region where plasmon dispersions are measured.<sup>2</sup> These states are accessible by the excited electrons in the EELS sampling, mainly the surface region, and are

likely to be responsible for collective and individual excitations. The resonance state,  $R$ , hybridizes with different bulk-conduction-band states along the  $[100]$  direction. At  $k=0$  this state is 1.9 eV above the filled  $D_1$  state. The individual excitation energy inferred from  $D_1$  and  $R$  is in fair agreement with the observed loss peak.<sup>1,2</sup> The calculated work function is 2.3 eV lower than the work function of the clean surface. This is also in accord with the observed reduction at the saturation coverage.<sup>1</sup>

The nature of the three states ( $D_1$ ,  $D_2$ , and  $R$ ), which are relevant for the excitation spectrum, can be deduced from the state charge distributions shown in Fig. 2. The charge-density contours of  $D_1$  and  $D_2$  emphasize the dangling-bond origin with minor deviations from those of clean  $\text{Si}(001)-(2 \times 1)$ . The contour plot of  $R$  gives an impression about how the charge density of a state having some origin from the K atom would form. All these facts corroborate our conclusion regarding the origin of the gap states. The contours of the total charge density in the K-overlayer plane, as presented in Fig. 3(a), prevail even above the monolayer with a decreasing magnitude. Their shape (with two maxima) and location with respect to substrate atoms indicate that the total charge density above the surface is peculiar to the substrate surface states, whereas those of the unsupported K monolayer exhibit a single maximum. The contours of the clean and K-covered surfaces in a plane above the K monolayer are similar in shape, but differ slightly in magnitude. The form of the charge distribution in the plane containing K chains is shown more clearly by a surface plot in Fig. 3(b). As depicted by Fig. 3(c) the charge in a vertical cut plane has the lowest density at the center of the sixfold hollow site, where the K atom is located. The local density of states above a horizontal plane bisecting the first and second Si layers yields 8.9 electrons (slightly less than 9). In this region the average electron density is close to that of the K bulk. Consequently, the screening of the K-core potential provided by the surface electrons is comparable to that of the K bulk.

From these results it becomes clear that the valence charge of the K atom is donated to fill the surface dangling-bond states which leads to the metallization of the Si surface. In contrast, the alkali-metal atoms adsorbed on metal substrates regain charge at the saturation coverage. The presence of the active dangling-bond states provides the crucial difference between a metal and a semiconductor substrate. In the present system the metal-insulator transition takes place through the metallization of the semiconductor surface, but not through a Mott-type transition (i.e., the formation of metallic bands on a K monolayer). The binding between adatom and Si is ionic. The attractive Coulomb interaction between the positively

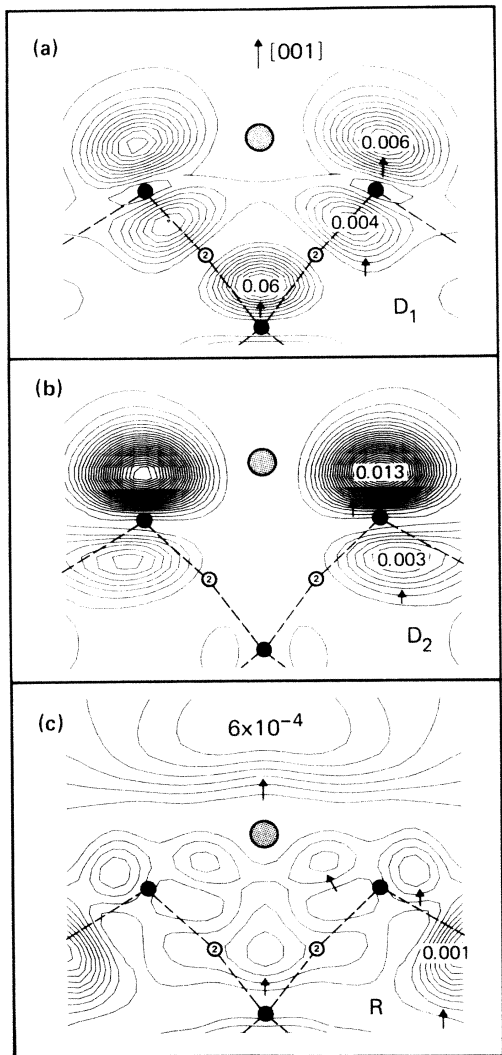


FIG. 2. Charge contour plots of  $D_1$ ,  $D_2$ , and  $R$  plotted in a vertical plane passing through K and two nearest surface Si atoms. Atoms in the plane and atoms projected to the plane are shown by filled and open circles, respectively. Charge density increases in the direction of small arrows. The contour spacings are (a)  $5 \times 10^{-4}$ , (b)  $5 \times 10^{-4}$ , and (c)  $10^{-4}$  in a.u.

charged core and the surrounding electron density of a Si surface is responsible for the strong binding. Such a conclusion is also supported by the total energy calculations. In the course of geometry optimization, even at a rather large K-surface distance ( $h = 5.1$  a.u.) the valence charge was already transferred to Si. As  $h$  is decreased, the Coulomb energy predominates other components of the total energy,<sup>7</sup> and pulls the ion to the equilibrium position. Strong Ewald forces, however, preclude it from entering into the substrate. Because of the strong interaction and charge relocation further deposition of K atoms to form a thick metal layer is not expected. This is also observed experimen-

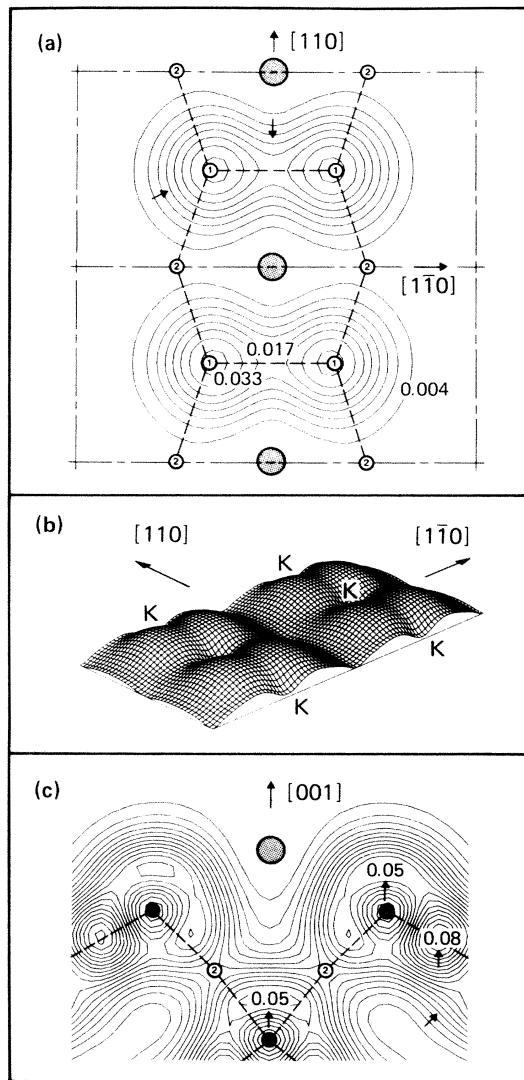


FIG. 3. (a) Contour plots of the total charge density in a horizontal plane containing the K monolayer with first- and second-layer Si atoms projected. Dash-dotted line delineates the unit cell. (b) The surface plot of (a) containing two parallel K chains. (c) Same as (a) but in a plane described in Fig. 2. The contour spacings are 0.004 a.u.

tally.<sup>1</sup> On the contrary, multilayer deposition occurs if the monolayer would be metallic.

The present results suggest that the 4s electrons are donated to Si at all coverages. Accordingly, at  $\theta \ll 1$  the 3p-core shift and the rapid decrease of the work function<sup>1</sup> are explained by a larger adatom-substrate distance and a comparably lower surface charge density. 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 the adatom-substrate distance becomes smaller and results in an effective core screening. This picture is also consistent with a work func-

tion receding at a lower rate near the saturation.

As revealed from the self-consistent-field microscopic theory of surface excitations,<sup>9</sup> the forms of the initial- and final-state wave functions play a decisive role in determining the dispersion of the excitation. In conjunction with this argument, the comparison of the observed dispersion with the relation  $\omega \sim (1 - \xi q)$ , obtained<sup>10</sup> from the dielectric response of a 2D degenerate electron gas, and deduction of the dimensionality

$$P_{zz}(\omega, \mathbf{q}) = \sum_{\mathbf{k}} \frac{F^*(z, \mathbf{k}, \mathbf{q}) [f(\mathbf{k}) - f(\mathbf{k} + \mathbf{q})] F(z', \mathbf{k}, \mathbf{q})}{E(\mathbf{k} + \mathbf{q}) - E(\mathbf{k}) - \hbar\omega - i\delta},$$

where  $\mathbf{r}$ ,  $\mathbf{q}$ , and  $\mathbf{k}$  are perpendicular to the  $z$  coordinate along the surface normal, and  $f$  is the distribution function. The logarithmic singularities of the above equation correspond to single-particle excitations. The transition energy from  $D_1$  to  $R$  at  $k=0$  indicates that the interband excitation is invoked mainly by parallel polarization with a negligible depolarization shift leading to positive dispersion at small  $q$ . To decide whether the dispersion is linear is a matter of detailed calculation. The anisotropic dispersion is an expected consequence from the bands shown in Fig. 1. Recall that an EELS peak at 1.7 eV was also observed<sup>11</sup> even in the clean Si(001)-(2×1) surface, and was assigned to an individual interband excitation from  $D_1$  to a surface resonance in the conduction band.<sup>6</sup> A major effort is currently under way for calculating the plasmon dispersion from first principles, and the results shall be reported in a complete article. However, for the present purposes it is more significant to point out that since the overlayer has not metallized because of the presence of active dangling bonds, the origin of the EELS peak has to be sought in single-particle excitations. The calculation of plasmon dispersion,<sup>12</sup> though interesting in its own right, is not essential for the conclusion drawn here.

In conclusion, the alkali-metal-Si system presents remarkable features in the adsorption phenomena. In spite of the fact that the adatom is a metal, the resulting binding is ionic, but the insulating substrate changes into a metallic state. Thus the observed dispersion cannot be associated with the 1D metal overlayer. As a unique metal-semiconductor system investigated so far, the Fermi level is pinned totally by the surface states and not by chemisorption or metal-induced states.<sup>13</sup> Since the Si surface makes a transition to a different charge state, we expect that co-adsorption of H, O, and some metals will lead to interesting features.

may lead to erroneous conclusions. The initial- and final-state wave functions in Fig. 2 do not display any free-electron-like, separable components. Consequently, in principle, a proper evaluation of the Fourier transform of the overlap

$$F(z, \mathbf{k}, \mathbf{q}) = \langle \psi(\mathbf{k} + \mathbf{q}, \mathbf{r}, z) | \exp(i\mathbf{q} \cdot \mathbf{r}) | \psi(\mathbf{k}, \mathbf{r}, z) \rangle$$

becomes necessary. Furthermore, all the initial surface states, especially the dimer bond states, need to be included in the polarization operator,

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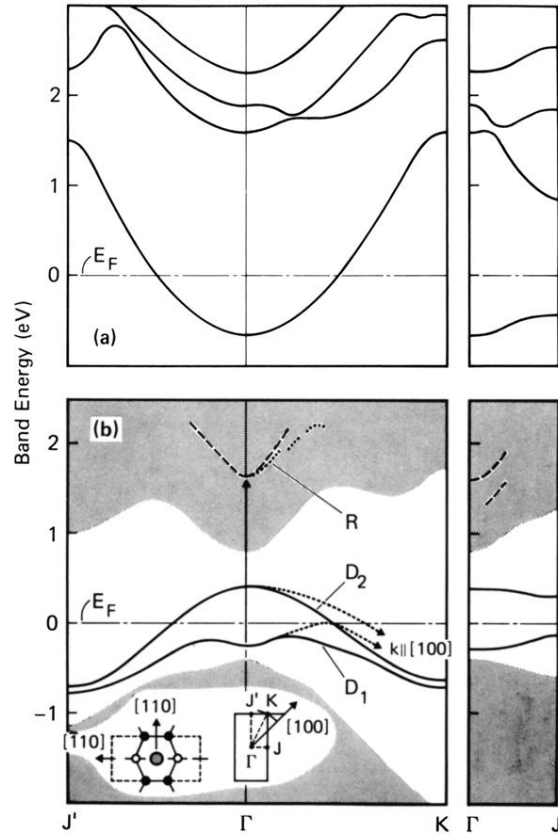


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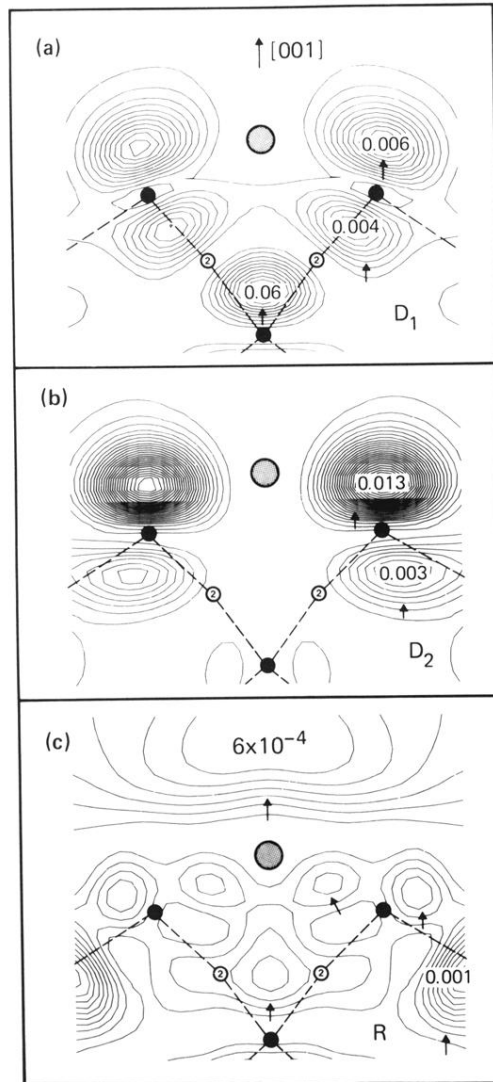


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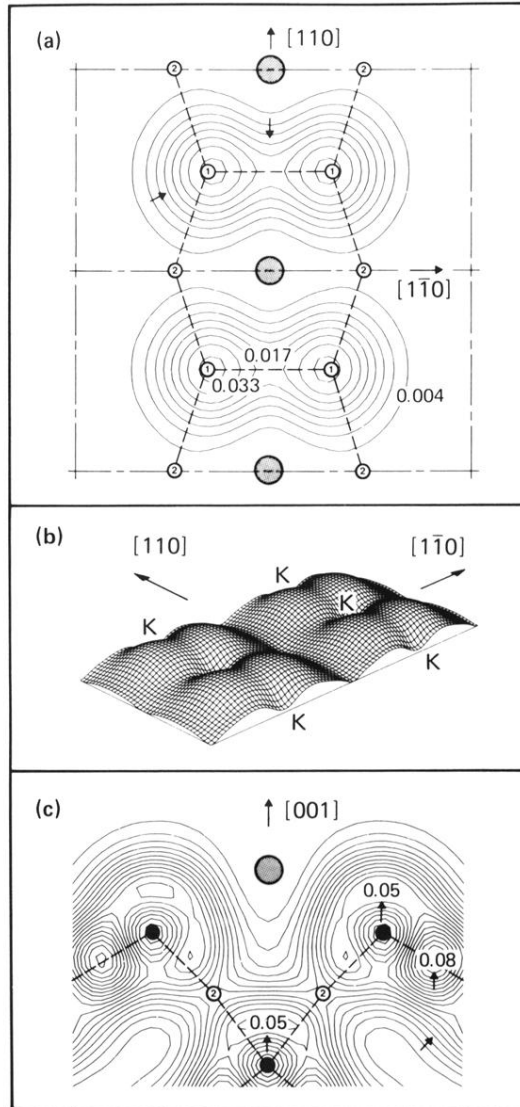


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