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Adsorption geometry of potassium on a Si(100) 2 × 1 surface

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Abstract. A 63-atom cluster is employed, in a self-consistent semi-empirical molecular orbital total energy algorithm, to calculate the binding energies of potassium atoms adsorbed on a Si(100) (2 × 1) reconstructed surface at various possible adsorption sites, namely, sites H, B and C. Our results strongly suggest that the B site is the most stable one. The results of a half-monolayer coverage calculation show that the double-layered structure of potassium atoms is feasible and in accordance with recent experimental observations. However, the bond length between Si and K, $d_{\text{Si-K}}$, is found to be around 15% lower than the experimental determination. From the Mulliken population analysis, the amount of charge transferred from Si to K atoms varies from 0.01 to 0.32 of the electronic charge at various adsorption sites.

1. Introduction

The adsorption of potassium atoms on a low-index semiconductor surface has been studied extensively for the past few years [1–10]. Interest in this adsorption system derives from its importance in device physics and microelectronics. Despite much effort devoted to the system both experimentally [7–10] and theoretically [1–6], some results are still controversial. For instance, the actual adsorption sites at various coverages and the amount of charge transfer between potassium and silicon atoms are still unknown. At present, we use a self-consistent semi-empirical molecular orbital method, also known as the complete neglect of differential overlap (CNDO) method [11] to investigate the preference site for adsorption, bond strength and the length of the K–Si interaction in the system and the amount of charge transfer between the K and Si atoms.

2. Molecular clusters and the CNDO method

The molecular cluster used to simulate the Si(100) surface is a 63-atom cluster, similar to the one used by Ong and Chan [12]. The cluster consists of four surface layers—a total of 35 Si atoms. The numbers of atoms in the first, second, third and fourth layers of the clusters are 8, 12, 9 and 6, respectively. The dangling bonds at the edges of the cluster are saturated by 28 pseudo-atoms, Si*, consists of sp^3 hybrid orbitals. In the CNDO calculation, the values of the three semi-empirical parameters, namely the orbital exponent ξ, the electronegativity E, and the bonding parameter β must be provided. For a given set of semi-empirical parameters, the CNDO method produces self-consistent calculations, yielding solutions similar to Hartree–Fock solutions and giving total energies and wavefunctions. It can also be used to calculate the Mulliken charge transfers

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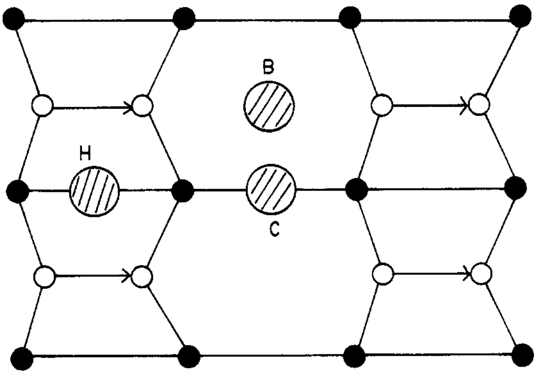

Figure 1. Top view of the positions of adsorbed potassium atoms on the Si(100) (2 × 1) surface. Surface Si atoms are shown as open circles and second-layer Si atoms are dark circles. The pairs of dimer atoms are indicated by the arrows, with the atoms having positive charge at the arrow end. Shaded circles denote K atoms adsorbed at various important sites labelled H, B, C.

among the various atoms in the cluster. The CNDO parameters for Si taken from the calculations of Harker and Larkins [13]) are used to fit the cohesive energy, lattice parameter and valence bandwidth of a 16-atom periodic Si large unit cell (LUC). The parameters of Si* are similar to those of Si except that the bonding parameter is set to zero. This was found necessary by Mainwood and Stoneham [14] in order to give a constant charge on the inner atoms of the silicon cluster and reproduce the valence bandwidth of the bulk silicon. The parameters for *K* are taken from Pople and Beveridge [11]. In the course of the study no attempt has been made to vary the CNDO parameters. The CNDO method has a good record in defect study [15] and the parameters for Si, Si* have been tested in surface problems [12, 16–18] as well as in defect studies [14, 15, 19, 20]. We used the Harwell computer code MOSES [21] to perform the CNDO calculations.

3. Calculations and results

It is established from LEED experiments that the 2 × 1 reconstructed pattern of Si(100) system does not change after the deposition of potassium. However, the exact geometry of the K-Si(100) 2 × 1 system is still unattainable. The only experimental information we know is the distance $d_{\mathrm{Si-K}}$ between the surface silicon and the adsorbed potassium which was obtained by Kendelewicz *et al* [22] from their SEXAFS experiment. The value determined by them is $d_{\mathrm{Si-K}} = 3.14 \pm 0.10$ Å. For clean Si(100) surfaces, most of the theoretical calculations predict that the (2 × 1) asymmetrical dimer is more stable than the symmetrical dimer [12]. However, for the K–Si(100) system, the charge mechanism that stabilises the (2 × 1) asymmetrical dimer on a clean Si(100) surface may not apply to the case studied here. Therefore, we follow the suggestions of Ishida *et al* [3] and Ye *et al* [1] and assume that the silicon substrate is a symmetrical dimer (2 × 1) surface. The dimer length was found to be 2.86 Å and each dimer atom moved 0.27 Å toward the bulk, from our total energy calculation.

We have investigated three possible adsorption sites on the silicon surface as illustrated in figure 1. The notation is the same as that adopted by Batra [23]. The first site

Table 1. The calculated results for binding energy (eV), $d_{\text{Si-K}}$ (Å) and charge transfer between potassium and substrate (electrons) for a single-potassium-atom adsorption site.

	H	C	B
d (Å)	2.77	2.70	2.63
Binding energy (eV)	4.43	5.50	7.13
Charge transfer to potassium atom (electrons)	0.04	0.05	0.25

Table 2. The calculated results for binding energy (eV), $d_{\text{Si-K}}$(Å) and charge transfer from Si substrate to potassium adsorbed for the case of two potassium atoms adsorbed on a Si substrate at various possible combinations of sites. The last column gives results corresponding to half-monolayer coverage.

	B + B	H + B	H + H	H + C	H + H + B + B
$d_{\text{Si-K}}$ (Å)	2.61	2.27	2.69	2.74	2.74
	2.61	2.61	2.69	2.62	2.61
Binding energy (eV)	7.53	6.50	4.59	5.32	6.74
Charge transfer to	0.31	0.31	0.05	0.12	0.09, 0.07
potassium atom (electrons)	0.31	0.06	0.06	0.24	0.32, 0.32

is a hollow site (H) which lies near the centre of a hexagon formed by two dimer pairs and two second-layer atoms and sits on top of a third-layer atom. The second site is the cave site (C), which has a second-layer atom as the nearest-neighbour atom. The third site is the long-bridged site B, the adsorbate being located above a fourth-layer Si atom connecting the rows of dimers.

In order to determine which of the above-mentioned sites is the preferred site, we have to calculate the binding energies for K adsorption on these sites. The binding energy, B, is calculated from the following relationship:

$$B = E_{\text{Si-K}} - (E_{\text{Si}} + E_{K})$$

where E_{Si} is the total energy of the clean reconstructed (2 × 1) surface cluster, E_{K} is the total energy of the potassium atoms and $E_{\text{Si-K}}$ is the total energy of the potassium adsorbed surface cluster.

Results from our total energy calculations for single potassium adsorbate are presented in table 1. Our results strongly suggest that the B site is the preferred one, giving support to the calculation of Ye *et al* [1]. However, our calculated bond length between potassium and the surface Si atom, $d_{\text{Si-K}}$, is about 15% shorter than that obtained from the experimental determination. In view of the uncertainty of the detailed geometry of the K–Si adsorbed system, the agreement with the experimental estimation can be considered quite good. The H site is found to be 0.15 Å off the centre of the hexagonal centre along the dimer direction. In the case of two potassium atoms adsorbed on a Si surface, four different combinations of sites are considered here, namely, the (B + B), (H + B), (H + H) and (H + C). The calculated results for the binding energies, $d_{\text{Si-K}}$, and charge transfer for each possible site are summarised in table 2. The (B + B) site is found to be most stable, followed by the (H + B) site. For the case of four potassium atoms adsorbed on our molecular cluster, which is equivalent to half-monolayer coverage, the binding energy is found to be high with a value for $d_{\text{Si-K}}$ of 2.74 Å and 2.61 Å for those potassium atoms adsorbed at H and B sites respectively. These results support the observation of a potassium double layer from the x-ray photoelectron diffraction experiments performed by Abukawa and Kono [7]. However, we are not able to investigate the linear chains of K at 0.5 ML due to the size of our molecular cluster.

Our calculated Mulliken charge transfer indicates that the charges are transferred from Si to K in all possible adsorption sites. The values vary from 0.04 to 0.33 of the electronic charge. These readings are in agreement with those obtained by Kasowski and Tsai [4] and contradict those obtained by Batra [2] and Ye *et al* [1]. Batra found that the valence electrons of the K atoms were donated to fill the empty surface states and Ye *et al* [1] found that about 0.63 of the electronic charge was transferred from K atoms to the substrate. We therefore conclude that the bonding between K atoms and the surface is probably not ionic.

4. Conclusions

We have calculated the binding energies of K/Si(100) 2 × 1 systems at various different adsorption sites by using the 63-atom molecular cluster. We conclude that the B site is the most stable one. The bond length between Si and K atoms, $d_{\text{Si-K}}$, is found to have different values for K at different adsorption sites. This suggests that a double-layer structure of potassium atoms is possible at higher potassium coverage. Our Mulliken charge analysis indicates that charge is transferred from the Si substrate to a potassium atom, and hence that the bond between Si and K is not ionic.

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