Size Effects for the Adsorption of Alkali Metal Atoms on the Si(001) Surface

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ABSTRACT The adsorptions of a series of alkali metal (AM) atoms, Li, Na, K, Rb and Cs, on a Si(001)-2×2 surface at 0.25 monolayer coverage have been investigated systematically by means of density functional theory calculations. The effects of the size of AM atoms on the Si(001) surface are focused in the present work by examining the most stable adsorption site, diffusion path, band structure, charge transfer, and the change of work function for different adsorbates. Our results suggest that, when the interactions among AM atoms are neglectable, these AM atoms can be divided into three classes. For Li and Na atoms, they show unique site preferences, and correspond to the strongest and weakest AM–Si interactions, respectively. In particular, the band structure calculation indicates that the nature of Li–Si interaction differs significantly from others. For the adsorptions of other AM atoms with larger size (namely, K, Rb and Cs), the similarities in the atomic and electronic structures are observed, implying that the atom size has little influence on the adsorption behavior for these large AM atoms on the Si(001) surface.

Keywords: size effects, adsorption, alkali metal atoms, Si(001) surface; DOI: 10.14102/j.cnki.0254-5861.2011-0620

1 INTRODUCTION

Adsorption of alkali metals (AM) on the Si surface has been the subject of extensive studies in the past few decades[1-6]. Because of the relatively simple electronic structure of AM, the AM-adsorbed Si(001) system is used as model systems for the investigations of metal-semiconductor junctions and the metallization of semiconductor surface. Up to now, there have been a large number of studies for the AM/Si(001) system over the years to reveal the bonding character between AM and substrate Si atoms, which is crucial in understanding the fundamental physics and technological applications of AM-adsorbed silicon surface.

It is well known that the adsorption behaviors of AM atom on the Si(001) are mainly affected by two factors, the coverage and the size of AM atom. Experimentally, Johansson et al. have carried out a series of typical work for the adsorptions of Li, Na, K and Rb on Si(001) by using angle-resolved direct and inverse photoemission[1-3]. In their results, the metallization of the silicon surface is observed for the cases of K and Rb with increasing the AM...
coverages, and the systematic differences in the electronic structures of different AM/Si(001) systems are caused by the sizes of AM atoms. A larger AM atom leads to a stronger AM–AM interaction and a weaker AM–Si interaction. Souda et al. have employed low-energy D⁺ scattering to explore the nature of the bonding of Na, K, Rb and Cs on the Si(001) surface in a low coverage regime (less than 0.25 monolayer)[4]. They found that Na atom has obvious covalency with Si, while other AM atoms are adsorbed almost completely ionized on the Si(001) surface. To explain the experimental observations and obtain a deep insight into the AM–Si interaction, theoretical investigations have been performed to study the atomic and electronic structures of AM/Si(001) systems[7-24]. However, much of such work focuses on the adsorptions of AM at the coverages of 0.5 and 1 monolayer (ML), and little attention has been paid to the cases of low coverages of AM on Si(001). Of all the alkali metals, according to our knowledge, only the adsorptions of lithium and sodium on the Si(001) surface have been investigated theoretically at the low coverage. Ko et al. have investigated the atomic and electronic structures of Li/Si(001) and Na/Si(001) systems using the first-principles method[22, 23]. Their results showed that at the coverage of 0.25 ML, the Li and Na adatoms prefer to be sit directly above the second-layer Si (B2 site in Fig. 1) and the fourth-layer Si (T4 site in Fig. 1) atoms, respectively. However, another theoretical calculation performed by Gravila et al. predicted that the Na atom tends to be adsorbed at the pedestal site between neighboring Si–Si dimers (HH site in Fig. 1)[24]. Therefore, there are still some controversies as to the most stable adsorption site of AM atom on the Si(001) surface at low coverage. Since the interactions among AM atoms are neglectable at the low coverages, the deposition process of AM on Si(001) is dominated by the interactions between AM and Si atoms. Then, the studies of the adsorption behavior of AM on the Si(001) surface at low coverages are important to obtain deep understanding of the bonding character between AM and substrate. On the other hand, the information about the effects of the size of AM atoms is still not clear because only one or two kinds of AM are involved in the previous theoretical work. The systematic investigation of the adsorption of AM atom with different sizes on the Si(001) surface is also necessary to reveal the topology and steric effects for the surface of this important semiconductor[25].

**Fig. 1.** A top view of some possible AM adsorption sites on the Si(001)-2×2 surface. The pedestal, valley bridge, cave, interdimer bridge, dimer bridge, and dangling-bond sites are denoted by HH, T3, T4, B2, HB, and TD, respectively. The rectangle area surrounded by the dashed line indicates a (2×2) unit cell employed in the calculations, and the Si atoms at different layers are denoted by circles with different sizes.
In this paper, we report the first-principles calculations of the adsorptions of Li, Na, K, Rb and Cs on a Si(001)-2×2 surface at the 0.25 ML coverage. The most stable adsorption site and the diffusion path on the surface for different adsorbates have been determined, and the differences among the electronic structure, including band structure and charge transfer, as well as the variation of work function have been discussed. Our systematic work can provide valuable information that allows us to investigate the effects of size of the AM atoms on the Si(001) surface.

2 COMPUTATIONAL DETAILS

The first principles calculations were carried out based on the density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP)[26, 27]. The Kohn-Sham equations were solved using a plane-wave basis set and periodic boundary conditions. Electron exchange and correlation were described by the Perdew-Burke-Ernzerhof (PBE) form[28] of the generalized gradient approximation (GGA). The ion cores were treated by projector-augmented wave (PAW) potential as proposed by Kresse and Joubert[29]. The kinetic cutoff energy for the plane-wave expansion was set to be about 250 eV, except a larger value of 700 eV used for the Na case. The valence atomic configurations of all AM atoms were (n–1)s²(n–1)p⁶ns¹. The Brillouin zone was sampled by a set of five special k points, and the effects of spin polarization and the dipole corrections were considered in the calculations.

A supercell consisting of a (2×2) surface unit cell was employed (corresponding to a 0.25 ML coverage of AM atom) and a periodic slab containing five Si layers was adopted to simulate the Si(001) surface. In this model, there were two alternating asymmetric Si–Si dimers on the top layer, and the dangling bonds at the bottom layer were saturated by H atoms. The thickness of vacuum region between two adjacent slabs was about 10 Å after the adsorption of AM atom. All the atoms were allowed to relax in all directions, except that two Si layers at the bottom were held at their bulk positions during the geometry optimization.

3 RESULTS AND DISCUSSION

3.1 Atomic structures of the AM/Si(001) systems

As displayed in Fig. 1, six special adsorption sites have been considered in the present work, in which the AM atom is located at the pedestal site (HH), valley bridge site (T3), bridge site (HB), cave site (T4), interdimer bridge site (B2), and dangling-bond site (TD), respectively[17]. Some optimized structural parameters for each AM atom with different adsorption sites are summarized in Table 1.

<table>
<thead>
<tr>
<th>AM atom</th>
<th>Adsorption site</th>
<th>d_{Si-Si}(Å)²</th>
<th>d_{AM-Si}(Å)²</th>
<th>Z_{AM}(Å)c</th>
<th>Relative energy (eV)d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>TD</td>
<td>2.365, 2.379</td>
<td>2.405</td>
<td>2.184</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>HB</td>
<td>2.344, 2.479</td>
<td>2.447</td>
<td>1.921</td>
<td>–0.27</td>
</tr>
<tr>
<td>Na</td>
<td>HH</td>
<td>2.386, 2.386</td>
<td>2.586</td>
<td>1.108</td>
<td>–0.67</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>2.357, 2.401</td>
<td>2.438</td>
<td>1.122</td>
<td>–0.53</td>
</tr>
<tr>
<td></td>
<td>T3</td>
<td>2.394, 2.394</td>
<td>2.686(2nd)</td>
<td>0.167</td>
<td>–0.42</td>
</tr>
<tr>
<td></td>
<td>T4</td>
<td>2.323, 2.451</td>
<td>2.641</td>
<td>0.130</td>
<td>–0.56</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>2.368, 2.371</td>
<td>2.732</td>
<td>2.498</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>HB</td>
<td>2.366, 2.403</td>
<td>2.820</td>
<td>2.115</td>
<td>–0.18</td>
</tr>
<tr>
<td></td>
<td>HH</td>
<td>2.376, 2.376</td>
<td>2.873</td>
<td>1.687</td>
<td>–0.53</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>2.366, 2.390</td>
<td>2.856</td>
<td>1.483</td>
<td>–0.38</td>
</tr>
<tr>
<td></td>
<td>T3</td>
<td>2.381, 2.382</td>
<td>3.062(2nd)</td>
<td>0.757</td>
<td>–0.50</td>
</tr>
<tr>
<td></td>
<td>T4</td>
<td>2.345, 2.395</td>
<td>2.870</td>
<td>0.875</td>
<td>–0.55</td>
</tr>
</tbody>
</table>

To be continued
For the clean surface, the calculated bond length of Si–Si dimer is 2.361 Å and the corresponding tilt angle is 21º, in good agreement with the previous theoretical calculations\(^{(30, 31)}\). After the adsorption of AM atom, as listed in Table 1, in many cases the configurations of two Si–Si dimers in the cell are similar to those of the clean surface. However, when the AM is located at the HB site, the Si–Si dimer beneath is elongated obviously, especially for the Li adsorption, in which the largest increase (about 0.1 Å) of the length of this dimer is observed. For comparison, the dimer configuration is almost unperturbed even when AM sits above the top of the first-layer Si atoms at the TD site. It is well known that the bonding between two Si atoms in the dimer can be described in terms of a strong \(\sigma\) bond and a weak \(\pi\) bond\(^{(32)}\), and consequently, the dimer bond is slightly shorter than the Si–Si bond in the bulk (about 2.40 Å). According to the above results, the \(\pi\) bond of dimer is broken obviously when the adsorption of AM happens on the HB site of dimer. For the case of Li atom, it is noted that besides the HB site, the adsorption at the T4 site also induces significant elongation of the Si–Si dimer near the T4 site. Hence, compared with other AM atoms, relative strong interaction between Li and Si atoms can be expected. Actually, the complicated reconstructions of Si(001) surface induced by the Li adsorption was observed experimentally at submonolayer coverage\(^{(33, 34)}\), suggesting obvious interaction between the Li and substrate.

The shortest distances between AM and Si atoms for different adsorption sites are also given in Table 1. For the T3 position, the AM adatom is far from the neighboring Si–Si dimer, thus the shortest AM–Si distance is from a second-layer Si atom at the substrate, not a dimer Si atom as in the cases of other adsorption positions. By examining the AM–Si distance, it shows following sequences for different AM atoms,

- For Li: \(\text{TD} \approx \text{HB} \approx \text{B2} < \text{HH} < \text{T4} < \text{T3}\)
- For Na: \(\text{TD} < \text{HB} \approx \text{B2} \approx \text{HH} \approx \text{T4} < \text{T3}\)
- For K, Rb and Cs: \(\text{TD} \approx \text{HB} < \text{B2} \approx \text{HH} \approx \text{T4} < \text{T3}\)

According to the above results, when AM atom sits at the T3 site, it exhibits the longest AM–Si distance. On the other hand, the AM adsorbed at the TD and HB sites tends to show the shortest AM–Si distance. Among various adsorption sites considered here, it seems that for the B2 site, the AM–Si distance is
somewhat sensitive to the size of AM atom. Owing to the small size of Li atom, the Li–Si distances for the B2 and TD sites are quite similar (2.438 vs. 2.405 Å), while for other AM atoms a longer AM–Si distance is found when the AM atom occupies the B2 site. It is noted that increasing the AM size from K to Cs causes the same sequence for the variation of AM–Si distance, implying they can be treated as AM atoms with large size. For the adsorption of Na, it represents the case for AM with medium size. Thus, this series of AM atom surface can be divided into the above three types, and this classification also can be deduced from other aspects discussed in following sections.

Fig. 2a displays the variation of the height of AM atom from surface, and as expected, when AM adatom resides on the top of a Si–Si dimer, namely, the TD or HB site. The AM atom occupies a higher position. However, the adsorption at the T3 or T4 site results in a lower height. Especially, due to the small size of Li atom, the T3 and T4 sites are located at nearly the same height as the surface layer. As displayed in Fig. 2a, the general tendency for the variation of the height is TD > HB > HH > B2 > T3 ≈ T4. Because of the obvious difference among the height of these sites, the multi-layer structure may be formed by introducing more AM atoms into the Si(001) surface. For example, at the saturation 1 ML coverage, the Na and K atoms tend to sit the HH and T3 sites, corresponding to a double-layer model proposed by Abukawa et al. [35].

Now let us focus on the stability of the AM-adsorbed Si(001) system. Fig. 2b shows the variation of the adsorption energy ($E_{\text{ads}}$) for different adsorption sites, which is defined as $E_{\text{ads}} = E_{\text{Si(001)}} + E_{\text{AM}} - E_{\text{AM/Si(001)}}$, where $E_{\text{Si(001)}}$, $E_{\text{AM}}$, and $E_{\text{AM/Si(001)}}$ are the total energies of the clean Si(001) surface, free AM atom, and the adsorbed system, respectively. In addition, the relative energies with respect to the TD site are also reported in Table 1. As shown in Fig. 2b, for all AM atoms, the TD site is found to be the least stable among the six sites considered here, and the next is the HB site. For other high symmetry positions, the relative stability is somewhat complicated and shows the dependence on the size of AM atom, and consequently, the most favorable adsorption site is different. The most stable position of Li adsorption is the HH site, and the T4 and B2 sites are metastable, while the T3 site is most unfavorable among these high-symmetry sites. For the adsorption of Na, except the B2 site that is less stable, other high-symmetry sites have nearly the same energies and are the candidates for the most stable adsorption sites. It is interesting that the adsorptions of K, Rb and Cs atoms exhibit similar trend of site stability, in which the most favored position is the T3 site, and the T4 site is found to be the next stable. According to the above analyses, the size of AM atom has an
obvious effect on the energy differences among HH, T4 and T3 sites. For Li atom with small size, the HH site is preferred, however, these three sites are nearly isoenergetic within 1.2 kcal/mol for the Na atom with medium size; and for AM with larger size (namely, K, Rb and Cs), the T3 site becomes energetically most favorable. Hence, the increasing AM size has a tendency to stabilize the T3 site and destabilize the HH site.

We have to mention that in the present work, the small coverage of AM (0.25 ML) and a large $2 \times 2$ unit cell of substrate imply the neglectable adatom-adatom interactions (the nearest-neighbor distance for the AM atoms is about 7.7 Å). Therefore, the stability of system is mainly determined by the interactions between AM atom and Si(001) surface. From Fig. 2b, it is noted that, for the same position, the adsorption energy changes non-monotonously with increasing the size of AM atom. The adsorption energy for Li addition is generally higher than that for other AM atoms, implying the strongest AM–Si interaction between Li and Si(001) surface. On the contrary, the weakest AM–Si interaction can be deduced for Na adsorption. For those AM atoms from K to Cs with larger size, the strength of the AM–Si interaction is between the cases of Li and Na. Therefore, our results suggest that the most favored adsorption site is AM size dependent, and according to the strength of AM–Si interaction, this series of AM atoms can be classified as strong, weak or moderate adsorbates, which have small, medium and large atomic sizes, respectively.

There have been many theoretical studies on the adsorptions of AM atom on the Si(001) surface over the years, however, most of them focus on the higher (namely 0.5 or 1 ML) coverages of AM atom and few attentions are paid to the early stage of AM adsorption. Ko et al. have investigated the Li-adsorbed Si(001) surface by using norm-conserving soft pseudopotentials within the local density functional approximation (LDA)\textsuperscript{[22]}. When the coverage of Li is 0.25 ML, the B2 site is found to be the most stable and the HH site is slightly unfavorable with the energy higher by 0.06 eV. This result disagrees with the present calculation that the HH site is more stable by 0.14 eV than the B2 position, which may be due to the different DFT functionals applied in their work. The same authors have also performed calculations for the Na adsorption\textsuperscript{[23]}, and similar to our results, the HH, T3 and T4 sites have nearly the same energies. However, in their work, as compared to these high-symmetry sites, a higher energy is predicted for the B2 site adsorption with respect to the present result. Gravila et al. have also explored the relative stability for the adsorption of Na at HH, T3 and T4 positions\textsuperscript{[24]}, and an obvious energy difference about 0.3 eV was observed between HH (or T4) and T3 sites, which is inconsistent with other theoretical work.

3.2 Diffusion of AM atom on the Si(001) surface

In order to obtain a better understanding of the similarities and differences among the adsorption of AM atom with different sizes on the Si(001) surface, and to gain insight into the energetics of their diffusion, we have also calculated the full migration energy profile of each AM atom. In the calculations, a rectangular region with the dimensions of Si(001)-$2 \times 1$ unit cell containing one Si–Si dimer was divided into a $26 \times 14$ uniform grid. The AM atom placed at each grid point was allowed to relax only in the direction perpendicular to the surface, while the positions of other atoms were relaxed as mentioned in section 2. The final potential energy surface (PES) reported in Fig. 3 is achieved by interpolating the results to a finer $104 \times 56$ grid. The energy values shown in pictures are calculated with respect to the free AM atom and clean Si(001) surface (namely, $-E_{\text{ads}}$), and for clarity the positions of six special sites as mentioned in the above sections are labeled in Fig. 3a. First of all, for all AM atoms, the brightest spots are corresponding to the TD sites, demonstrating that they are the points with the highest energy in the PES. It is interesting that for the Li and Na adsorptions, the T3 site is a saddle point to connect two adjacent T4 sites.
However, it appears as a global minimum in PES for the adsorptions of other AM, demonstrating the stabilization of T3 site as the size of AM is increased. Another difference among them can be observed for the topography around the HH site, which is also sensitive to the AM size. For the Li case, the HH position is a global minimum, and with increasing the AM size, the HH site is located in the bottom of a flat basin, and finally for the Cs adsorption, the basin becomes a narrow valley between two adjacent dimer rows. Therefore, it can be concluded that the small AM atoms, namely, Li and Na atoms, prefer the HH and T4 sites, while other AM atoms with large size favor the T3 site.

![Fig. 3. Contour plots of the potential energy surface for the adsorption of different AM adsorbates.](image)

(a) Li, (b) Na, (c) K, (d) Rb, and (e) Cs on Si(001)-2×2 surface. The energy range shown in figures is from –2.35 eV (dark region) to –1.25 eV (bright region)

We turn next to the motions of AM atom on the Si(001) surface. Since the AM atom is difficult to come across the Si–Si dimers, here, we focus on two possible diffusion paths. One is along the HH–B2–T3 sites and another is along the T3–T4 sites. As shown in Fig. 3a, for Li, the first path is exactly along the dimer row direction ([110] direction, see Fig. 1), and the second one is perpendicular to the dimer row ([110] direction). However, obvious divergences from the [110] and [110] directions are observed for the cases of AM atoms with large size. Actually, careful examining the coordinates of each site shows that, the T4 and B2 sites tend to depart from the atop positions of the fourth- and second-layer Si atoms, respectively, as increasing the size of AM atom. These displacements of the T4 and B2 sites lead to obvious distortions of the diffusion paths for K, Rb and Cs adatoms (See Fig. 3c–3e).
To obtain more accurate descriptions of the diffusion behavior, we define two energy barriers, \( E_b^1 \) and \( E_b^2 \), corresponding to the above two paths, and the results are listed in Table 2. For all AM atoms, we find that the difference \( \Delta E_b = E_b^1 - E_b^2 \) is always positive. This indicates that the AM atoms will have more changes to migrate along the T3–T4 path at low temperature. Furthermore, it is noted that the energy barriers along two directions for Na are small (not exceeding 0.15 eV), which means the easier Na diffusion on the Si(001) surface with respect to other AM atoms. To estimate the attempts that AM atom will move along the T3–T4 path versus migration along the HH–B2–T3 path, the ratio \( \gamma \) of movements along two paths is calculated by the expression of \( \gamma = \exp(\Delta E_b / kT) \). As shown from Table II, the values of \( \gamma \) at room temperature are small for the Li and Na atoms, suggesting that the motion along the T3–T4 path is not predominant. On the other hand, the motion of those large AM atoms will be more strongly restricted to the path along the T3–T4 sites at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_b^1 ) (eV)</td>
<td>0.25</td>
<td>0.15</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>( E_b^2 ) (eV)</td>
<td>0.14</td>
<td>0.05</td>
<td>0.10</td>
<td>0.11</td>
<td>0.10</td>
</tr>
<tr>
<td>( \Delta E_b ) (eV)</td>
<td>0.11</td>
<td>0.10</td>
<td>0.17</td>
<td>0.16</td>
<td>0.17</td>
</tr>
<tr>
<td>( \gamma ) (T = 300 K)</td>
<td>70</td>
<td>48</td>
<td>718</td>
<td>488</td>
<td>718</td>
</tr>
</tbody>
</table>

3.3 Electronic structures of the AM/Si(001) systems

The band structures of the clean Si(001)-2 \( \times \) 2 surface and some adsorption systems along the \( \Gamma \rightarrow J \rightarrow K \rightarrow J' \rightarrow \Gamma \rightarrow K \) directions in the surface Brillouin zone are shown in Fig. 4. For the clean Si(001) surface (Fig. 4a), it is well-known that the occupied energy bands just below the Fermi level and the empty bands appearing in the band gap of bulk Si are corresponding to the \( \pi \) and \( \pi^* \) surface states, respectively. Further analyses for the components of these energy bands show that they are mainly originated from the \( 3p_z \) orbital of Si–Si dimers. As shown in Fig. 5a, the contributions of two Si atoms in the same dimer are different, and for the occupied \( \pi \) states, the component of higher-lying Si atom is dominant while the lower-lying Si atom has large contribution for the empty \( \pi^* \) states. This different distribution of the charge is due to the tilted arrangement of two Si atoms in the dimer, and as a result, the Si–Si dimer possesses a zwitterionic character, namely, the upper atom is nucleophilic and the lower Si atom is electrophilic.\(^{[36, 37]}\) This difference also implies that the lower Si of dimer will carry more electrons after the AM addition (see section 3.4). In addition, because two Si–Si dimers exist in the unit cell, there are two energy bands associated with the \( \pi \) (or \( \pi^* \)) surface states, and they are degenerated in the region of \( K \rightarrow J' \). In the followings, we will see that the adsorption of AM atom results in the redistribution of the above \( \pi/\pi^* \) surface states, which depends on the position of AM atom.

We first focus on the band structures of Li-adsorbed Si(001) systems. In six adsorption models, except HH and T3 structures, the spin-polarized solution is preferred when the Li atom is adsorbed on other sites, and the corresponding magnetic moments of these systems are close to 0.33 \( \mu_B \). The energy bands associated with \( 3p_z \) state of Si–Si dimers as well as the Li 2s state are denoted in Fig. 4 by circles and crosses, respectively. For the HH and T3 models, their band structures are similar, and the arrangements of \( \pi/\pi^* \) surface states in two configurations are nearly identical to the case of clean surface. As an example, for the most stable HH structure, the distributions of partial charge density for \( \pi \) and \( \pi^* \) surface states in the range of \( K \rightarrow J' \) region (Fig. 5b) are nearly unperturbed by the adsorption of Li with respect to the clean surface.
Therefore, the adsorptions of Li atom at HH and T3 positions have weak effects on the surface states. However, it is noted that, compared with the clean surface, the Fermi level is shifted upwards, and as a result the π* states in HH and T3 structures are partly occupied, indicating some electrons transfer from the Li atom to the substrate and the metallization of silicon substrate by Li adsorption is observed. For other sites, the Li adsorptions introduce obvious changes of surface states for both energy positions and compositions, especially for the π* states. First of all, the distributions of two π* states differ significantly and one π* energy band (spin-up) becomes fully occupied, implying that the π* state is more sensitive to the Li addition than the π surface state. Secondly, the mixing of Li 2s states with substrate π* states are observed for some adsorption systems, implying obvious interactions between Li and the Si(001) surface. One typical example is the TD model, which has the shortest AM–Si distance. In this structure, certain components of Li 2s are found for the π state derived from the Si–Si dimer just under the Li atom (Fig. 4b). As presented in Fig. 5c, the direction and topology of this π surface state demonstrate the σ-bonding interactions between Li and upper Si atom of the dimer, and consequently, the position of this π band shifts towards higher binding energy. On the other hand, there are also some Li 2s states found in the highest π* surface state. Interestingly, in the TD configuration, besides four energy bands derived from the surface states, there is an additional energy band in the gap of bulk and is located just above the highest π* band. From Fig. 5(d), this energy band is dominated by the Li atom, corresponding to the metal induced gap states (MIGS). The appearance of MIGS can be seen as a character of the TD structure, which is not found in other configurations.

For the adsorptions of other AM atoms, they exhibit very similar band structures for the same adsorption pattern and like Li, at this coverage the substrate metallization induced by AM adsorption is also observed for all systems. However, since the interactions between adatom and substrate vary with the type of AM atom, there are some differences among the band structures. Herein, we select the TD model to probe the interactions between different AM atoms and Si(001) surface. Fig. 4h and 4i present the band structures of the TD configuration for Na and K-adsorbed surfaces. For the case of Na, similar to the Li adsorption, the shift of the π state originating from dimer just below the Na atom is also remarkable, indicating the obvious interactions between Na and substrate. However, the contributions of Na state for this π state are small with respect to the Li case, and no significant component of Na atom is observed (See Fig. 4h), indicating that the Na–Si interaction is weaker than Li–Si. As the size of AM is increased, for the K adsorption, the distributions of two π surface states are similar to those of the clean surface (one indication is that two π surface states are still nearly degenerated in the region of K → J). Therefore, when the size of AM is larger than Na, the AM–Si bond is predominantly ionic. Actually, our calculated results show that except Li and Na, nearly identical arrangements of two π surface states are achieved for the adsorption of other AM atoms with large size at different surface positions.

Now let us discuss the distributions of spin density of the AM-adsorbed Si(001) surface at 0.25 ML coverage. As mentioned above, except HH and T3 structures, the spin-polarized state is favorable when AM atom is adsorbed at other sites. Since π* surface states are partly occupied after AM adsorption, and according to Fig. 5a, the π* state is mainly localized on the lower Si atom of the dimer, we can expect that the spin density may be also located on this lower Si atom. This conclusion is consistent with the pictures shown in Fig. 6. However, it is noted that there are two Si–Si dimers on the 2×2 unit cell. The final distributions of spin density on the low-lying Si atom depend on the site of AM adsorbate. As an example, when the Li atom is adsorbed at the TD (or HB) site, the spin density is
located on the lower Si atom of the dimer just below adatom (See Fig. 6a), while for the T4 (or B2) adsorption model, the lower Si atom close to the Li atom is preferred (See Fig. 6b). Moreover, for the TD site, the distributions of spin density also differ with the kind of AM atom. With respect to the Li adsorption that spin charges are distributed on the lower Si of the dimer just underneath of Li, for other AM atoms, the spin density is found on the lower Si atom of another dimer. Additionally, part of spin density still keeps on the AM atom (See Fig. 6c). Therefore, this different distribution of spin density also implies the distinct feature for the Li–Si interactions.

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**Fig. 4.** Band structures for (a) the clean Si(001)-2 × 2 surface, and the systems for the Li atom adsorbed at the (b) TD, (c) HB, (d) B2, (e) HH, (f) T3, and (g) T4 sites, respectively. The band structures for (h) Na and (i) K atom adsorbed at TD position are also shown for comparisons. Except HH and T3 models, the spin-polarized solution is preferred for other models and only the band structures associated with spin-up states are presented. In the pictures, the energy bands that contain obvious components of Si 3p\(_z\) states of the dimer, and valence s states of AM atom are labeled by circles and crosses, respectively. The Fermi level is taken as energy zero.
3.4 Charge transfers and work functions of the AM/Si(001) systems

The charge transfer (CT) between AM and Si(001) surface at different surface sites have been calculated by means of the Bader analysis\[^{38}\], and the final results are presented in Fig. 7. In the figures, the darker the region is, the more electrons transfer from AM to the Si(001) substrate. Examining the topology of CT pictures shows that the common feature lies in the brightest regions in Fig. 7 found at
the TD sites for all AM/Si(001) systems, indicating
the smallest CT around the TD positions. Overall for
the adsorptions of Li and Na atoms, they show
distinct patterns for the CT distribution, while a
similar arrangement of CT is observed for the K, Rb
and Cs adsorptions. This result is also consistent
with the above classification of this series AM atoms
based on the adsorption configurations.

![Contour plots](image)

**Fig. 7.** Contour plots of the charge transfer from AM atom to the Si(001) surface of
different AM adsorbates. (a) Li, (b) Na, (c) K, (d) Rb, and (e) Cs at different surface sites

Compared the CT of different adsorbates, the CT
magnitudes of Li adsorption at different surface sites
are close to the value of 0.8 e. However, for other
AM atoms, the distributions of CT are sensitive to
the adsorption sites, and the variation of CT is larger
than 0.2 e. Moreover, for the adsorption of Na, the
darkest region is located around the T3 site. For
other AM atoms, the largest CT is observed at the
top site above the lower Si atom of dimer. This may
be due to the fact that, the $\pi^*$ band of substrate
becomes partly occupied after the AM adsorption,
and as mentioned above, the $\pi^*$ surface state is
mainly originated from the compositions of the
lower dimer Si atom, so obvious CT can be expected
for this Si atom.

The variations of the work function (WF) after the
AM adsorption at different surface positions are also
determined with respect to the clean Si(001) surface,
and the results are displayed in Fig. 8. In the figures,
the darker regions mean the more decrease of WF.
For the clean surface, the predicted WF (4.88 eV)
agrees well with the experimental value (4.8 eV)\cite{39}.
Since the charges transfer from the AM atom to the
substrate, the raise of the Fermi level leads to the
drop of WF. Hence, if the change of WF is only
relative to CT, Figs. 7 and 8 must exhibit similar
arrangement of the bright or dark regions. However,
the general opposite relationship between the
variations of CT and WF is observed. For instance,
in the case of Li adsorption, the darkest region in Fig.
8a is around the TD site, implying the most
significant decrease of WF in this region. On the
other hand, the CT of this region is small and corresponding to the brightest spot in Fig. 7a. Therefore, it seems that the change of WF for the AM-adsorbed Si(001) surface can not be well explained only by considering the effect of CT.

Actually, according to the definition of WF, the value of WF ($\Phi$) is expressed as\textsuperscript{[40]},

$$\Phi = 4\pi D - E_F$$

where $D$ and $E_F$ are the dipole moments per surface area and the Fermi level, respectively. So, the change of WF is obtained as

$$\Delta \Phi = 4\pi \Delta D - \Delta E_F$$

where the first and second terms represent the changes of surface dipole moment per surface area and the Fermi level, respectively. Therefore, in addition to CT, the effect of surface dipole moment must be included to explain the variation of WF.

Table 3 lists the change of dipole moment per surface area along the surface normal direction ($\Delta D$) when the AM atom is adsorbed at different sites. Except the T4 site of Li adsorption, negative values of $\Delta D$ are obtained, indicating the decrease of $D$. It can be seen clearly that the depolarization effect induced by ionized AM atom depends strongly on the size and the height of AM atom. Overall, for the same adsorption site, the depolarization effect becomes more significant with increasing the AM size. As an example, for the T3 site, the magnitude of $\Delta D$ increases gradually from $0.3 \times 10^{-3}$ e/Å of Li to $10.5 \times 10^{-3}$ e/Å of Cs adsorption. In addition, $D$ also decreases more obviously when AM is adsorbed on the site with large height. So for the adsorption of the same AM atom, the large magnitudes of $\Delta D$ are found for the TD and HB sites.

On the contrary, relatively smaller changes of $D$ are observed for the T3 and T4 sites, in which the AM atoms are located at the positions with low height. Therefore, the obvious decrease of WF can be expected for the regions around TD or HB sites, while relatively smaller changes of WF occur at the regions around T3 or T4 positions. This distribution for WF change is consistent with the pictures in Fig. 8, thus the WF change is dominated by the change of surface dipole moment.

Fig. 8. Contour plots of the change of work function with respect to the clean Si(001) surface of different AM adsorbates. (a) Li, (b) Na, (c) K, (d)Rb, and (e) Cs at different surface sites
4 CONCLUSION

First-principles calculations based on DFT method have been performed on Li, Na, K, Rb and Cs adsorbed on the Si(001)-2x2 surface at 0.25 ML coverage. Our calculated results indicate that the smallest Li adatom prefers to be adsorbed at HH position and the adsorption at the T3 site is most unfavorable among four high symmetry sites; for the case of Na atom, except the B2 site, the other three high symmetry sites, namely the HH, T3 and T4 sites, are almost energetically identical; for other AM atoms with large size, the adsorptions of these AM atoms favor the T3 site of Si(001) surface. Besides the adsorption site, the strength of interaction between AM and silicon substrate is also size dependent, implying that the nature of AM–Si bond may be different. Comparing the calculated adsorption energy, the strongest interaction between AM and substrate is found for the Li adatom, and on the contrary, the adsorption of Na atom represents the case of the weakest interaction. After the adsorption of AM atom, there are obvious charge transfers between AM and substrate, and the Si(001) surface appears metallic character because the energy bands derived from surface π* state are partly occupied. In addition, the adsorption of AM also results in the decrease of surface work function, and this change of work function is mainly relative to the depolarization effect introduced by the ionized AM atom.

In summary, the present work shows that the systematic differences appeared in the site preferences, diffusions on the surface, and the electronic structures (including the band structure, distribution of the spin density, and the charge transfer between AM and substrate) can be attributed to the sizes of AM atoms. It is likely that this series of alkali metal atoms can be divided into three classes. For Li and Na, they exhibit unique adsorption behaviors on Si(001) surface, while the similarity is observed for other AM atoms with larger size. Although this conclusion is obtained at 0.25 ML coverage of AM atom, the above classification may be applicable to other cases with larger AM coverages.

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