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Adsorption site of alkali metal overlayers on Si(001) 2 × 1

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The alkali metal semiconductor interfaces are currently being investigated by a variety of tools. Most studies to date at half a monolayer coverage have shown preference for either a quasi-hexagonal (H) site or a long-bridge (B) site. At this coverage one-dimensional chain structure for K on Si(001)2×1 have now been confirmed by scanning tunneling microscopy (STM). The data, however, is consistent with either of the two sites. STM investigations at low coverages suggested that alkali metals like K and Cs occupy a novel site, Y, which is a bridge site between two Si atoms belonging to different dimers along the dimer row [110] direction. The total energy calculations for this new Y site, discovered by STM, have shown that it is indeed a site of (local) energy minimum. The ability of the surface silicon atoms, which are not adjacent to the alkali metal atom, to buckle makes the Y site a competitive adsorption site. We deduce the nature of bonding between alkali metals and Si using the STM data. It is concluded that the bond is substantially ionic in nature.

The adsorption of alkali metal (AM) overlayers on Si(001)2 × 1 has attracted considerable attention recently [1–4]. One of the outstanding issues has been the geometrical [5–8] arrangement and registry of the overlayer with respect to the substrate. This fails naturally within the scope of the scanning tunneling microscopy (STM) [9] which is well suited for providing the local atomic arrangement. Much of the pioneering work [10–13] of deducing structure from the STM data for AM on Si(001)2 × 1 has been carried out by our Japanese colleagues. Since STM approximately probes [14] the local density of states around the Fermi level, the detection of alkali metals on Si(001)2 × 1 surface is a non-trivial issue. The difficulty arises from the fact that the Si(001)2 × 1 surface has partly occupied dangling bond states. The local density of states around E_F is thus dominated by these states. Furthermore, the valence (ns) orbital of the AM atom which is obliged to interact with these states is rather diffuse. In the extreme ionic interaction picture, these AM atoms will decorate the dangling bond states to be detected by STM. In the weak interaction case, the dangling bond states and the valance states of the metallic overlayer occupy the same narrow region around E_F making discrimination difficult.

In spite of all these complications, STM work [10–13,15] has provided valuable information about the geometrical arrangement for AM on Si(001)2 × 1. By carefully monitoring the density of bright spots and deposition time the adsorbed AM atoms have been identified. Six probable adsorption sites labelled by the letters H, B, C, D, T and Y are shown in fig. 1. At half a monolayer

(ML) coverage there is one AM atom per 2×1 cell (3.39×10^{14} atoms/cm^2) in one of the above-mentioned sites.

Levine [16] in 1973 proposed for Cs adsorption on Si(001) that at low coverages this metal occupied a quasi-hexagonal hollow site (H) above the rows of dimers. The H-site occupancy offered [16] a simple explanation for negative electron affinity (NEA) because it left the long-bridge (B) sites, where the adatom connects two dimers in adjacent rows, unoccupied. The coadsorption permits the oxygen atoms to submerge under the B sites to cause additional (beyond that produced by AM) lowering of the work function required to achieve NEA. The C site has adsorbates above the third layer of Si and due to reconstruction this is a more open site than H. Others have called [4,11] the C site as a valley bridge site (T3) and B site as a cave site (T4). The dimer bridge
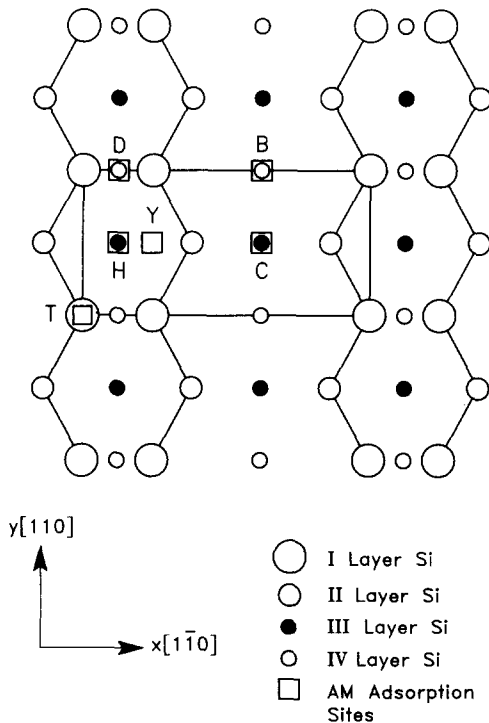

Fig. 2. Total energy of an AM overlayer as a function of vertical height h at $\frac{1}{2}$ML coverage adsorbed above the Si(001)2 × 1 surface at various competitive sites. All energies are referenced with respect to the minimum energy of the H site. The Abraham–Batra [19] symmetric dimer model was employed for the substrate.

site, D, locates the adsorbate above the mid-point of the Si dimer. In the top site T, adsorbate is above one of the dimer-forming Si atoms. The Y site is an off-centered site between the H and the C sites and has been recently revealed by STM work [13] at low coverages.

Atoms in the top Si layer of clean Si(001) surface normally have two dangling bonds each for an ideal bulk truncated structure. The 2×1 structure is obtained when these atoms dimerize along the x direction (generating a σ bond) resulting in rows of dimers along the y [110] direction. Each surface atom nominally has a single dangling bond. Since there are two Si atoms per surface unit cell, one gets two bands (π and π^*) in the gap region which are only partially occupied. The AM atoms interact with these dangling bond orbitals located near the Fermi level. The STM images thus have to be carefully analyzed to detect real alkali metal atoms.

Our total energy calculations for the adsorption of Na on Si(001)2 × 1 at $\frac{1}{2}$ML coverage are illustrated in fig. 2. Other AM atoms are expected to show similar qualitative trends. All

y[110]

x[1$\bar{1}$0]

○ I Layer Si
○ II Layer Si
● III Layer Si
○ IV Layer Si
☐ AM Adsorption Sites

Fig. 1. A top view of the Si(001)2 × 1 surface. Various likely adsorption sites in a 2 × 1 unit cell for an alkali metal (AM) are labelled by squares and denoted by the letters H, Y, C, B, D and T. Rows of Si dimers are oriented along the y direction.
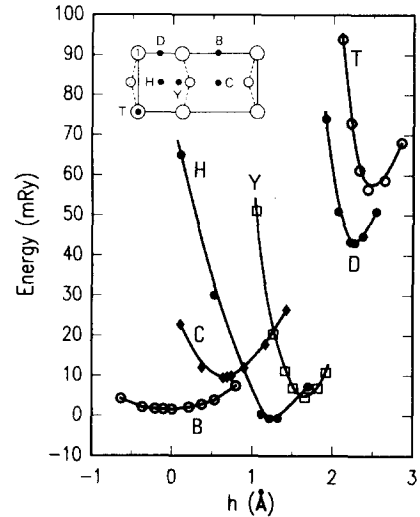
calculations were performed using the pseudopotential method and have been described in detail elsewhere [17,18]. We have shown computed total energy versus vertical height of AM overlayer at various sites. All energies are referenced with respect to energy of the stable configuration at the H site and are computed using a 4.5 Ry energy cutoff. Here the optimization consisted of only moving the AM overlayer along the z direction while the substrate atoms were held fixed at the positions given by the Abraham–Batra [19] symmetric dimer model. The energy sequence for Na/Si system in the order of decreasing stability is $E(H) \simeq E(B) < E(Y) < E(C)$. The D and T sites are found [17,18] to be much less stable and thus are not likely adsorption sites at this coverage.

It thus emerges that the H, B, Y and C sites are competitive adsorption sites at $\frac{1}{2}$ML coverage. Consequently we decided to study a potential energy line passing through the likely adsorption sites. The local dip in total energy at the Y site (with the Si–Na–Si plane being perpendicular to substrate surface) suggests that the Y site is a good candidate to be an adsorption site. We must credit the STM work [13] for the suggestion of the Y-site which was never considered by any-

one else earlier. We have only carried out a limited relaxation at every structural point. But we have shown earlier [17,18] that the adsorption induced relaxation of Si substrate plays a key role in selecting among sites which have close energy minima on the Born–Oppenheimer surface. Therefore, the results shown in fig. 3 are only good for qualitative or semi-quantitative purposes. It turns out that the C site at this level of accuracy is not a true minimum. As shown in fig. 3, it is an inflection point along the y direction. The AM atoms may well be trapped in this site before finding an absolute minimum. A general conclusion to be drawn from fig. 3 is that even at $\frac{1}{2}$ML coverage several adsorption sites are nearly equally favored. A detailed cluster calculation [20] initially indicated strong site dependency of the energy surface. It was subsequently realized [21] that the inclusion of substrate relaxation [17,18] makes many of those sites highly competitive.

Our above assertions are consistent with the conclusions drawn from the STM data. It was concluded [13] that at low coverages (< 0.1 ML) K and Cs adsorb near the Y site. We note that STM data was first interpreted [10] in terms of the T site where AMs bond directly with the Si dangling bonds. This site was eliminated a long tune ago by Ciraci and Batra [3]. Now the interpretation of the STM data has been revised [13]. It is argued that K and Cs atoms form bonds with two neighboring Si atoms, which belong to adjacent and parallel dimer bonds. We called this site the Y site. In the original suggestion by Hashizume, Hasegawa and Sakurai [13] the plane of two Si and K atoms was not perpendicular to the surface but tilted towards the H site. At $\frac{1}{2}$ML coverage the well known one-dimensional linear chains parallel to the Si dimer rows have been confirmed [15] for K on Si(001)2 × 1. Although they were unable to deduce a definitive adsorption site, the H site is fully compatible with this STM data [15]. At ~ 0.2 ML coverage they [15] noted the coexistence of adsorption in several sites consistent with our earlier conclusions [3,17,18] and the inference drawn from fig. 3.

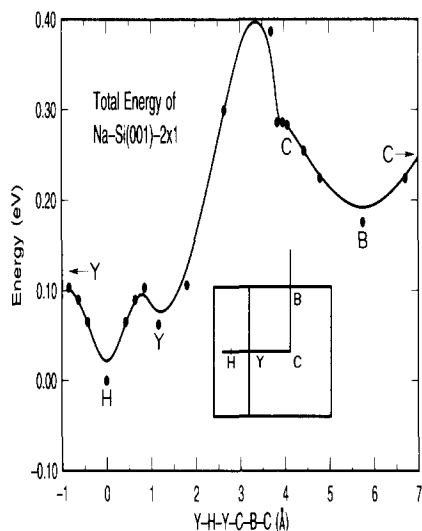The Y site is a novel and unique site first [13] brought to light by STM. They also showed that

Fig. 3. Total energy of Na–Si(001)2×1 (referenced with respect to the H site) for various structural arrangements along the line shown in the 2×1 cell. Positive energies correspond to less stable structures.

the buckled dimerization is stabilized by AM adsorption on these sites. We fully concur with this conclusion. Our optimized geometry given in table 1 shows that the surface Si atoms located away from the AM can lower the total energy by inward relaxation. A slight asymmetry in the dimer is also noted. A net lowering of energy with respect to the symmetric unbuckled dimer was found to be ~ 0.05 eV.

Since the Y site has not been discussed much in the literature, we also take this opportunity to show total valence charge density plots. Figs. 4 and 5 show two orthogonal planes both containing the Y site. The AM valence charge is mostly taken up by Si dangling bonds. Our conclusion is that the nature of bonding is rather similar to the other sites [3,17,18], namely, there exists a large ionic component in the bond. We describe below the nature of bonding as we infer from the STM data.

There have been some suggestions [22,23] in the literature that the interaction between AM and Si is weak at $\frac{1}{2}$ML coverage. It is difficult to reconcile this with STM data where AM atoms have been shown to form one-dimensional chains parallel to the substrate Si dimer row directions. In the proposed geometry for, say, K on Si(001) 2 × 1, the nearest neighbor K–K interatomic distance of 3.8 Å is considerably shorter than the bulk equilibrium distance of 4.6 Å. For Cs, the deviation from the bulk bond length (5.2 Å) is even greater. This suggests that AM atoms are being forced to locate on the repulsive part (≥ 0.5 eV) of the potential energy surface in the AM–
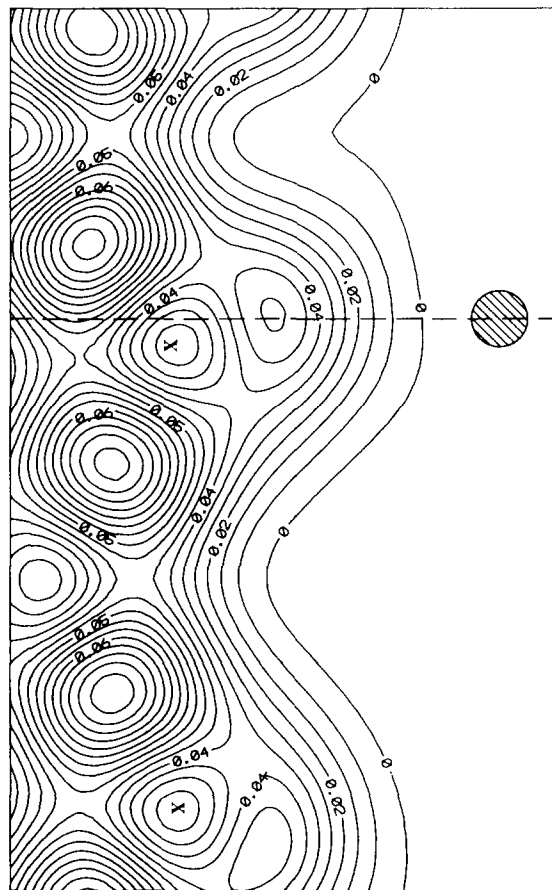

Fig. 4. Contour plots of the valence change density for $\frac{1}{2}$ML coverage of Na on Si(001)2 × 1 adsorbed at the Y site. The plane shown is (110) passing through the Y site. Na atom is shown by a cross-hatched circle under which charge density is somewhat enhanced. In this plane there are no Si atoms directly below Na in the first Si layer. Approximate location of the second-layer Si atoms is shown by the letter X.

Table 1
Optimized atomic coordinates (in a.u.) for Na overlayer at the Y site at $\frac{1}{2}$ML coverage and the corresponding top two Si layers in the 2×1 cell. Each Si layer contributes two atoms per unit cell which are denoted by numbers with and without primes on them. These calculations were performed with 4.5 Ry energy cutoff and 32 k-points in the Brillouin zone

Atom	x	y	z
Na(Y)	2.20	3.63	2.47
Si(1)	2.27	0.0	−0.62
Si(1′)	−2.13	0.0	−0.83
Si(2)	3.40	3.63	−2.80
Si(2′)	−3.45	3.63	−2.76

AM coordinate. From thermal desorption experiments [24] binding energies of 1.6 and 1.9 eV have been obtained depending on the adsorption site. The overall stabilization of the structure must then arise from AM–Si interactions. This interaction has to be substantial and in fact most theoretical calculations [3,4,17,18,20,21,25] estimate this number to be in the 2 eV range. The origin of the stabilization energy lies in the image interaction between the alkali ion and the Si surface.
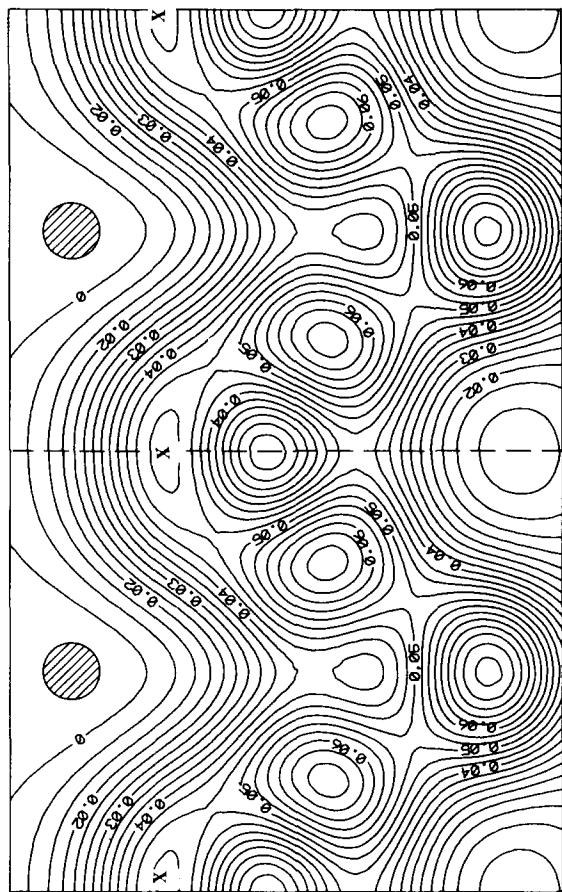
Fig. 5. The plane shown is (1$\bar{1}$0) passing through the Y site. The dotted line divides two identical unit cells. AM charge is mostly taken up by surface Si dangling bonds. Approximate location of the first-layer Si atoms is shown by the letter X.

The predominantly covalent AM–Si interaction proposal [23] is also not being supported by the STM data. At intermediate coverages (~ 0.2 ML) the AM atoms have been shown [15] to occupy a variety of adsorption sites. Covalent bonds are usually highly directional [26] in nature and tend to be site specific. Our earlier total energy calculations and the Na potential-energy line shown in fig. 3 support multiple adsorption sites in agreement with the STM data. Thus both the data and the current calculations argue against a purely covalent bond. Multiple sites can be consistent with a weakly interacting metallic overlayer on Si(001) 2 × 1 surface. But we have noted

above that the bond energy is ~ 2 eV which is certainly not weak. Hence, the overall interactions must have a strong ionic contribution. This conclusion is also supported by cluster calculations [20,21,25].

The precise quantitative value of the charge transfer, ΔQ, from AM to Si lacks consensus. This is not too surprising since there is no unique definition for ΔQ. The spatial and spectral distribution clearly suggest that the bond is substantially ionic. We believe that the STM observations are consistent with the Langmuir–Gurney [27] picture of ionic interaction at low coverages. A more direct confirmation is provided by recent inverse photoemission experiments [28]. Here an empty state attributable to K overlayer is detected at 2.4 eV above for the Fermi level at a K coverage of less than $\frac{1}{2}$ML.

In summary, our total energy calculations show that several adsorption sites for AM on Si(001) 2 × 1 are competitive in energy. At least three sites lie within 0.2 eV of each other. This explains in part the controversy regarding the adsorption sites. Most authors have noted that there is no single site which uniquely stands out as the most stable site. (Those who disagree with this are obviously in error because then the controversy would not have arisen in the first place). STM experiments have confirmed that several adsorption sites must indeed lie close in energy as they are simultaneously observed. We can thus reconcile that different sites can coexist. A pronounced lack of directionality is also a hallmark of ionic bonds which we believe is the conclusion of STM experiments.

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