

## Structure of the K/Si(100)-(2×1) surface: Semiempirical self-consistent-field crystal orbital analysis

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The electronic structure of the K/Si(100)-(2×1) surface at a K coverage  $\Theta=0.5$  has been studied by a semiempirical self-consistent-field Hartree-Fock crystal orbital (CO) formalism supplemented by an INDO (intermediate neglect of differential overlap) Hamiltonian. A symmetric dimer model has been used to represent the structure of the Si(100)-(2×1) surface. Four possible adsorption sites for the K atoms have been investigated. The relative stabilities of the adsorption sites have been determined by total energy calculations. The Si(100)-(2×1) surface covered with chemisorbed K atoms is stabilized by multicenter Si-K bonding, which favors K adsorption at surface sites where the coordination to the Si atoms is maximized. The charge transfer from the K overlayer to the Si substrate indicates that the nature of the Si-K bonding is partially ionic. At a K coverage  $\Theta=0.5$  the K/Si(100)-(2×1) system is metallic. The charge carriers at the Fermi level are located at the outermost Si layer. The semiconducting Si(100)-(2×1) surface is, therefore, metallized upon deposition of K atoms.

### I. INTRODUCTION

Deposition of alkali metals on semiconductors has been studied extensively in the past decade.<sup>1</sup> The changes of the electronic properties, especially the decrease of the work function, with alkali coverage make these systems interesting for technical applications, e.g., as electron emitters of high efficiency<sup>2</sup> or as spin-polarized electron guns.<sup>3</sup> Multilayer deposition of alkali metals on Si surfaces is of great technological relevance due to the promoter effect in low-temperature oxidation of Si.<sup>4</sup> From a fundamental point of view, the determination of the surface structure and the microscopic description of the interaction between adsorbate and substrate are essential for the understanding of the properties of these materials. In a large number of experimental<sup>5-9</sup> and theoretical investigations,<sup>10-14</sup> the deposition of K atoms on the Si(100)-(2×1) surface has been analyzed. This system is an ideal model for metal-semiconductor interfaces because no interdiffusion takes place in the adsorption process.

The clean Si(100) surface is reconstructed into a (2×1) structure. Many models, e.g., vacancy models, conjugated-chain-type models, and dimer models, have been proposed for the surface reconstruction, but only the dimer model shows a satisfactory agreement with theoretical and experimental data.<sup>15</sup> A scanning-tunneling microscopy study<sup>16</sup> has confirmed recently the existence of both symmetric and buckled Si dimers in roughly equal amounts on the reconstructed surface, as well as a high density (10–20 %) of vacancy-type defects. The valence-charge distribution in the buckled dimers is nearly symmetrical, as can be inferred from high-resolution photoemission experiments.<sup>17</sup>

The reconstructed Si(100)-(2×1) surface has been

found to be semiconducting.<sup>18</sup> Upon adsorption of K atoms, the electronic structure of the Si substrate is modified remarkably. Measurements of the work-function change present a minimum at a K coverage of  $\Theta=0.5$ .<sup>8</sup> The value  $\Theta=0.5$  means that the number of adsorbed K atoms is one-half the number of Si atoms at the (100) surface, i.e.,  $6.78 \times 10^{14}$  (Si atoms)/cm<sup>2</sup>. An insulator-metal transition has been observed via the onset of metallic overlayer plasmons.<sup>12-14</sup> The metallization of the surface was first interpreted as a Mott transition due to the formation of one-dimensional K chains at a given alkali coverage.<sup>13,14</sup> Recently, Ciraci and Batra<sup>10</sup> have proposed a new suggestive model based on pseudopotential calculations within the local-density approximation. They explain the insulator-metal transition in terms of a charge transfer from the alkali atoms to the empty dangling-bond states of the Si surface; i.e., the Si substrate is thereby metallized and not the K overlayer. Very recent experimental data favor the interpretation based on the Si metallization. At a K coverage  $\Theta=1$ , the dangling-bond states are saturated and the surface becomes semiconducting.<sup>5</sup>

The nature of the chemical bond in the K/Si(100)-(2×1) surface has been the subject of controversy. The numerical results in Ref. 10 lead to a description of the Si-K bonding as being purely ionic, i.e., the 4s electrons of the K atoms are completely transferred to the Si surface. On the contrary, a nonempirical linear combination of atomic orbitals (LCAO)  $X\alpha$  calculation,<sup>13</sup> as well as a tight-binding study with a parametrized Hamiltonian,<sup>11</sup> predict a partial electron transfer from the alkali atoms to the surface. The electronegativity difference between Si and K [ $\chi(\text{Si})=1.74$ ,  $\chi(\text{K})=0.74$  (Ref. 19)] suggests a polarized Si-K bonding but not a purely ionic one. Crystal chemical studies of the binary Si/K system lead to

two stable potassium silicides with composition KSi (Ref. 20) and  $K_8Si_{46}$ .<sup>21</sup> The crystal structure and physical properties of these phases are not typical for strong ionic compounds. The crystal structure of the semiconductor KSi contains tetrahedral  $Si_4$  clusters surrounded by K atoms, while the compound  $K_8Si_{46}$  shows a clathrate structure and metallic conductivity.<sup>22</sup>

The determination of the adsorption site of the K atoms on the Si(100)-(2×1) surface is an important structural problem which has not been clarified definitely until now. The structural model accepted commonly for the K/Si(100)-(2×1) system has been suggested by Levine<sup>23</sup> on the basis of low-energy-electron-diffraction (LEED) data. Although a large number of studies<sup>7,11-14</sup> have assumed the validity of this model, no direct experimental support has been provided so far. Only the above-mentioned numerical investigation in Ref. 10 has treated the relative stabilities of different adsorption sites for the alkali atoms on the Si(100)-(2×1) surface. The results of the calculation support a structure for the adsorbed surface that corresponds to Levine's model. The calculated equilibrium bond length between Si and K amounts to 2.6 Å. This value represents an underestimation when compared with the experimental value of 3.1 Å, which has been recently reported in a surface-extended x-ray-absorption fine-structure (SEXAFS) study.<sup>24</sup>

It is the purpose of the present contribution to study the electronic structure of K/Si(100)-(2×1) in the framework of a semiempirical self-consistent-field (SCF) Hartree-Fock (HF) crystal orbital (CO) scheme as derived in the tight-binding approximation.<sup>25,26</sup> The employed CO approach is based on the intermediate neglect of differential overlap (INDO) approximation. The model has been applied to elucidate band-structure features of complicated Zintl phases,<sup>27,28</sup> highly conducting metal-macrocycles,<sup>29,30</sup> as well as intercalation compounds.<sup>31</sup> Geometrical parameters (i.e., bond angles and bond lengths) of lithium silicides could be reproduced satisfactorily by the computational approach.<sup>27,28</sup> Subsequently it will be shown that the present study suggests a structure for the K/Si(100)-(2×1) surface at a K coverage of  $\Theta=0.5$  that differs from the model given by Levine. Adsorption of K atoms over the grooves that are built at the reconstructed Si(100)-(2×1) surface is calculated to be energetically more favorable than alkali deposition over the rows that are formed by the Si dimers. Structural preferences are rationalized on the basis of a bonding model that describes the interactions between adsorbed and substrate atoms. The organization of the paper is as follows. The structural models for the surface are presented in Sec. II. Relevant computational conditions are given in Sec. III. The results of the geometry optimization in the K/Si(100)-(2×1) system are discussed in Sec. IV. The band structure and bonding model for the adsorbed surface are presented in Sec. V. The conclusions are reserved for Sec. VI.

## II. STRUCTURAL MODELS

The model chosen in the calculation to represent the reconstructed Si(100)-(2×1) surface is the symmetric di-

mer model. Figure 1 shows schematically the geometrical ordering of the substrate atoms. At the top of the figure a projection along a direction perpendicular to the surface is shown. The outer most Si atoms [ $=(1)$ ] build dimers which are arranged in rows along the [110] direction (i.e.,  $y$  direction in the representation). The side projection at the bottom of Fig. 1 shows the typical profile of the Si(100) surface. There are elevations corresponding to the above-mentioned dimer rows and grooves between them. The reported Si—Si bond length at the dimer is 2.4 Å.<sup>32</sup> With the exception of the Si dimers, Si atoms in the reconstructed surface show only a small displacement from their ideal positions (always less than 0.15 Å);<sup>32</sup> this displacement was not considered in the model. The Si-Si bulk distance amounts to 2.35 Å.

LEED data have shown<sup>7,33</sup> that the deposition of K atoms on the Si(100)-(2×1) substrate does not change the (2×1) reconstruction of the Si surface. Figure 2 shows the rectangular unit cell of the Si(100)-(2×1) system. The surface symmetry is characterized by the space group  $p2mm$ . The corresponding lattice parameters are  $a=7.68$  Å and  $b=3.84$  Å. Four possible adsorption sites for the K atoms have been considered in the calculations. They are symbolized in the unit cell as  $A$ ,  $B$ ,  $C$ , and  $D$ , respectively. If only one of these sites is occupied by K atoms, the corresponding K coverage will be  $\theta=0.5$ . Sites  $A$  and  $D$  are located over the dimer rows, while sites  $B$  and  $C$  are found over surface grooves. The number of Si(1) nearest neighbors for a K atom at site  $A$

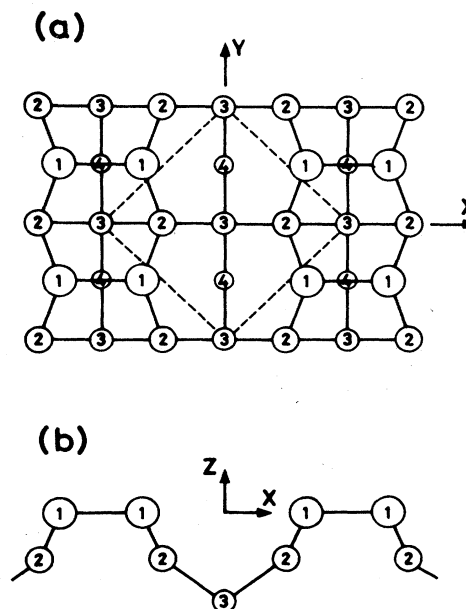


FIG. 1. Schematic representation of the reconstructed Si(100)-(2×1) surface. (a) Projection of the structure along a direction perpendicular to the surface. The successive Si layers are numerated. The number 1 is associated to the Si dimers at  $z=0$ . The dashed lines represent a projection of the fcc unit cell corresponding to the bulk Si. (b) Side view of the surface structure. Grooves are formed between the Si dimers. The Cartesian-coordinate system used in the calculations is shown.

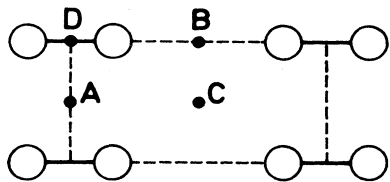


FIG. 2. Rectangular unit cell of the reconstructed Si(100)-(2 $\times$ 1) surface. Only the Si dimers are displayed. The sites labeled *A*, *B*, *C*, and *D* represent four possible adsorption positions for the K atoms.

or *C* is four. This number is reduced to two for a K atom located at site *B* or *D*.

### III. COMPUTATIONAL CONDITIONS

The employed semiempirical SCF HF CO formalism has been described in detail in Refs. 25 and 26. The basic equations are therefore not repeated in this context. The numerical model requires a fragmentation of the infinite crystal into two types of spatial domains, I and II, respectively. Domain I is a sphere that has to be defined for each atomic center in the unit cell.<sup>34</sup> Within this sphere the exact SCF HF CO expansion is used; i.e., the interactions are treated quantum mechanically in the adopted formalism. For larger interatomic separations (domain II) the interaction is expressed in terms of the conventional electrostatic Madelung approximation. In the present calculation a common sphere radius of 8 Å around each atomic site has been chosen. The numerical capability of such a condition has been analyzed in Ref. 34. The Si(100)-(2 $\times$ 1) surface has been represented by a slab comprising four Si layers. One side of the slab has been saturated by H atoms. Other reported numerical studies on the K/Si(100)-(2 $\times$ 1) system have adopted as model a slab that comprises four,<sup>13</sup> six,<sup>35</sup> or eight<sup>36,10</sup> Si layers, respectively. A cluster calculation including Si atoms distributed in three layers has been recently used as model for the adsorption of atomic K at the Si surface.<sup>36</sup> Geometrical relaxation effects on the Si surface upon adsorption of K atoms were calculated and found to be very small.<sup>10</sup> Therefore, a slab model of four Si layers seems to be adequate enough for the computation of energy differences relating deposition of atomic K at different surface sites. The value of the one-electron core integral associated with the H atoms (i.e., the energy of an electron in the atomic 1s orbital) has been slightly modified in order to simulate a nonpolarized Si—H bond. The composition of the adopted unit cell for a K coverage of  $\Theta=0.5$  corresponds to  $H_4Si_8K$ .

The *k*-dependent CO equations have been solved at nine *k* points in the irreducible part of the Brillouin zone (IBZ) associated with the two-dimensional space group  $p2mm$ . This grid represents an ensemble of 36 *k* points in the full BZ. Simple geometric criteria to generate *k* grids for any two- or three-dimensional space groups have been given in Ref. 37. A sampling of *k* points covering the whole BZ is necessary in order to determine the elements of the charge-density matrix via Fourier trans-

formation. For the corresponding numerical integration, the plain discrete summation has been used. The SCF iterations have been controlled by an accelerated Hartree damping of the charge-density matrices.<sup>38</sup> An energy criterion of  $10^{-4}$  a.u. has been established to terminate the iterative process. The density-of-states (DOS) distributions are determined by the classical histogram technique in a grid of 144 *k* points over the BZ. A step size of 0.15 eV has been used. The final curves were smoothed via Gauss-type functions with a mean width of 0.4 eV.

### IV. GEOMETRY OPTIMIZATION

In this section the results of the geometry optimization which has been carried out within the unit cell of the K/Si(100)-(2 $\times$ 1) system are presented. The calculations correspond to a K coverage of  $\Theta=0.5$ . Four possible adsorption sites (*A*, *B*, *C*, and *D*; see Fig. 2) for the K atoms were considered. For each site the *z* coordinate which defines the position of the K overlayer relative to the Si surface was modified to determine the energy minimum. Using an interatomic force calculation<sup>10</sup> it was estimated that geometrical relaxation effects on the Si surface upon adsorption of K atoms are very small. They were therefore not considered in the geometry optimization.

In Fig. 3 the relative total energies of the K/Si(100)-(2 $\times$ 1) system has been given for the four investigated adsorption geometries. The structures are labeled *A*, *B*, *C*,

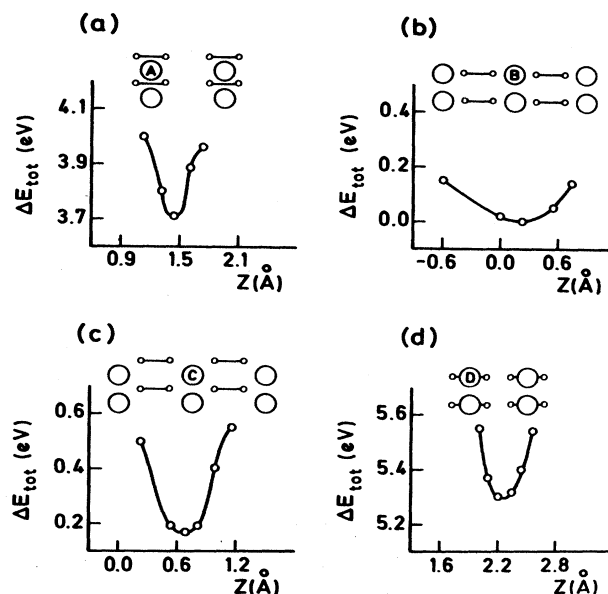


FIG. 3. Relative total energies (in eV) of the K/Si(100)-(2 $\times$ 1) system as a function of the *z* coordinate (in Å) defining the height of the K overlayer relative to the Si surface [ $z(\text{Si}(1))=0$ ]. Four possible adsorption sites (*A*, *B*, *C*, *D*) have been considered for the K atoms. The coordination of the K atoms relative to the Si dimers of the Si(100)-(2 $\times$ 1) surface is shown schematically for each case. The small circles symbolize Si atoms and the large ones K atoms. The energy of the most stable geometry has been taken as internal reference.

or  $D$  according to the site occupied by the alkali atoms. The total energy for the most stable structure has been taken as internal standard. The order of increasing stability of surface structures is given by the sequence  $D < A < C < B$ . At site  $D$  the K atoms are located over the Si dimer bonds. The structure  $A$  corresponds to Levine's model. Common to both geometries  $D$  and  $A$  is that the alkali atoms are coordinated above rows of Si dimers. Nevertheless, the coordination number of the metal atoms is different. Four Si(1) nearest neighbors are found for the K atoms in model  $A$  but only two are found in model  $D$ . At the equilibrium geometry structure  $A$  is predicted to be 1.6 eV/(unit cell) more stable than structure  $D$ .

An important result of the present work is that the deposition of K atoms above the grooves of the Si(100)-(2×1) surface (i.e., at sites  $B$  or  $C$ ) is found to be energetically more favorable than at sites  $A$  or  $D$ . The lowest energy corresponds to structure  $B$ , where the K atoms are located as if they would saturate the Si dangling bonds (see Fig. 3). The calculated equilibrium distances between the alkali centers and the Si dimer atoms [ $=(1)$ ] are summarized as follows for the structures  $A, B, C$ , and  $D$ , respectively: structure  $A$ ,  $d(\text{Si}(1)\text{-K})=2.69 \text{ \AA}$ ; structure  $B$ ,  $d(\text{Si}(1)\text{-K})=2.65 \text{ \AA}$ ; structure  $C$ ,  $d(\text{Si}(1)\text{-K})=3.34 \text{ \AA}$ ; structure  $D$ ,  $d(\text{Si}(1)\text{-K})=2.52 \text{ \AA}$ . The value  $d(\text{Si}(1)\text{-K})=2.69 \text{ \AA}$  determined for structure  $A$  agrees well with the calculated distance  $d(\text{Si}(1)\text{-K})=2.59 \text{ \AA}$  reported in Ref. 10. It was mentioned in the Introduction that an estimation of the Si(1)—K bond length in the K/Si(100)-(2×1) system via SEXAFS leads to a value of  $d(\text{Si}(1)\text{-K})=3.1 \text{ \AA}$ .<sup>24</sup> Without further experimental evidence one cannot determine which Si-K distance (i.e., 2.6 Å versus 3.1 Å) is correct. The bond length  $d(\text{Si}(1)\text{-K})=2.52 \text{ \AA}$  found for structure  $D$  is shorter than the value corresponding to structure  $A$  (2.69 Å). This can be understood as an effect of the reduction of the coordination number of the K atoms from four to two. The largest distance  $d(\text{Si}(1)\text{-K})=3.34 \text{ \AA}$  was obtained for structure  $C$ , where  $z(\text{K}) \approx (\text{Si}(1))$  so that shorter Si(1)-K distances are impossible. For this site, the nearest Si neighbors of the K centers correspond to Si atoms of the second layer [ $=\text{Si}(2)$ ], with  $d(\text{Si}(2)\text{-K})=2.81 \text{ \AA}$  at equilibrium geometry. For the most stable surface structure (model  $B$ ) predicted by the INDO SCF HF CO calculation, the optimized Si—K bond length is 2.65 Å.

In order to assess the reliability of the applied numerical method a geometry optimization of the  $\text{K}_4\text{Si}_4$  cluster as realized in the crystal structure of the  $\text{KS}_i$  phase<sup>20</sup> was performed. The experimental geometry corresponds to a  $\text{Si}_4$  tetrahedron [ $d(\text{Si-Si})=2.43 \text{ \AA}$ ] surrounded by four K atoms. Each of the K atoms is coordinated to the three Si centers of a tetrahedral face. The average experimental Si-K distance is 3.48 Å. The numerical model reproduces that coordination of K atoms to a tetrahedral face is more stable than coordination to a tetrahedral vertex. The calculated equilibrium Si-K distance amounts to 3.05 Å, i.e., the numerical method underestimates the experimental value by about 12%. Assuming that this deviation in the calculated Si—K bond lengths is systematic,

the optimized Si-K distance for the K/Si(100)-(2×1) system (2.65 Å) converts to a value (3.00 Å) very near to the experimental one (3.1 Å)<sup>24</sup>. The calculated coordinate  $z(\text{K})=0.25 \text{ \AA}$  for K adsorption at site  $B$  (see Fig. 3) leads to a value for the surface dipole moment which is too small to explain the decrease of the work function for the Si(100) surface upon alkali deposition.<sup>8</sup> The corrected distance  $d(\text{Si-K})=3.0 \text{ \AA}$  would correspond to  $z(\text{K})=1.3 \text{ \AA}$ , consistent with the observed decrease of the work function.<sup>8</sup>

Very recently, Abukawa and Kono<sup>39</sup> proposed a K double-layer model to interpret photoelectron diffraction measurements on K/Si(100)-(2×1) at a K coverage of  $\Theta=1$ . The vertical separation between the two K layers is reported to be  $1.1 \pm 0.1 \text{ \AA}$ . The authors suggest tentatively a structural model where the K atoms are adsorbed at sites  $C$  and  $A$ . However, the stability sequence of adsorption sites given by our numerical method for a K coverage of  $\Theta=0.5$  is  $D < A < C < B$ . For a coverage of  $\Theta=1$  two adsorption sites are occupied by K atoms. Considering the former energetic sequence, the K double-layer formation is expected to take place via alkali adsorption at sites  $A$  and  $B$ . Notice that after occupation of site  $B$ , adsorption of K at site  $C$  is hindered by steric effects. It can be seen in Fig. 3 that the vertical separation (i.e., difference in the  $z$  coordinates) between sites  $B$  and  $A$  at the calculated equilibrium geometry amounts to 1.2 Å, in good agreement with the experimental value (1.1 Å) of Abukawa and Kono.<sup>39</sup> To confirm this hypothesis, the total energy of the two alternative double-layer models was calculated, having taken all atomic coordinates from the optimized model at a K coverage of  $\Theta=0.5$ . The results of this calculation indicate that the double layer with K atoms adsorbed at sites  $B$  and  $A$  is 1.1 eV/(unit cell) more stable than the double layer proposed by Abukawa and Kono<sup>39</sup> with the K atoms located at sites  $C$  and  $A$ .

## V. BAND STRUCTURE AND CHEMICAL BONDING

The surface energy bands of the K/Si(100)-(2×1) system are shown in Fig. 4. The calculation corresponds to the optimized geometry with the alkali atoms adsorbed at site  $B$ . The valence and conduction bands with bulklike character are located in the hatched regions. The energy gap  $E_g$  calculated for the bulk bands in the employed slab model amounts to 4.5 eV. The experimental energy gap of bulk Si is 1.1 eV.<sup>40</sup> The overestimation of the  $E_g$  value by LCAO HF CO approaches is a well-known mean-field error which is caused by the neglect of quasiparticle corrections (i.e., electronic correlations and relaxations) as well as the employment of an unphysical potential in the virtual Fermi sea.<sup>41</sup> Two surface bands appear in the gap region. They are labeled  $a_1$  and  $b_1$  according to the irreducible representations of the point group  $C_{2v}$  of the  $k$  vector at the symmetry point  $\Gamma$ . The surface K/Si(100)-(2×1) is metallic and the Fermi energy crosses the band  $a_1$ .

The one-electron energies and localization properties corresponding to the surface bands  $b_1$  and  $a_1$  are given in Table I for the symmetry points  $Y, \Gamma, X$ , and  $S$  of the BZ.

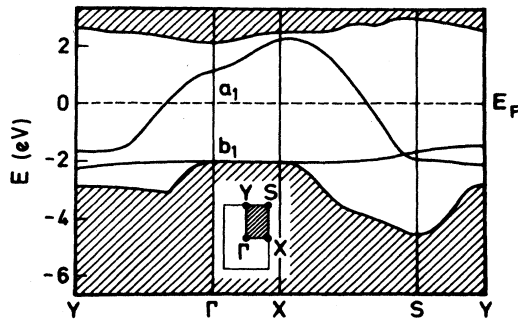


FIG. 4. Surface bands of the K/Si(100)-(2×1) slab model for the optimized geometry corresponding to adsorption of K atoms at site B. Bulklike bands are displayed as shaded areas. The surface bands are labeled  $a_1$  and  $b_1$  according to the irreducible representations of the surface point group  $C_{2v}$  at the symmetry point  $\Gamma$ . The BZ and the irreducible part of the BZ (hatched area) are shown in the inset. The Fermi energy  $E_F$  has been taken as zero of the energy scale.

The CO microstates are localized at the Si dimers [=Si(1)] with amplitudes between 47% and 87%. The contribution from the Si centers of the second layer [=Si(2)] varies between 17% and 27% for band  $b_1$ . These values are reduced to 2–20% for band  $a_1$ . Admixtures from the third and fourth Si layers [=Si(3), Si(4)] are, with only two exceptions, less than 10%. Significant contributions from the alkali atoms are found only at the symmetry point S in the band  $a_1$ . The one-electron energies associated to the band  $b_1$  are lower than those corresponding to the band  $a_1$  for all the symmetry directions in the BZ except for the directions  $S \rightarrow Y$ . The stabilization of the band  $a_1$  at the symmetry point S is due to the bonding interaction between the Si surface states and the AO's centered at the K atoms. The relative stability of the surface bands  $b_1$  and  $a_1$  agrees with the LCAO  $X\alpha$  slab calculation of Ref. 14.

The calculated density of states (DOS) corresponding to the K overlayer and the first three Si layers of the K/Si(100)-(2×1) slab model is shown in Fig. 5 for an en-

ergy window of 13 eV. The projected DOS associated with the valence AO's of the Si dimers alone is represented for comparison. The electronic states at the Fermi level are almost exclusively located at the Si dimers. The SCF HF CO calculation agrees therefore with the results of Ref. 10 with reference to the metallization of the Si surface upon adsorption of alkali atoms up to a coverage of  $\theta=0.5$ . The maximum in the DOS curve below  $E_F$  is due to the surface bands  $b_1$  and  $a_1$ .

A Mulliken population analysis<sup>42</sup> of the electronic wave function predicts a transfer of 0.26 electrons from the alkali atoms to the Si substrate at the optimized geometry corresponding to the adsorption of K atoms at site B. Nevertheless, the charge transfer is almost independent of the adsorption site of the K atoms; the largest value is found for K adsorption at site A (0.32 electrons). These values are in good agreement with the results of Flores *et al.*,<sup>11</sup> who report a charge transfer of 0.28 electrons. The electronic charge located at the K atoms amounts to 0.74e. This population spreads over the manifold one-electron states associated with the valence bands of the chemisorbed system and therefore is not confined to the surface bands where the alkali character is small (see Table I). The bonding between the K and Si centers is partially ionic, as can be expected from the electronegativity difference between Si and K atoms.

The bonding interactions responsible for the stability of the different adsorption sites of the K atoms over the Si(100)-(2×1) surface are of two types: (i) stabilization of the substrate s valence band; (ii) stabilization of the surface bands. An important feature of type-(i) interaction is that is not restricted to the Si atoms of the first layer [=Si(1)]. Additional Si—K bonding interactions with the Si atoms of the second and third layers [=Si(2), Si(3)] are also important. However, the stabilization of the surface bands [type-(ii) interaction] is determined by the coordination of the K atoms to the outermost Si(1) centers.

Type-(i) interaction is responsible for the relative stabilities of the adsorption sites for the K atoms. The stabilization of the substrate s band as a function of the adsorption geometry follows exactly the same sequence  $D < A < C < B$  found for the total energies. Table II shows the relative energy of the center of gravity of the

TABLE I. Band-structure data for the surface bands  $b_1$  and  $a_1$  of the K/Si(100)-(2×1) slab model according to the semiempirical SCF HF CO approach. The optimized Si-K distance for adsorption of K atoms at site B has been employed in the calculation. The band energies  $\epsilon_i$  are given for the symmetry points in the BZ. The CO microstates have been decomposed into contributions (in %) from the different atomic centers.

	$b_1$ band				$a_1$ band			
	Y	$\Gamma$	X	S	Y	$\Gamma$	X	S
$\epsilon_i$ (eV)	-2.1	-2.0	-2.1	-1.7	-1.6	1.2	2.4	-1.9
K (%)	0.7	0.7	1.4	0.1	0.0	4.0	1.6	9.7
Si(1) 1st layer (%)	81.0	65.5	46.8	75.9	86.7	51.6	67.8	72.6
Si(2) 2nd layer (%)	17.4	22.6	26.4	17.6	2.0	19.8	15.5	5.7
Si(3) 3rd layer (%)	0.0	9.7	18.2	2.9	1.4	13.3	7.7	1.0
Si(4) 4th layer (%)	0.1	0.7	6.6	2.3	8.4	10.0	6.7	8.9
H saturators (%)	0.5	0.7	0.6	1.2	1.4	1.0	0.5	2.1

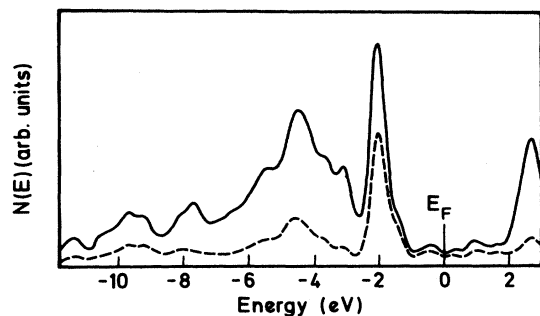


FIG. 5. Density of states  $N(E)$  calculated for the K overlayer and first three Si layers of the K/Si(100)-(2×1) slab model. The surface structure corresponds to adsorption of K atoms at site *B*. The projected DOS corresponding to the valence AO's of the Si dimers is shown by a dashed line.  $E_F$  symbolizes the Fermi level.

six lowest valence *s* bands, which are mainly located at the Si(1), Si(2), and Si(3) surface atoms, as well as the site coordination found for the K atoms at positions *D*, *A*, *C*, and *B*, respectively. The *s*-band stabilization is larger when the alkali atoms are adsorbed at the grooves of the Si(100)-(2×1) surface (i.e., at sites *C* and *B*). At these positions the K atoms are found at lower heights *z* so that the distances from the second- and third-layer Si atoms have values between 2.8 and 3.5 Å, compared with values of 3.4–5.3 Å for sites *D* and *A*. A K atom at the most stable adsorption site (model *B*) is coordinated most effectively to the Si atoms. Multicenter bonding is therefore an important feature of the stability of arrangement *B* in the system K/Si(100)-(2×1). A similar stabilization mechanism has been presented recently in *ab initio* pseudopotential calculations of small  $M_n\text{Si}_n$  clusters ( $M = \text{Li, Na}$ ;  $n = 2, 3$ ).<sup>43</sup>

It is not expected that the employed numerical method, which is not *ab initio*, will be able to reproduce quantitatively all the energetics associated with alkali adsorption on the Si surface. The energy difference (3.7 eV) between alkali adsorption at sites *A* and *B* is too high and seems unrealistic. Nevertheless, the numerical method provides useful information about trends of increasing

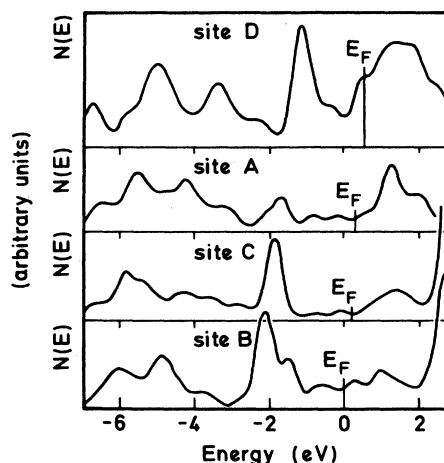


FIG. 6. Projected density of states corresponding to K atoms adsorbed at sites *D*, *A*, *C*, and *B*, respectively. An energy window of 10 eV has been chosen to show the interaction between alkali states and surface bands. The Fermi energy of model *B* has been taken as the origin of the energy scale.

stability of adsorption sites, as well as about the interaction mechanism between adsorbate and substrate. Very recent experimental results<sup>44</sup> based on titration with physisorbed Xe of the Si(100)-(2×1) surface for several K coverages ( $\Theta = 0.0$ – $0.6$ ) confirm that the relative stabilities of the K adsorption sites found in the present work are correct.

The interaction between adsorbate and the surface bands can be monitored by means of the projected DOS curves corresponding to the valence AO's of K atoms in the energy region associated with the surface bands. In Fig. 6 these projected DOS curves are displayed in an energy window of 10 eV that includes the Fermi level. The scale of the DOS curves has been amplified by a factor of 55 with respect to the plot shown in Fig. 5. The reason for this amplification is that the electron density associated with the alkali atoms in the K/Si(100)-(2×1) system is rather small. The total number of valence electrons in the unit cell is  $37e$ . The valence electrons associated with the K atoms represent only a small fraction (about 1:55)

TABLE II. Coordination between adsorbed K atoms and the Si centers of the first three layers at the optimized geometries of the K/Si(100)-(2×1) slab model corresponding to the adsorption sites *D*, *A*, *C*, and *B*, respectively. The number of Si-K nearest neighbors and the corresponding Si-K distances are given for each Si layer. In the last column the  $\Delta\epsilon_s$  values represent the relative energies of the center of gravity of the six lowest valence *s* bands for each adsorption site. The energy value corresponding to site *B* has been taken as internal reference. Positive energy increments indicate destabilization of the band energies. Distances are given in Å, energies in eV.

	Si(1) 1st layer	Si(2) 2nd layer	Si(3) 3rd layer	$\Delta\epsilon_s$
K at <i>D</i>	2×2.52	4×4.49	2×5.29	2.29
K at <i>A</i>	4×2.69	2×3.40	1×4.16	1.21
K at <i>C</i>	4×3.34	2×2.81	1×3.40	0.58
K at <i>B</i>	2×2.65	4×3.16	2×3.53	0.00

of this total number. The maximum in the partial DOS curves found at about 2 eV below the Fermi level corresponds to electronic states characterized by an admixture between AO's centered on the alkali atoms and the surface bands of the Si substrate. The area of this peak in the DOS curves is therefore an indication of the degree of hybridization between alkali states and Si surface bands. The larger the area, the more effective the interaction (hybridization) between adsorbate states and substrate surface bands. Figure 6 shows that the area of the above-mentioned peak in the DOS curve increases in the sequence  $A < C < B < D$ , identical with the sequence found for the total energies except for site  $D$ . At geometry  $D$  the alkali atoms are located above the Si dimer bonds with the shortest Si(1)-K distance; therefore they interact very effectively with the Si surface states.

## VI. CONCLUSIONS

The main conclusion of the present work is the identification of the grooves of the Si(100)-(2×1) surface as the most stable adsorption site for K atoms at a coverage of  $\Theta=0.5$ . The analysis of the band structure of the K/Si(100)-(2×1) surface leads to a bonding model that rationalizes the microscopic origin of the interaction be-

tween adsorbate and substrate. Two electronic factors determine the structure of the surface: (i) the stabilization of the substrate  $s$  band; (ii) the interaction between adsorbed atoms and the surface bands. The most stable adsorption site of the alkali atoms on the Si(100)-(2×1) surface is characterized by the most effective coordination between K and Si atoms. This condition is best realized in model  $B$ , where the K atoms are located as if they would saturate the Si dangling bonds. The chemisorbed K atoms and the Si(100)-(2×1) surface are stabilized by multicenter Si-K bonding.

The odd number of electrons in the unit cell of the K/Si(100)-(2×1) surface at a K coverage  $\Theta=0.5$  leads to a metallic configuration. The highest occupied electronic states are provided by the Si dimers. It is therefore the Si surface that is metallized by deposition of K atoms up to a coverage  $\Theta=0.5$ .

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