# Spectroscopic examination of the Na/Si(111)-(3×1) surface structure

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We have examined a recently proposed experimental model for the alkali-metal induced Si(111)-(3×1) surface structure, based on density-functional theory calculations and their comparison with experiments on the structural and electronic properties of Na/Si(111)-(3×1). This model, characterized by the alkali-metal adsorption in empty channels and the resulting honeycomblike substrate reconstruction, is energetically favored and reproduces well the experimental scanning-tunneling-microscope images, surface-state band structure, and Si 2$p$ surface core-level spectra, which together provide a convincing theoretical demonstration that the employed model is acceptable both in energetics and in spectroscopic examination. [S0163-1829(98)52444-7]

Alkali-metal (AM) adsorbates are known to induce (3×1) reconstructions of the Si(111) surface,[1] and very similar (i.e., AM-insensitive) low-energy-electron-diffraction (LEED) patterns,[2,3] scanning-tunneling-microscopy (STM) images,[4,5] and surface core-level shifts (SCLS)[6–8] have strongly suggested that the same substrate reconstruction is induced by different AM adsorbates. More interestingly, similar (3×1) reconstructions were also reported for other than alkali metals, such as Ag and Mg.[2–4,9] The construction of a correct structural model for the AM/Si(111)-(3×1) surfaces has been a longstanding issue. Of several qualitative structural models proposed earlier, only two survived the energetics test based on density-functional theory (DFT) calculations,[11,12] which have been referred to as the extended-Pandey-chain model (EPC) and the missing-top-layer (MTL) (or Seiwatz-chain) model (see Fig. 1). While

each of these two models could possibly explain the AM-insensitive LEED I-V curves,[2,3] the observed semiconducting property,[5] and the chemical passivation for surface oxidation,[10] both had serious difficulty in reproducing the measured surface band structures and STM images.[8,11,12]

Recently, a structural model for Ag/Si(111)-(3×1) was proposed based on direct phasing of transmission electron diffraction data,[13] and a similar and more refined model for the alkali adsorbates (Li, Na, and Rb) was also derived by combining surface x-ray diffraction and LEED measurements and DFT calculations.[14] This model is characterized by the AM adsorption in empty channels and the resulting reconstruction of the surface Si atoms in between the channels (see Fig. 1). The channel in this model can be regarded as a removal of the Pandey chain in the EPC model, and therefore we refer to it as a missing-Pandey-chain (MPC)
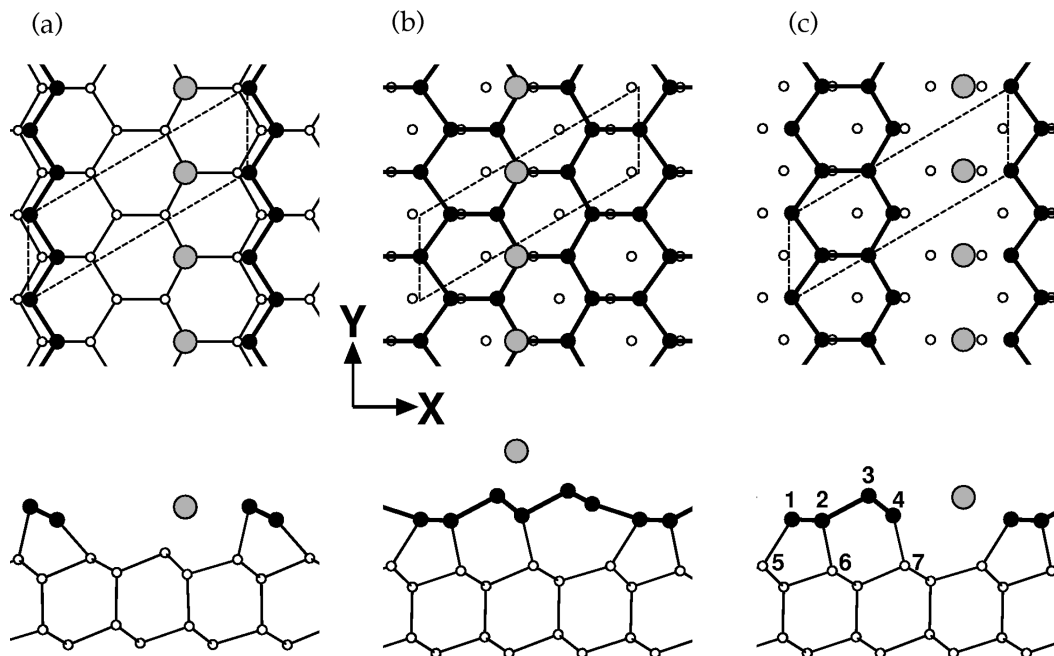


FIG. 1. Schematic diagrams of structural models for AM/Si(111)-(3×1): (a) the missing-top-layer (MTL), (b) the extended-Pandey-chain (EPC), and (c) the missing-Pandey-chain (MPC) models. The gray circles represent AM.
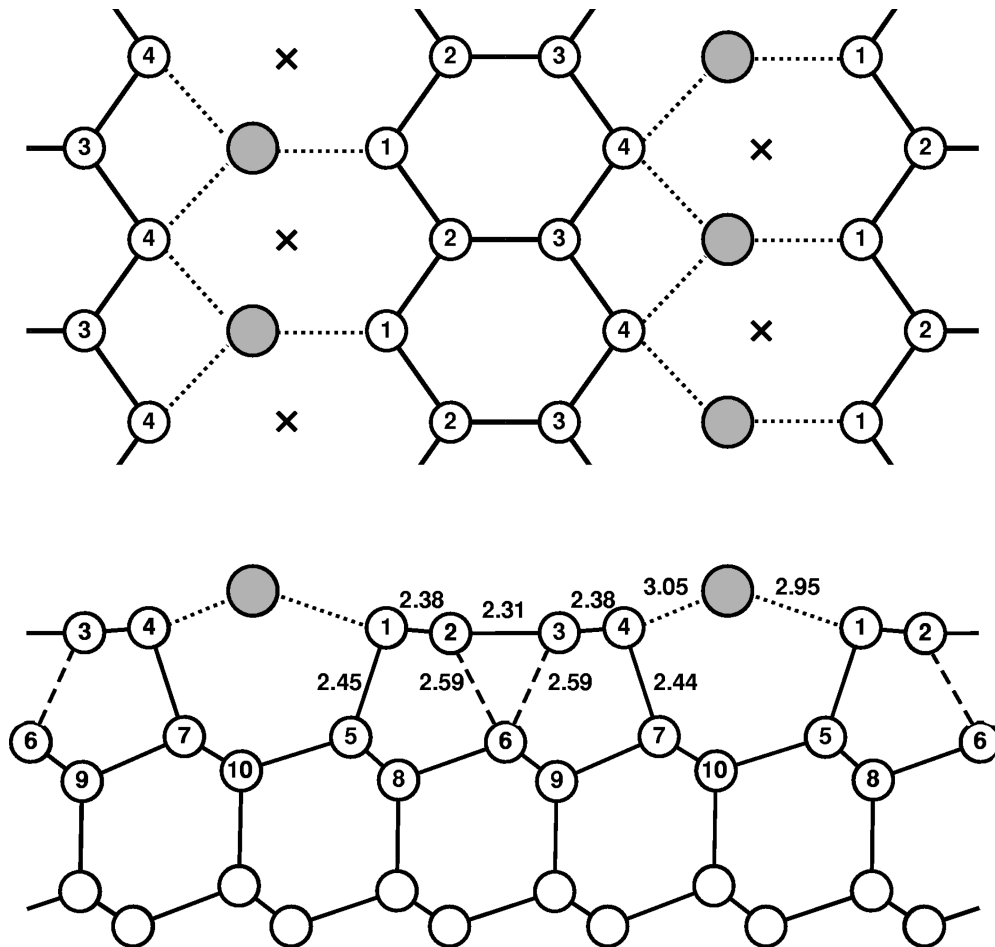
FIG. 2. Equilibrium geometry of Na/Si(111)-(3×1) within the MPC model. The gray circles represent Na. The characteristic surface bond lengths are given in Å, and the bulk reference value is 2.38 Å.

model, hereafter. Since it is based on both direct methods to surface diffraction data and DFT total-energy calculations, the MPC model is very promising, but there still remains an interesting question whether it can account for the experimental surface electronic data. This test is compelling since a *correct* structural model should survive quantitative spectroscopic examination.

In the present work, we have theoretically investigated the proposed MPC model for the prototypical Na/Si(111)-(3×1) system, based on DFT calculations and their comparison with experiments on the structural and electronic properties. The main results we will report in this paper include (1) an energetical confirmation of the MPC model as the lowest-energy structure, (2) a successful theoretical reproduction within the MPC model of the measured angle-resolved photoemission spectroscopy (ARPES) band structure, STM images, and SCLS data, and (3) an electronic-structure-based explanation of the interesting substrate reconstruction found in this system, which together are sufficient to provide a convincing theoretical confirmation that the MPC model is correct both in energetics and in spectroscopic examination.

The total-energy and force calculations were carried out by employing the norm-conserving pseudopotentials[15,16] and density-functional theory within generalized-gradient approximation.[17,18] We simulate the Si(111) surface by a periodic slab geometry of 12 atomic and 6 vacuum layers with the use of a plane-wave basis of 10 Ry. More details and the

convergence of the computations can be found in our previous work on the (Na, K)/Si(111)-(3×1) surface.[12]

First, we determined the equilibrium MPC structure of Na/Si(111)-(3×1) starting from the initial geometry shown in Fig. 1(c) where the top-layer Pandey chain of the EPC model was replaced by a Na chain. In the final structure shown in Fig. 2, the Na chain stays in a position of nearly equal distance from the top-layer Si atoms labeled 1 and 4, and noticeable is a large relaxation of the Si atom 2 resulting in a $sp^2$-like plane bonding configuration. The physical origin of this interesting reconstruction pattern and the nature of AM bonding will be discussed later in connection with the calculated electronic structure. We also found another stable Na adsorption site (denoted as crosses in Fig. 2): its adsorption energy is only 0.03 eV/Na higher than that of the reference minimum-energy structure, and the energy barrier between them is as low as 0.1 eV/Na. In both adsorption cases, however, the underlying Si substrate geometries were found to be nearly identical. In energetics, the MPC structure is much more favored than the previous MTL or EPC model (see Table I). The present results on the equilibrium structure and the energetics of Na/Si(111)-(3×1) are very similar to the DFT results on Li/Si(111)-(3×1) by Lottermoser *et al*.[14]

The calculated MPC band structure is shown in Fig. 3(a). We found four surface-state bands near the bulk gap: three

TABLE I. Surface energies $E_{\text{surf}}$ (relative to the extended Pandey chain) and band gaps $E_g$ calculated for different models for Si(111)-(3×1). Energies are given in eV/Na for $E_{\text{surf}}$ and eV for $E_g$.

| Structural models | $E_{\text{surf}}$ | $E_g$ |
| --- | --- | --- |
| EPC | 0.00 | 0.49 |
| MTL | −0.09 | 0.27 |
| MPC | −0.62 | 0.74 |

filled ($S_1$, $S_2$, and $S_3$) and one empty ($S_4$). The filled-state band dispersions and relative positions compared well with recent ARPES data on Na/Si(111)-(3×1).[19] This good agreement is in contrast with the previous MTL and EPC models, which had difficulty in reproducing ARPES data available on the Li and K cases.[8,12]

The charge character of representative surface states, shown in Fig. 3(b), provides insights into the Na-induced interesting substrate bonding configuration. The states $S_2$ and $S_3$ represent clearly the saturated dangling-bond states of the Si atoms 1 and 4. It is apparent from simple counting of surface electrons that the electrons needed for their saturation are supplied from the Na atom and the Si atom 3. Hence, the bonding of Na atoms on Si(111)-(3×1) is mainly ionic, and the major factor governing its equilibrium will be the Coulomb interaction with the saturated dangling-bond states of both Si atoms 1 and 4. With its dangling-bond state empty, the Si atom 3 can get a large electronic energy gain associated with a rehybridization from $sp^3$ to more stable $sp^2$ and



FIG. 3. (a) Surface band structure of Na/Si(111)-(3×1): All energies are given relative to the valence band maximum at $\overline{\Gamma}$ point. The (3×1) surface Brillouin zone is shown as a reference. Shaded areas are the projected bulk-band structure. Surface (resonance) states are represented by solid (dashed) lines. Filled circles represent the ARPES data of Okuda et al. (Ref. 19), which were uniformly shifted by 0.42 eV for a better comparison. (b) Charge character of the representative surface states at $\overline{A}$. Contour spacings are 0.006 e/Å$^3$.

less stable $p_z$, where the $sp^2$ bonding leads to a strengthened honeycomb-like flat lattice and the remaining $p_z$ orbital would be the main character of the empty surface-state band.

More interesting in this sense is the character of $S_1$ and $S_4$. The character of $S_4$ is apparently not the $p_z$ orbital of the Si atom 3. As a matter of fact, the main character of $S_1$ ($S_4$) is essentially that of a $\pi$ bonding ($\pi^*$ antibonding) between the $p_z$ orbitals of the Si atoms 2 and 3, slightly modified by subsurface interactions. This can be understood as follows: By the $sp^2$-like relaxation of the atom 3, the Si atom 2 is also left in a very similar plane bonding configuration. This drives the otherwise stable $sp^3$ bonding between the atoms 2 and 6 so unstable as to break, allowing the atom 2 to undergo a favorable rehybridization into $sp^2$ and $p_z$. Then, two electrons released from the broken bond favorably fill the stable $\pi$ bonding state, newly formed between the atoms 2 and 3. In this way, the in-plane bonding of the atoms 2 and 3 is much strengthened while the interlayer bonding becomes weaker (in fact, there exists no direct bondings between the atom 6 and any of the surface atoms 2 and 3, and this is why we denoted the corresponding bonds by dashed lines in Fig. 2).

The band gap in this system, defined as the energy difference between the band $S_4$ and the bulk valence band maximum, is 0.74 eV in good agreement with a STM measurement of about 0.8 eV.[5] This gap is associated with a large split of the bands $S_1$ and $S_4$ (i.e., the $\pi$-$\pi^*$ split between the atoms 2 and 3). In the MTL and EPC models, on the other hand, the band gap is caused by the buckling of the Seiwatz or Pandey chain, which leads to a somewhat weaker split and thus a smaller band gap (see Table I).

Simulated STM images could be another crucial test for the MPC model. We have shown in Fig. 4 some images simulated by integrating the electronic charge density near the Fermi level. The filled-state image of a double-row zigzag chain represents the saturated dangling-bond states $S_2$ and $S_3$ shown in Fig. 3. It is noteworthy that the triangular image of the electronic states is nearly equilateral while the underlying lattice is not. The main character of the empty-state image is an AM-related line image, but the $\pi^*$ antibonding character of the band $S_4$ also weakly appears. In fact, these simulated images are in perfect agreement with the STM data on the Li or Na adsorbed Si(111)-(3×1) surface.[4,5] The previous MTL and EPC models were not so successful: the MTL model has serious difficulty in explaining the double-row filled-state image,[12] and the EPC model produces a double-row image with too narrow width to be properly compared with the STM data.[11]

In their SCLS experiment on Na/Si(111)-(3×1), Okuda et al.[6] obtained two well-resolved Si 2p surface core-level spectra of equal intensity (one in higher and the other in lower binding sides). Since SCLS reflects well the underlying surface geometry and bonding configuration, it is also interesting to see whether the MPC model is compatible with the measured SCLS data. We have examined it within initial-state theory, where SCLS is defined as a binding-energy difference of core electrons at different sites and can be estimated in pseudopotential formalism by the expectation value of the self-consistent potential on the Si 2p atomic orbital located at each site.[20] As shown in Fig. 5, the calculated
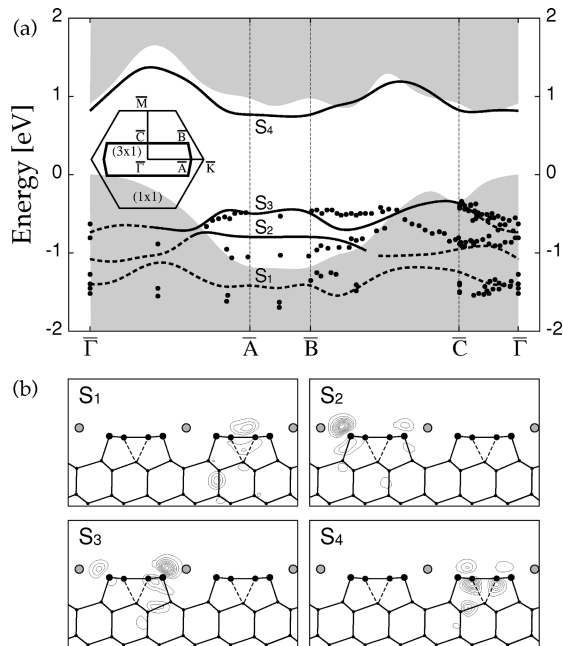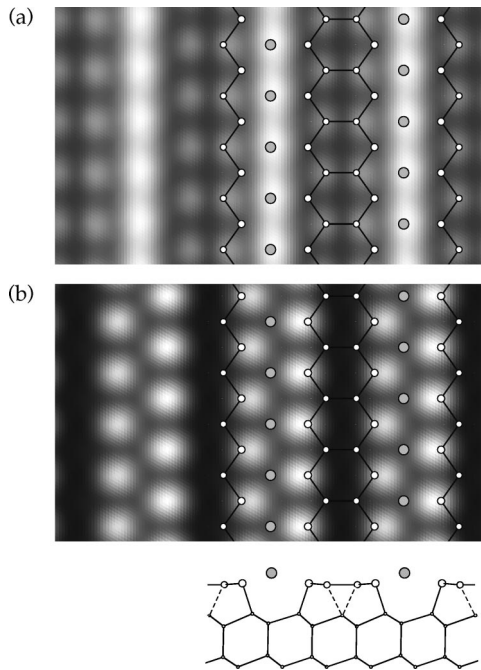
(a)



(b)

FIG. 4. Simulated STM images of Na/Si(111)-(3×1). (a) The empty-state image obtained by integrating $\rho(r,\varepsilon)$ from $\varepsilon_F$ to $\varepsilon_F +2.0$ eV. (b) The filled-state image from $\varepsilon_F-1.0$ eV to $\varepsilon_F$. The images were taken at 3.0 Å above the top Si atom.



FIG. 5. Calculated Si $2p$ core-level shifts on the MPC Na/Si(111)-(3×1) surface using initial-state theory in comparison with the experimental data of Okuda et al. (Ref. 6). The numbers over the calculated core levels represent the corresponding surface Si atoms as denoted in Fig. 2.

SCLS is in quantitative agreement with the experimental data and reflects well the underlying structural feature; that is, the lower (higher) binding shifts for the Si atoms 1 and 4 (2 and 3) can be attributed to a gain (depletion) of electronic charge associated with the aforementioned charge transfer. It is also noticeable that the Si atoms 2 and 3 show the same core levels in their symmetric bonding configurations, while the core levels of the Si atoms 1 and 4 are separated by about 0.1 eV due to their inequivalent bonding with Na.

In summary, on the basis of density-functional calculations for the Na/Si(111)-(3×1) surface, we have demonstrated that the recently proposed structural model (MPC) is not only energetically favored, but also can incorporate the
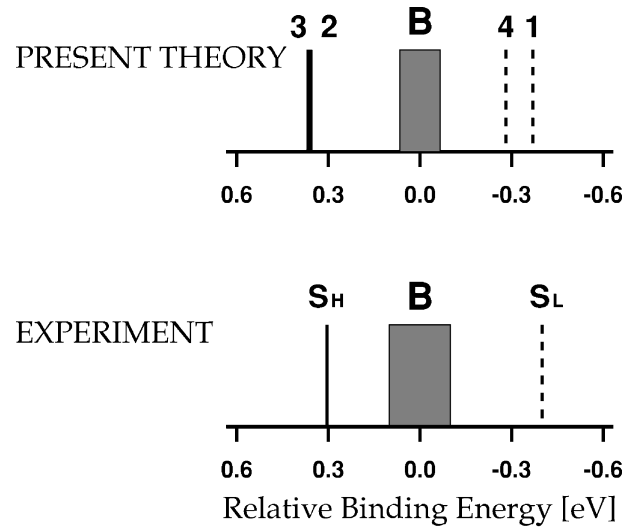
available experimental (ARPES, STM, and SCLS) surface electronic data. The origin of the interesting substrate reconstruction has also been addressed in connection with the charge character of surface electronic states. Hence, the present study provides an extensive theoretical confirmation of the proposed experimental model as a *correct* one that is acceptable both in energetics and in spectroscopic examination.

*Note added.* A density-functional electronic-structure study of the (Li; Ag)/Si(111)-(3×1) surfaces has just been published by Erwin and Weitering.[21] The reported structural and electronic properties for the Li case are very similar to the present result for the Na case.

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