

Theoretical support to the double-layer model for potassium adsorption on the Si(001) surface

Y. Morikawa, K. Kobayashi, K. Terakura, and S. Blügel*

Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

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K adsorption on the Si(001)- 2×1 surface is studied by first-principles molecular dynamics based on a norm-conserving pseudopotential. The theoretically optimized structure for full coverage ($\Theta=1.0$) agrees fairly well with the double-layer model analyzed by x-ray photoelectron diffraction. At $\Theta=0.5$, the configuration with K adsorbed along the trough is more stable than the Levine model. The mean desorption energies for the two peaks in the thermal-desorption-spectrum are well accounted for by the present calculation. The calculated work-function change also agrees quantitatively with the observed one. Based on these analyses, it is concluded that the double-layer model should be appropriate for the saturation coverage of K on the Si(001) surface.

An alkali metal adsorbed on the Si(001) surface is a system which has been actively studied with various experimental techniques and with heavy theoretical calculations,¹⁻³ and yet some fundamental aspects are in debate. Among them, the most fundamental issue is concerned with the absolute coverage of adsorbed alkali-metal atoms at saturation coverage. Levine⁴ proposed a model in which Cs atoms were assumed to be adsorbed at the hollow site along the hill of the dimer row (called the HH site hereafter) at the saturation coverage. The saturation coverage in Levine's model corresponds to $\Theta=0.5$ with Θ defined as the ratio of the number of adsorbed atoms to that of the topmost substrate Si atoms, and the surface is metallic with a half-filled π^* band. Levine's model was accepted widely not only for Cs adsorption but also for Na and K adsorption until a model corresponding to $\Theta=1.0$ was proposed by Enta *et al.*⁵ based on angle-resolved photoemission measurements. They found that the Si(001) surface with saturation coverage of K is insulating, in contradiction to Levine's model, and Abukawa and Kono⁶ proposed a double-layer model in which K would be adsorbed along the trough between the dimer rows as well as at the HH sites. Several experiments have been performed since then to judge which of the two models is appropriate. At the present stage no consensus has been attained yet about the Θ value at saturation coverage. The Auger intensity measurement⁷ supports $\Theta=0.5$, the reflection high-energy electron-diffraction (RHEED) analysis⁸ favors $\Theta=1.0$ and the low-energy electron-diffraction (LEED) analysis⁹ cannot answer definitively. However, a recent measurement of the thermal-desorption spectrum¹⁰ (TDS) clearly suggests the existence of two inequivalent adsorption sites for K on the Si(001) surface. Furthermore, it suggests that the populations of K atoms at the two inequivalent sites are nearly the same at the saturation coverage. These results seem to give strong support to the double-layer model. Another piece of evidence for $\Theta=1.0$ at saturation coverage was also given by a medium-energy ion-scattering experiment for K and Cs.¹¹

The main purpose of the present work is to elucidate the adsorption states of K on the Si(001) surface at $\Theta=0.5$ and 1.0 with the first-principles molecular-dynamics method (FPMD).¹² From our calculation, we found that

the T3 site (along the trough, on top of the third-layer Si atom, called the valley bridge site in other papers), and the HH site can be simultaneously occupied stably with a significant adsorption energy. [See Fig. 1 for the possible adsorption sites on the Si(001)- 2×1 surface.] The optimized geometry of adsorbed K atoms at $\Theta=1.0$ agrees well with an analysis by x-ray photoelectron diffraction (XPD) measurement⁶ and the calculated adsorption energies at $\Theta=0.5$ and 1.0 are in good agreement with TDS results.¹⁰ These results lead us to conclude that the saturation coverage of K on the Si(001) surface should be $\Theta=1.0$.

Our calculation is based on the local-density approximation in density-functional theory^{13,14} with the Wigner interpolation formula¹⁵ for the exchange and correlation, and a norm-conserving pseudopotential¹⁶ with a modification by Kleinman and Bylander.¹⁷ Following the suggestion by Gonze *et al.*,¹⁸ we tune a local potential of K, which is a d potential in our case, to remove a ghost band in the bulk K calculation and to achieve good energy dependence of logarithmic derivatives for $4s$ and $4p$ states of a K atom. We also incorporate the partial core correc-

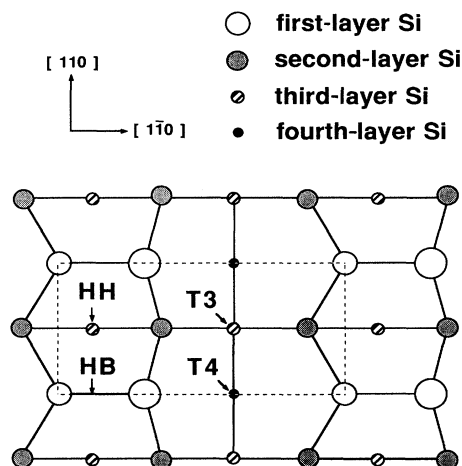


FIG. 1. A top view of the Si(001)- 2×1 asymmetric surface. The 2×1 unit cell is indicated by dashed lines. The HH, HB, T3, and T4 sites are indicated.

tion developed by Louie *et al.*¹⁹ to the K pseudopotential because K has a relatively large core.²⁰ We adopt a repeating-slab geometry and the plane-wave basis. The substrate is represented by a ten-layer Si(001) slab and a vacuum region of the same thickness is inserted in between Si slabs.²¹ The alkali-metal atoms are introduced on each surface of the Si slab. The cutoff energy of the plane-wave basis is 6.25 Ry which results in the maximum number of 1488 plane waves.²² The surface Brillouin zone is divided into 4×8 meshes and 32 inequivalent k points are used to construct the charge density. The optimization of the electronic and ionic degrees of freedom is performed by a modified version of FPMD. We adopt a steepest-descent type of algorithm for the electronic degrees of freedom as proposed by Williams and Soler.²³ More details of the numerical procedure are described in Refs. 24 and 25. We use the optimized (2×1) asymmetric dimer structure as a starting configuration of the substrate Si(001). In case of $\Theta = 0.5$, we consider three possible adsorption sites for K atom, HH, $T3$, and $T4$ sites as shown in Fig. 1. In case of $\Theta = 1.0$, we consider two possibilities, a combination of HH and $T3$ sites, and that of HH and $T4$ sites. In order to make sure whether these adsorption sites are local minima of the Born-Oppenheimer surface, the starting positions of K atoms are away from these sites by about 0.48 \AA along the dimer row. The adsorption at the bridge site of the Si-Si dimer is not considered in the present calculation, because we found it very unstable in the previous calculation for Na adsorption.^{24,26,27} In the process of structural optimization, the Si atoms in the two center layers of each Si slab are fixed at their bulk positions while other atoms are moved by using the classical molecular dynamics with the Hellmann-Feynman force.

For $\Theta = 0.5$, we find out that the HH and $T3$ sites are well-defined local minima for K adsorption with the latter being 0.39 eV/atom more stable than the former. On the other hand, even if we put a K atom near the $T4$ site, it moves toward the $T3$ site. This is so even for a starting position with only 0.2 \AA apart from the $T4$ site. For $\Theta = 1.0$, we find out that two K atoms are adsorbed at the HH and $T3$ sites in the 2×1 unit cell. Even if we put two K atoms near the HH and $T4$ sites, the K atoms move toward the HH and $T3$ sites, respectively. A side view for the optimized structure for $\Theta = 1.0$ is illustrated in Fig. 2(a). The substrate Si dimer becomes symmetric because of filling of the π^* band. The relative position of the two K atoms agrees very well with the results of XPD:⁶ one K atom sits in the $[110]$ direction of the other K atom and their vertical separation is 1.1 \AA . The corresponding value by the recent RHEED experiment⁸ is 1.25 \AA . As for the K-Si bond length, the present result is about 7% larger than the surface extended x-ray absorption fine-structure result.²⁸ The Si dimer bond length becomes 0.27 \AA larger than that of the clean asymmetric dimer and is also larger than the bulk Si-Si bond length by 0.19 \AA . Therefore we expect that the dimer bond becomes rather weaker by K adsorption. The stable adsorption site for $\Theta = 0.5$ [Fig. 2(b)] is the $T3$ site in the present work²⁹ in contradiction to the prediction of the $T4$ site by Ye, Freeman, and Delley.³⁰ Experimentally, the Auger electron-

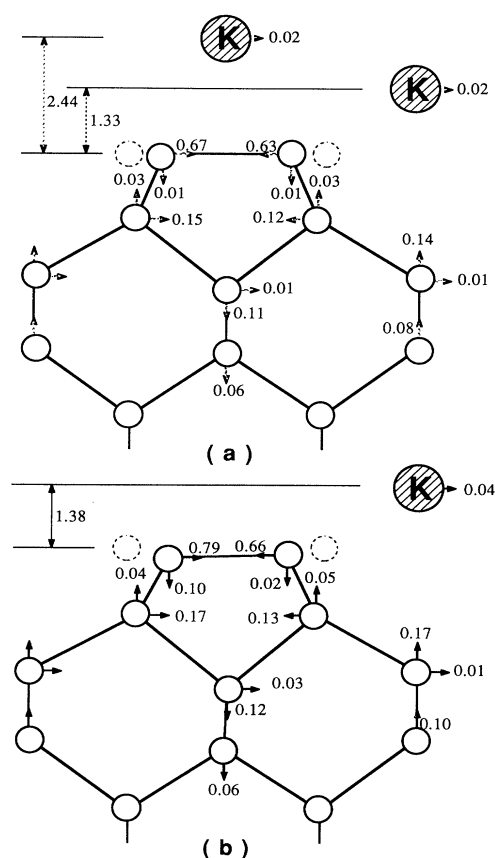


FIG. 2. The side views of the optimized structure at (a) $\Theta = 1.0$ and (b) $\Theta = 0.5$. Displacements from the bulk terminated ideal surface are indicated in angstrom. The first layer Si atoms of ideal surface are indicated by the dotted circles, with reference to which the height of K atoms (hatched circles) are measured. The horizontal displacements of K atoms are measured with reference to the third layer Si atoms of the ideal surface.

diffraction measurement by Asensio *et al.*³¹ concluded the K adsorption at the $T3$ site for submonolayer coverage.³² The same conclusion was reached by the analysis of TDS of Xe for the coadsorption of Xe and K on the Si(001) surface.³³

The total-energy diagram is illustrated in Fig. 3 for $\Theta = 0.0, 0.5$, and 1.0 . The energy of a free K atom is estimated by a total-energy calculation for a bcc structure with a large lattice constant of 30.0 a.u. with the same cutoff energy of 6.25 Ry ,³⁴ and the spin-polarization energy (-0.25 eV/atom) is separately estimated by an all-electron free atom calculation. From Fig. 3, the mean adsorption energy from $\Theta = 0.0$ to $\Theta = 0.5$ (the $T3$ site adsorption) and that from $\Theta = 0.5$ to $\Theta = 1.0$ are 2.12 eV/atom and 1.74 eV/atom , respectively. The important point is that the latter is still significantly large and roughly comparable with the former. We, therefore, conclude that the double-layer model is stable and that the saturation coverage may be $\Theta = 1.0$. The present estimation of the adsorption energies can be compared with the TDS results by the following argument. Let us consider the pro-

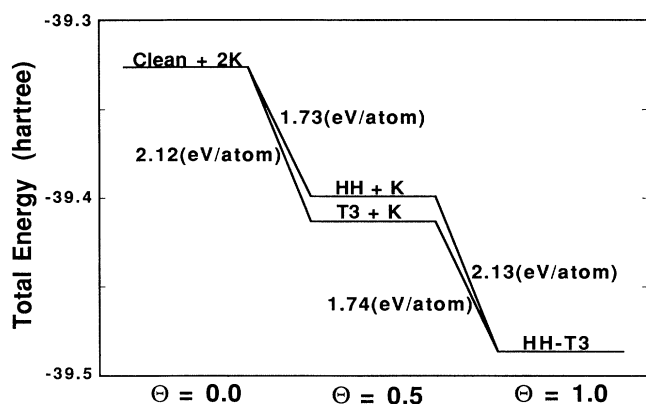


FIG. 3. The total energy for the system composed of the (2×1) surface unit cell of the Si substrate per surface and two K atoms. Two K atoms are free for $\Theta=0.0$, one K atom is adsorbed at the $T3$ site (or the HH site) with one additional free K atom for $\Theta=0.5$, and the two K atoms are adsorbed for $\Theta=1.0$. The energy difference corresponds to the mean adsorption energy for each adsorption configuration.

cess of thermal desorption starting from the saturation coverage. As the temperature increases, K atoms contributing to the α peak (Fig. 1 of Ref. 10) are first desorbed. The integral of the desorption energy curve (Fig. 2 of Ref. 10) for the α peak over the relevant coverage range should correspond to the energy required to remove all K atoms contributing to the α peak. The initial configuration and the final one in this process correspond to $\Theta=1.0$ (HH- $T3$ configuration) and $\Theta=0.5$ ($T3$ configuration), respectively. Therefore the experimental mean desorption energy of the α peak of 1.59 eV/atom should be compared with the theoretical adsorption energy of 1.74 eV/atom from $\Theta=0.5$ to $\Theta=1.0$ in Fig. 3. Similarly the experimental mean desorption energy for the β peak of 2.03 eV/atom should be compared with the theoretical adsorption energy of 2.12 eV/atom from $\Theta=0.0$ to $\Theta=0.5$. The very good agreement between the theoretical estimate and the experimental one can be taken as an additional strong support to the double-layer model for the saturation coverage.

One of the most important properties of the alkali-metal adsorption is a significant lowering of the work function, whose mechanism was extensively discussed by Ishida and co-worker^{35,36} recently. We present our results for $\Theta=0.5$ and $\Theta=1.0$ in Fig. 4.²¹ The theoretical results in Fig. 14 of Ishida and Terakura³⁶ are different from the present ones because the structural optimization was not done in their work. The calculated work-function lowering $\Delta\Phi(\Theta=1.0)$ in Fig. 4 agrees well with the experimental value at the saturation coverage: -3.3 eV by Tochiyama⁷ and -3.2 eV by Enta *et al.*,⁵ both measured at room temperatures. In both measurements, $\Delta\Phi(\Theta)$ decreases monotonously with increasing Θ . In the experiment by Oellig and Miranda³⁷ at 200 K, $\Delta\Phi(\Theta)$ takes a minimum value of about -3 eV and saturates to about -2.6 eV. However, there is a possibility of multilayer adsorption at low temperatures. In fact, -2.6 eV is just the difference of the work functions of Si (4.8 eV) and K (2.2

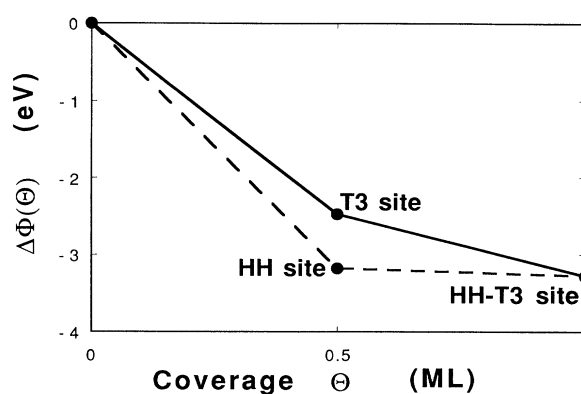


FIG. 4. The work-function change due to the K adsorption for the three different adsorption configurations.

eV). As discussed above, K atoms occupy the $T3$ sites at $\Theta=0.5$, and after that they also occupy the HH sites, so the work-function change will behave like the solid line in Fig. 4. The work function will not take a minimum up to $\Theta=1.0$. From the scanning-tunnel microscope image,³⁸ it is suggested that the stable adsorption site at low coverages is the interdimer bridge site between the two raised Si atoms of the neighboring asymmetric dimers along the dimer row. Our preliminary calculation^{24,27} for the Na adsorption with $\Theta=\frac{1}{6}$ correctly predicts this adsorption site. In this geometry, the alkali-metal atoms are located relatively far into the vacuum and thereby, may contribute to a steep lowering of the work function. More extensive arguments in the low-coverage region will be given in a future publication.²⁵

In summary we obtained the optimized structure with the first-principles molecular-dynamics method. The calculated optimized structure at $\Theta=1.0$ agrees very well with the double-layer model of Abukawa and Kono⁶ and the adsorption energies agree well with the desorption energies obtained by TDS.¹⁰ Based on these observations, we conclude that the saturation coverage at room temperatures is $\Theta=1.0$. At $\Theta=0.5$, the $T3$ site is the most stable site and for higher coverages, K atoms will be adsorbed at the HH site. The work function will not take a minimum at a submonolayer coverage on this surface.

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- *Present address: Institute für Festkörperforschung, Forschungszentrum Jülich, D-5170 Jülich, Germany.
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 - ²²With this cutoff energy and with the present pseudopotential, the lattice constant and the bulk modulus of bulk Si are 5.452 Å and 0.98 Mbar both of which agree with the experimental values within 1% error. As for the optimized geometry of the 2×1 asymmetric dimer model for the Si(001) surface, the dimer bond length is 2.262 Å and the amount of buckling is 0.537 Å.
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