Atomic and electronic structure of the Si(001)2 × 1–Li chemisorption system at 1.0 monolayer coverage

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Abstract

Ab initio plane-wave pseudopotential density functional theory (DFT) calculations have been performed to determine the atomic and electronic structure of the Si(001)2 × 1–Li adsorption system at 1.0 monolayer (ML) coverage. Chemisorption of the lithium atoms is found to result in a minimum energy configuration characterized by symmetric Si dimers in agreement with the results of high-resolution core-level photoelectron spectroscopy. The transition from the asymmetric Si dimers of the clean Si(001) surface to the symmetric dimers of the Li chemisorbed surface is due to charge transfer from the Li adatoms to the substrate. The dispersion of the occupied electronic surface state bands is found to be in good agreement with the angle-resolved photoemission data. The nature of the lowest energy unoccupied surface state band suggests that silicide formation may occur at coverages greater than 1.0 ML.

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1. Introduction

Systems involving the interaction of alkali metals (AM) with silicon surfaces have attracted a great deal of attention in semiconductor surface science due to both their fundamental interest and possible technological applications [1–3]. Of all of the alkali metals, potassium and sodium on the Si(001) surface have been the most widely studied [4–12]. Lithium, the lightest of the alkali metals, has attracted much less interest, and while some experimental work devoted to studying the adsorption of lithium on the Si(001) surface has been reported in the literature [13–23], very few theoretical calculations have been carried out for this system [10,24–27]. This is perhaps somewhat surprising as lithium, with an atomic number of 3, has a very simple electronic structure, and Si(001) is the most widely studied and best...
characterized of all semiconductor surfaces. The Si(001)–Li system could thus be regarded as the ideal model system for studying the basic properties of the interaction of AM’s with semiconducting substrates.

Several questions concerning the basic properties of the Si(001)–Li chemisorption system remain unanswered. These include the actual chemisorption sites of the lithium atoms, the nature of the Li–Si bonds, whether the Li atoms penetrate deeply into the Si subsurface and, finally, whether the interaction of the Li and Si atoms results in the formation of a surface silicide or a metallic Li overlayer. Johansson et al. [18] and Grekh et al. [19] investigated the Si(001)–Li system for low (<1.0 ML) and high (>1.0 ML) Li coverage using high-resolution core-level photoelectron spectroscopy. They showed that the Si surface reconstruction changed from asymmetric to symmetric dimers for a Li coverage of 1.0 ML, and that beyond this coverage the Li atoms reacted with the substrate indicating the possibility of silicide formation. This data was supported by Auger electron spectroscopy (AES) and electron energy loss spectroscopy (EELS) experiments carried out by Tochihara and Murata [13] which indicated intermixing of the Li and Si at coverages greater than 1 ML, and the absence of metallic overlayers. Kleine et al. [16], however, on the basis of similar experiments, argued against the creation of silicides and suggested that Li multilayers were formed. Results obtained from the metastable deexcitation spectroscopy (MDS) and thermal desorption spectroscopy (TDS) experiments of Hongo et al. [23] supported silicide formation and suggested that intermixing of the Li adatoms with the substrate starts at coverages of about 1.0 ML. The comparative ARUPS and IPES studies of the chemisorption of K, Na and Li on the Si(001) surface carried out by Johansson and Reihl [14] demonstrated that Li adsorption is very different to that of K and Na in that the 2 × 1 reconstruction is destroyed for high Li coverage. Tochihara and Murata [13] also studied the lithium overlayer on the Si(001) surface using low energy electron diffraction (LEED). They found that, in contrast to the behaviour for the other alkali metals, the LEED pattern for Li changed from 2 × 1 to 1 × 1 with increasing coverage in the monolayer range.

The electronic structure of the Si(001)–Li system was experimentally investigated by Kim et al. [22] using synchrotron UV radiation. The observed variations in the behaviour of the occupied surface state bands along the Γ–J and Γ–J’ directions of the surface Brillouin zone (SBZ), compared to those of the clean Si(001)2 × 1 surface, were interpreted by these authors as arising from strong interactions between the Li and Si surface atoms. This behaviour, as well as that of the surface Si2p core level shifts, was considered to indicate the presence of asymmetric Si dimers on the Li chemisorbed Si(001)2 × 1 surface. The ARUPS data of Johansson and Reihl [14] for the Γ-point of the SBZ showed that the strong photoemission peak corresponding to the Si dangling bonds of the clean Si(001)2 × 1 surface split into two peaks with increasing Li chemisorption. The splitting of these peaks at 1.0 ML coverage was around 0.3 eV. A Li-induced unoccupied surface state also appeared in the IPES spectra that moved downward in energy with increasing coverage. The energy of this empty state at 1.0 ML coverage, relative to the Fermi energy, was 2.0 eV, giving a surface band gap of 3.1 eV. This unoccupied state was also observed for Na and K chemisorption on the Si(001) surface, but at different energies. This was attributed by Johansson and Reihl as being due to the varying sizes of the alkali metal atoms [14].

Theoretical calculations carried out by Kobayashi et al. [24] for monolayer coverage (two Li atoms per Si(001)2 × 1 surface unit cell (SUC)) found two almost degenerate configurations with a very small energy difference of 2.5 meV per 2 × 1 SUC. In their most energetically stable structure, the Li adatoms occupied asymmetric positions 0.36 Å from the pedestal site A along the A–C direction in Fig. 1, and 1.00 Å from the valley bridge site C along the C–D direction in Fig. 1. Theoretical calculations carried out by Morikawa et al. [10] predicted that the most energetically favourable structure for 1.0 ML coverage would result from the two Li atoms sitting essentially at the pedestal (A) and valley bridge (C) sites. This structure was virtually identical to the so-called
double layer (DL) model that had been proposed by Abukawa and Kono [6] for the atomic structure of the Si(001)\(2 \times 1\)-K adsorption system at 1.0 ML coverage. Later calculations performed by Ko et al. [26] predicted that chemisorption of the Li atoms at the pedestal and cave sites (sites A and D in Fig. 1) resulted in the most energetically stable configuration at 1.0 ML coverage. This structure, however, was found to be just 0.01 eV lower in energy than the DL model [26]. No explanation has been given for these discrepancies between the different theoretical studies. Moreover, while the electronic structure of the Li/Si(001) chemisorption system at 1.0 ML coverage has been calculated by Ko et al. [26], no attempt has been made to analyse the nature of the electronic surface states of the Si(001)\(2 \times 1\)-Li system and compare the results with the available experimental data.

In a previous paper we have performed detailed calculations of the atomic and electronic structure of the Si(001)\(2 \times 2\)–Li chemisorption system at 0.5 ML coverage [27]. The goal of this paper is to carry out analogous calculations for the Si(001)\(2 \times 1\)–Li system at 1.0 ML coverage, and to compare the results of these calculations with the currently available experimental data and theoretical calculations. The predicted minimum energy Li adatom configuration is found to be similar to the second lowest energy structure obtained by Kobayashi et al. [24], and marginally lower in energy than the structures found by Morikawa et al. [10] and Ko et al. [26]. It is also shown that the Li adatoms in this minimum energy configuration transfer their charge to the silicon dimer atoms. This results in both the formation of symmetric Si dimers on the Si(001)\(2 \times 1\)-Li surface at 1.0 ML coverage, and the surface remaining semiconducting. The calculated electronic structure for the Li/Si(001) chemisorption system is found to closely follow the electronic structure of the clean reconstructed Si(001) surface and is very sensitive to the geometry of the substrate. The character of the low lying unoccupied electronic surface states is shown to support the formation of silicides, rather than metallic overlayers, at coverages of greater than 1 ML.

2. Method and procedure

Our calculations have been carried out using the ab initio total-energy and molecular dynamics program VASP (Vienna ab-initio simulation package) [28–30]. This code is based on the density functional theory (DFT) pseudopotential plane wave method. It is well known that core-valence overlap can produce significant changes in the cohesive
properties of alkali metals due to their shallow core states and low density of valence electrons. To overcome this problem, we have used PAW potentials [31] for all of the component atoms within our periodic slab unit cell. The exchange and correlation contributions to these potentials have been described by the Ceperly–Alder formulation of the Local–Density approximation. For the Li atoms the 1s state was treated as a valence state. The Kohn–Sham equations were solved using plane waves with kinetic energies up to ~20 Rydbergs and 4 special k points in the irreducible symmetry element of the SBZ of the Si(001)2×1 SUC. The 2×1 periodic cell consisted of 6 layers of silicon plus 4 hydrogen atoms to saturate the dangling bonds of the bottom layer silicon atoms, and a vacuum region of ~8 Å. All of the coordinates of the silicon atoms in the top four layers of the slab, plus those of the chemisorbed lithium atoms, were allowed to vary, and the lowest energy structure was found by minimizing the forces using the Hellmann–Feynman theorem. To verify the accuracy of our obtained results convergence tests were also carried out for the three lowest energy structures using respectively 8 layers with 6 allowed to vary, 16 special k-points, a vacuum of 12 Å, and an energy cut-off of 25 Rydbergs.

To identify the electronic surface states we calculated the function \( \rho_{nk}(z) \) defined by

\[
\rho_{nk}(z) = \int_{\text{SUC}} |\Psi_{nk}(x,y,z)|^2 \, dx \, dy,
\]

where \( x \) and \( y \) lie in the surface plane, \( z \) is out of the surface, and the integration is performed over the SUC. In order to unambiguously determine the nature of the individual surface state bands, three-dimensional (3D) charge/probability density distributions were also calculated for all of the identified electronic surface states. To simplify the resulting pictures, these latter calculations were carried out using the ultrasoft (US) pseudopotentials contained in the VASP code [28–30]. States were identified as surface states if the \( \rho_{nk}(z) \) function showed clear exponential decay into the bulk and the corresponding 3D density plots evidenced large surface contributions with negligible contributions from the bulk layers.

3. Results

3.1. Atomic structure

To determine the minimum energy structure for the Si(001)2×1–Li chemisorption system at 1.0 ML coverage many different configurations for the two lithium atoms in each SUC were considered. The three lowest energy structures were all found to correspond to one of the Li atoms occupying the pedestal (A) site while the second Li atom was positioned along the valley midway between the dimer rows (i.e. along the line D–C–C′–D in Fig. 1). For the lowest energy configuration the second lithium atom was predicted to lie at the C′ site which is displaced along the positive \( y \) axis from the C site by 0.82 Å. This structure is quite similar to the second lowest energy configuration found by Kobayashi et al. [24]. Our calculations, however, predict that the lithium atom at the A site sits somewhat higher than predicted by Kobayashi et al. and the Si–Li bond lengths are approximately 3.5% longer. The second lowest energy structure determined by our calculations was the double layer (DL) model in which the two lithium atoms are positioned at the A and C sites. This was the minimum energy structure determined by Morikawa et al. [10]. Our third lowest energy structure corresponds to chemisorption of the lithium atoms at the pedestal (A) and cave (D) sites, and is the model predicted by Ko et al. [26]. We find these two latter models to be 0.013 eV and 0.024 eV per 2×1 SUC higher in energy than our minimum energy A–C′ configuration. To test the reliability of these predicted energy differences additional calculations were performed using increased values for the number of layers, size of vacuum, energy cut-off and number of k-points in the irreducible symmetry element of the SBZ. The results of these calculations are presented in Table 1. It is clear that increasing the various calculational parameters produces little change in the relative stability of these structures. The predicted topologies for these three structures were also found to be accurately reproduced by our original parameter set.

Values for some of the important parameters of our three lowest energy structures for the
Si(001)2×1–Li chemisorption system at 1.0 ML coverage are given in Table 2. The most significant feature of our minimum energy structure is that the Si dimers are predicted to be symmetric. This is in agreement with the experimental results of Johansson et al. [18] and Grekh et al. [19] but disagrees with Kim et al. [22] who claim that line shape analysis of their measured Si2p core level shifts as a function of coverage indicates asymmetric dimers for the Si(001)2×1–Li chemisorption system at monolayer coverage. Reconstruction of the substrate from asymmetric dimers (for the clean Si(001) surface) to symmetric dimers (for the Li chemisorbed Si(001)2×1 surface at 1.0 ML coverage) was also predicted by Morikawa et al. [10] and Ko et al. [26] for their minimum energy A–C and A–D site Li adatom configurations. The bond length of the symmetric Si dimers for our minimum energy configuration was found to be 2.63 Å, which is considerably larger than the Si dimer bondlength for the clean Si(001) surface of 2.26 Å [32]. This observed behaviour of the Si–Si dimers is due to the transfer of charge from the Li adatoms to the down Si dimer atoms. This charge transfer compensates for the charge deficiency of these atoms and leads to the formation of symmetric dimers with expanded bondlength [26]. Similar behaviour was observed for the Si(001)–Li chemisorption system at 0.5 ML coverage [27]. In this case, all of the charge of the Li adatoms was transferred to just one of the Si–Si dimers in the 2×2 SUC. The resulting topology was thus characterized by alternating symmetric and asymmetric Si–Si dimers along each dimer row. The bondlength of the symmetric dimer (~2.5 Å) was again substantially longer than the clean surface value. Two essentially degenerate minimum energy Li adatom configurations were found for the Si(001)2×2–Li chemisorption system at 0.5 ML coverage. In both of these structures one of the Li atoms is chemisorbed in the vicinity of the pedestal (A) site while the other is chemisorbed near a cave (D) site [27]. This is similar to our minimum energy structure for 1.0 ML coverage except for the observed preference of one of the Li adatoms to chemisorb near the valley bridge (C) site rather than the cave (D) site.

Table 1
Total energies of the three lowest energy structures of the Si(001)2×1–Li chemisorption system at monolayer coverage relative to that of the minimum energy AC0 structure

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Reference</th>
<th>Vacuum</th>
<th>Layers</th>
<th>Cut-off</th>
<th>K points</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>AC</td>
<td>0.013</td>
<td>0.013</td>
<td>0.013</td>
<td>0.014</td>
<td>0.015</td>
</tr>
<tr>
<td>AD</td>
<td>0.024</td>
<td>0.023</td>
<td>0.025</td>
<td>0.025</td>
<td>0.021</td>
</tr>
</tbody>
</table>

The different columns correspond to: Reference—employing the default set of calculational parameters (6 layers varying 4, 4 k-point sampling, 8 Å vacuum, and 20 Rydberg energy cut-off); Vacuum—increasing the vacuum to 12 Å; Layers—using 8 layers varying 6; Cut-off—increasing the cut-off to 25 Rydbergs; K points—employing 16 k-point sampling.

Table 2
Important parameters of the optimised geometry (in Å) of the Si(001)2×1–Li chemisorption system at 1.0 ML coverage compared with the theoretical calculations of Morikawa et al. [10], Kobayashi et al. [24] and Ko et al. [26]

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>zLi1</td>
<td>6.76</td>
<td>6.76</td>
<td>6.51</td>
<td></td>
</tr>
<tr>
<td>zLi2</td>
<td>5.99</td>
<td>5.89</td>
<td>5.85</td>
<td></td>
</tr>
<tr>
<td>zSi(1a)</td>
<td>5.52</td>
<td>5.45</td>
<td>5.42</td>
<td></td>
</tr>
<tr>
<td>zSi(1b)</td>
<td>5.52</td>
<td>5.45</td>
<td>5.41</td>
<td></td>
</tr>
<tr>
<td>Δx Li1</td>
<td>0.02</td>
<td>0.00</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>Δy Li1</td>
<td>0.00</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Δx Li2</td>
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<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Δy Li2</td>
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<td>0.82</td>
<td>1.12</td>
<td>1.82</td>
</tr>
<tr>
<td>dSi(1a)-Si(1b)</td>
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<td>2.57</td>
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<td>2.57</td>
<td>2.62</td>
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<tr>
<td>dSi(1b)-Li1</td>
<td>2.66</td>
<td>2.66</td>
<td>2.56</td>
<td>2.62</td>
</tr>
<tr>
<td>dSi(1a)-Li2</td>
<td>3.13</td>
<td>2.76</td>
<td>2.67</td>
<td>2.66</td>
</tr>
<tr>
<td>dSi(1b)-Li2</td>
<td>3.12</td>
<td>2.77</td>
<td>2.65</td>
<td>2.66</td>
</tr>
</tbody>
</table>

Z is the vertical distance relative to the fifth layer, Δ is the displacement relative to the A and C sites of the ideal bulk terminated surface, and d denotes the various bond lengths. The labeling of the silicon atoms is the same as in Fig. 1. Li1 denotes the lithium atom at the A site (Li(A)), while Li2 indicates the lithium at the C, C', C'' or D site for the four configurations.
3.2. Electronic structure

Electronic structure calculations have been carried out for our minimum energy Si(001)2×1–Li A–C’ structure at 1.0 ML coverage. The energy bands obtained from calculating the eigenvalues in the vicinity of the energy gap for 120 k-points along the Γ–J–K–J’–Γ symmetry directions of the SBZ are plotted in Fig. 2. The electronic structure is seen to be semiconducting in agreement with the ARUPS and IPES data of Johansson et al. [18]. In order to identify the electronic surface states, the function \( \rho_{\text{xy}}(z) \) has been calculated at 30 k-points along Γ–J–K–J’–Γ for all of the bands within several electron volts of the Fermi energy. The identified surface states are indicated in Fig. 2a by the empty circles. The photoemission data obtained by Kim et al. [22] for the Si(001)2×1–Li system is also shown in Fig. 2a, with the filled circles and triangles indicating strong and weak peaks in the angle-resolved photoemission spectra, respectively. The experimental data has been shifted up by approximately 0.18 eV to match the theoretically predicted values. This shift is required because of the neglect of self-energy effects in the standard DFT theory and the difficulty in accurately determining the Fermi energy experimentally.

As can be seen from the data presented in Fig. 2a, there is good overall agreement between the theoretical results (empty circles) and the experimental data of Kim et al. [22] (filled symbols). This is especially true along the Γ–J’ symmetry direction of the SBZ where both theory and experiment predict two separate surface state bands close to the Fermi energy. The splitting of these bands at the J’ point is predicted by our calculations to be 0.40 eV in good agreement with the value of \( \sim 0.52 \) eV determined from the ARUPS photoemission data of Kim et al. [22]. The predicted splitting of these occupied surface state bands at the Γ point of the SBZ of 0.41 eV is in excellent agreement with the value of 0.42 eV derived from the ARUPS data of Kim et al. [22]. In addition to these two occupied surface state bands lying close to the Fermi energy, our calculations find lower-lying surface states with a strong downward dispersion along the Γ–J’ symmetry direction in agreement with the photoemission results.

Along the Γ–J direction of the SBZ our calculations reveal the presence of three well-defined occupied surface states close to the Fermi energy. The ARUPS experiments of Kim et al. [22], however, have evidenced only two such surface state bands (filled circles in Fig. 2a). The photoemission data of Kim et al. [22] also indicated the occurrence of a weak lower-lying occupied surface state band along the Γ–J direction of the SBZ (filled triangles in Fig. 2a). While our theoretical calculations determine a band in this energy region, the
corresponding states are not localized in the vicinity of the surface. Our theoretical calculations do, however, predict the occurrence of a surface state band lying about 0.5 eV lower in energy in the vicinity of the Γ point and extending along the J–K symmetry direction of the SBZ. Well-defined electronic surface states have also been predicted to occur along the J–K–J′ symmetry directions of the SBZ. Unfortunately, there is no experimental data for Li for these symmetry directions. The dispersion of these bands is, however, very similar to that of the surface states of the Si(001)2×1–K chemisorption system at 1.0 ML coverage obtained by Abukawa et al. [8] using synchrotron radiation angle resolved photoelectron spectroscopy (SR-ARPES).

The electronic structure of the Si(001)2×1–Li chemisorption system at 1.0 ML coverage was also calculated by Ko et al. [26] using their A–D site minimum energy structure. The predicted topology and dispersion of the two highest energy occupied surface states (denoted by S and S* in [26]) are very similar to those derived from our A–C adatom configuration. The results in [26] show, however, a clear splitting of up to 0.40 eV between the S and S* surface state bands along the J–K–J′ symmetry directions of the SBZ. The splitting predicted by our calculations along the J–K symmetry direction is significantly less (see Fig. 2a). Experimental studies of the surface states along the J–K–J′ symmetry directions of the SBZ are needed to discriminate between these two theoretical predictions.

3.3. Nature of the surface states

The nature of all of the electronic surface state bands in the vicinity of the Fermi energy has been determined by calculating the corresponding 3D charge/probability density plots. Altogether, we have identified six different occupied surface state bands, and three unoccupied surface state bands. These are indicated by the different symbols in Fig. 2b. The first important observation is that all of the occupied electronic surface states of the Si(001)2×1–Li surface at 1.0 ML coverage look like the surface states of the clean Si(001)2×1 reconstructed surface with symmetric Si dimers. Three dimensional charge density plots, along with the corresponding $\rho_{nk}(z)$, for the occupied surface state bands denoted in Fig. 2b by the empty triangles, crosses and plus signs are shown in Figs. 3a–c, respectively. These charge density plots correspond to the surface states at the J and J′ symmetry points of the SBZ, and a wave vector between the J′ and Γ symmetry points, respectively. It is obvious that these occupied surface state bands represent a combination of the first and third (Fig. 3a), second (Fig. 3b), and third (Fig. 3c) silicon back bond surface states, respectively.

3D charge density plots for the surface state band denoted by the empty squares in Fig. 2b at the K point of the SBZ are presented in Fig. 4a. Also plotted in this figure is the corresponding $\rho_{nk}(z)$. These plots show a clear contribution from the occupied dangling bond orbitals and can be regarded as π orbitals formed on the symmetric Si dimer. 3D charge density plots for the electronic surface state band represented by the empty diamonds in Fig. 2b at the J point of the SBZ are presented in Fig. 5a. This surface state band corresponds to the Si dimer σ bonds. The corresponding antibonding π* (asterisks) and σ* (empty circles) orbitals are shown in Fig. 4b and Fig. 5b, respectively. These plots correspond to the surface states at the J and K points of the SBZ. It should be noted that the density plots in Fig. 5b include contributions from both the σ* antibonding orbitals and the lithium adatom orbitals.

The remaining two unoccupied surface state bands that we have determined from our VASP first-principles calculations are denoted by the inverted triangles and the arrowheads in Fig. 2b. Three-dimensional probability density plots for these unoccupied surface state bands are presented in Fig. 6a (inverted triangles) and Fig. 6b (arrowheads). Fig. 6a corresponds to a wave vector at the K point of the SBZ, while Fig. 6b is for a wave vector lying between the J and K points. Also plotted in these figures are the corresponding $\rho_{nk}(z)$ functions. The first of these unoccupied surface states (inverted triangles in Fig. 2b) has a contribution from the lithium that is almost entirely from the upper lithium adatom along the Γ–J–K symmetry directions of the SBZ, with this contribution
being mainly of $s$ character. Along the $K'-\Gamma'$ symmetry directions, however, both lithium atoms contribute more or less equally. For the unoccupied surface states indicated by the arrowheads in Fig. 2b, it is again mainly the upper lithium adatoms that contribute, but now this contribution is mostly of $p$ character (see Fig. 6b).

4. Discussion

Of particular interest in our results is the change in the dispersion and occupation of the electronic surface states following the chemisorption of the Li adatoms, and the observed differences between these results and those reported by Ko et al. [26]. Two significantly different Li-induced features are the observed reduction in the magnitude of the $\pi-\pi^*$ surface state energy band gap from $\sim 0.7$ eV for the clean buckled dimer Si(001)2×1 surface [33] to zero for the Li-chemisorbed surface, and the complete occupation of the $\pi^*$ surface state band. The transfer of charge from the Li adatoms to the down silicon dimer atoms produces two effects: symmetrisation of the dimers and an expansion of the Si dimer bond. Both of these effects result in a reduction of the $\pi-\pi^*$ surface state gap. Going from the clean Si(001) surface with buckled dimers to the symmetric dimer configuration (with a bondlength of 2.25 Å) results in roughly parallel $\pi$ and $\pi^*$ surface state bands, which are separated by 0.6–1.0 eV at each wave vector $k$, but overlap at different wave vectors to yield an electronic structure which is now metallic.
The further reduction of the separation of the \( \pi \) and \( \pi^* \) surface state bands to effectively zero for the Li-chemisorbed Si(001) surface is due to the significant weakening of the Si dimer bond and the resulting expansion of its bond length from the clean symmetric dimer surface value of 2.25 Å [33] to 2.63 Å. To confirm these conclusions we carried out electronic structure calculations for the clean Si(001)2\( \times \)1 reconstructed substrate which is obtained by removing the Li adatoms from the Li-chemisorbed surface. The resulting electronic structure for the occupied states was found to be essentially the same as that shown in Fig. 2, only now the Fermi energy had shifted downward so that it crossed both the \( \pi \) and \( \pi^* \) bands. The separation of the \( \pi \) and \( \pi^* \) bands for this symmetric dimer reconstructed surface with expanded Si–Si dimer bonds was found to be very small, in agreement with our observations for the Li-chemisorbed surface. We thus conclude that the observed reduction of the \( \pi–\pi^* \) gap for the Si(001)2\( \times \)1–Li chemisorbed surface at monolayer coverage arises from both the symmetric dimer reconstruction, and the weakening of the dimer bond, produced by the charge transfer from the Li adatoms to the originally unoccupied \( \pi^* \) surface state band of the substrate. The above considerations may also explain the similarities and differences between the electronic structure calculated here and that discussed by Ko et al. [26]. The Si dimer bondlength of 2.57 Å determined by Ko et al. is shorter than the value of 2.63 Å predicted for the minimum energy A–C′ configuration. This shorter dimer bondlength would be expected to increase the \( \pi–\pi^* \) gap for the Si(001)2\( \times \)1 symmetric dimer structure.

Analysis of the unoccupied electronic surface states indicates that despite the shift of the \( \pi^* \) band below the Fermi energy, and the corresponding
large reduction in the size of the \( \pi-\pi^* \) gap, the Li covered Si(001) surface still remains quite reactive. This is due to the presence of the low-lying unoccupied surface state band indicated by the empty circles in Fig. 2b. This band can be characterized as a mixture of antibonding dimer \( \sigma^* \) orbitals and predominantly s-like and/or p-like orbitals associated with the lower Li adatoms (see Fig. 5b). Along the \( \Gamma-J-K \) symmetry directions of the SBZ, the contribution from the lower Li adatom is predominantly of s character, but becomes almost entirely of p character along \( J'-\Gamma \). The dispersion of this empty surface state band is very similar to that of typical p, atomic orbitals due to the phases of the Si dimer \( \sigma^* \) and Li orbitals included in the mixture. The \( \sigma^* \) antibonding character of this surface state suggests that doping the Si(001)2 \( \times 1 \)-Li 1.0 ML configuration by an additional charge of 2e may break the Si–Si dimer bond, and change the symmetric dimer 2 \( \times 1 \) topology of the 1.0 ML reconstruction into a 1 \( \times 1 \) substrate configuration at higher coverages. Experimental evidence for such a reconstruction has, in fact, been observed in the LEED data of Tochihara and Murata [13], and Johansson and Reihl [14]. Geometry optimisation calculations for the chemisorption of 2.0 ML of Li on the Si(001)2 \( \times 1 \) surface by Morikawa et al. [10] and Ko et al. [26] have also predicted that the Si dimers will be broken, in agreement with the experimental data. The mixture of Si and Li character in this low-lying unoccupied surface state band also suggests that the bonding between the Li adatoms and the Si surface atoms for 2.0 ML coverage (when an additional valence charge of 2e will be added to the system) may be somewhat different from the ionic bonding that occurs at 1.0 ML coverage. Such behaviour would be consistent with the formation of silicides. This conclusion agrees with the work of Morikawa et al. [10] who found that for 2.0 ML coverage the first layer of lithium penetrated into the substrate and resided close to the second Si layer, while the topmost Li atoms interacted directly with the Si dimer atoms.

The empty surface states of the Si(001)2 \( \times 1 \)-Li system have been studied experimentally by Johansson and Reihl [14]. Using normal incidence IPES they observed a single unoccupied surface state which shifted down in energy with increasing Li coverage. At a saturation coverage of 1.0 ML this unoccupied surface state was found to lie 2.0 eV above the Fermi energy and the measured surface band gap was 3.1 eV. Our calculations predict the presence of an unoccupied surface state in the vicinity of the \( \Gamma \) point of the SBZ (empty circles in Fig. 2b) that is separated from the highest occupied level at \( \Gamma \) by 2.4 eV. Given that density functional calculations generally underestimate the energy gap of silicon by about 0.6 eV [34], this latter value is in very good agreement with the experimental data. The IPES measurements of Johansson and Reihl also indicated that the unoccupied surface state was essentially dispersionless [14]. Our theoretically predicted surface state, however, exhibits considerable dispersion as shown in Fig. 2b.

Fig. 2. Side and top views of the 3D probability density distributions, and the corresponding \( \rho_{\text{IPES}}(z) \), for the unoccupied surface state bands of the Si(001)2 \( \times 1 \)-Li system at 1.0 ML coverage indicated in Fig. 2b by (a) inverted triangles at the K point of the SBZ, and (b) arrowheads for a wave vector lying between the J and K points of the SBZ. The density isosurface value in each case was \( 2.0 \times 10^{-2} \) \( \text{Å}^{-3} \).
5. Summary

In this paper we have investigated the atomic and electronic structure of the Si(001)2\times1–Li system at 1.0 ML coverage using the plane wave pseudopotential DFT method contained in the VASP code. It has been found that predominantly ionic bonds are formed between the chemisorbed lithium atoms and the first layer silicon atoms. The calculations have also shown that the associated transfer of charge causes the substrate to reconstruct into a symmetric dimer topology in agreement with experiment. The predicted electronic structure of the occupied surface states has been found to closely follow that of the reconstructed substrate and to be in good agreement with the current experimental data. The electronic structure of the unoccupied surface states, on the other hand, has been found to be significantly influenced by the Li adatoms. The mainly antibonding character of the lowest energy unoccupied surface state band along the Γ–J–K symmetry directions of the SBZ explains how doping the Si(001)2\times1–Li 1.0 ML configuration with an additional two electrons per SUC by increasing the lithium coverage from 1.0 ML to 2.0 ML could change the symmetric dimer 2\times1 reconstruction into the 1\times1 reconstruction. The hybrid Li/Si character of this surface state band also supports the formation of silicides at Li coverages beyond 1 ML.

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References


