Buckled reconstruction of the alkali-metal (Na, K)-adsorbed Si(111)-(3×1) surfaces

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The atomic and electronic structures of the alkali-metal (Na, K)-adsorbed Si(111)-(3×1) surface are studied by the pseudopotential density-functional total-energy scheme for the structural models proposed to date: the missing-top-layer (MTL), π-bonded chain, and overlayer models including their variations. From the extensive investigation of them, we propose the MTL model as the ground-state structure of this system based both on the energetics and on the comparison of the calculated electronic structures with recent angle-resolved ultraviolet photoemission data. [S0163-1829(96)02828-7]

I. INTRODUCTION

The investigation of adsorption geometry (i.e., adsorbate coverages, bonding sites, and substrate reconstructions) is an important research subject in surface physics, since it forms a basis of proper understanding of the adsorbed surface systems. Of great interest, in this sense, is the alkali-metal (AM) adsorbed Si(111)-(3×1) surfaces because, despite recent extensive investigations, we have not constructed yet a successful structural model that can incorporate the reported intriguing experimental facts. The (3×1) reconstruction of the AM/Si(111) surface was first reported a decade ago,[1] but we do not have any conclusive structural information, except for the saturation coverage of AM. In fact, although it is a basic component in building a right structural model, the problem of the AM saturation coverage has long been a matter of controversy,[1–13] but more recent works[6–13] on Na- and K-covered Si(111)-(3×1) surfaces arrived at a consensus of 1/3 monolayer (ML), disputing the earlier proposal of 2/3 ML based on scanning-tunneling-microscopy (STM) images.[4,5] Another structural information, which may be helpful in constructing structural models, is provided by recent STM studies of Olthoff, McKinnon, and Welland[11] and Paggel *et al.*[13] Their conclusion was that the structural changes from the clean (7×7) phase to the AM-covered (3×1) phase require considerable mass transport, which implies that the numbers of Si atoms in both phases are much different. We have more quantitative results on the electronic structures: the STM measurement of the semiconducting band gap of about 0.8 eV for Na/Si(111)-(3×1) (Ref. 4) and the surface-state band structure of K/Si(111)-(3×1) measured by angle-resolved ultraviolet photoemission spectroscopy (ARUPS),[8] but we have yet to develop a proper structural model that can provide a consistent explanation of the semiconducting nature and other experimental results including the AM-insensitive low-energy-electron-diffraction (LEED) *I-V* curves,[2] the chemical passivation for surface oxidation,[3] and the surface-core-level-shift (SCLS) spectra.[9,10]

Based on the saturation coverage of 1/3 ML, several structural models have been proposed to date in different experimental contexts (see Fig. 1). The missing-top-layer (MTL) model is characterized by the AM linear chain adsorbed on the empty channel between the top-layer Si chains.

This model was proposed to explain the observed semiconducting nature.[7,8] In the π-bonded chain model, the AM chain is adsorbed on a reconstructed Si substrate, which is similar to the π-bonded chain type found in the Si(111)-(2×1) surface.[14] This model and the above MTL model are compatible with the recent SCLS analysis.[9,10,15] In the overlayer model, the AM chain is adsorbed on the bulk-terminated Si(111) surface. This model was suggested first by Jeon *et al.*[4] from their double-row STM images on Na/Si(111)-(3×1) assuming 2/3-ML coverage, but it was shown in our previous theoretical study[12] that the result for the coverage of 1/3 ML is in better agreement with the experiments. So far, however, none of the above models are quite satisfactory: the MTL and π-bonded chain models are only qualitative, and the previous quantitative study of the overlayer model[12] failed to produce the measured surface electronic structure. In order to be successfully compared with the measured semiconducting electronic structure, therefore, these models require some assumptions not justified yet.[16]

In the present work, we examine on an equal basis all the proposed models of AM/Si(111)-(3×1) by investigating the equilibrium atomic and electronic structures of the Na- and K-covered surfaces, using the density-functional pseudopo-
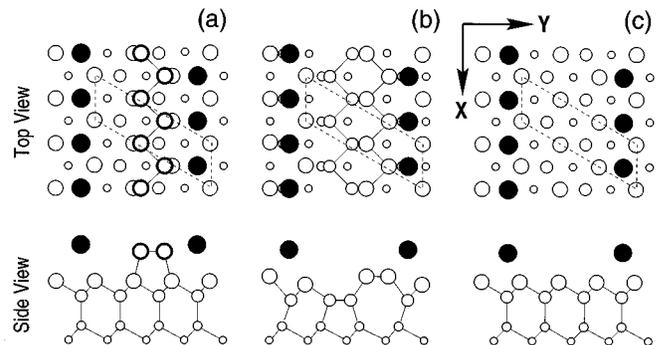
FIG. 1. Schematic diagrams of structural models for AM/Si(111)-(3×1): (a) the missing-top-layer (MTL), (b) the π-bonded chain, and (c) the overlayer models. Filled and empty circles represent AM and Si atoms, respectively. Thick circles in the MTL model indicate the top-layer Si atoms. Each (3×1) unit cell is represented by dashed lines. For convenience, each AM is put on the threefold filled (T_4) site, but on-top adsorptions are also considered.

tential total-energy scheme. The key result is that the most stable is a *buckled* MTL structure that is characterized by the linear chain of alkali atoms adsorbed on a stable three-fold site in between the *buckled* top-layer Si chains. This buckling is found to induce a band separation between the two otherwise nearly degenerate dangling-bond states localized on the top-layer Si atoms, and thus makes this surface semiconducting. The resulting surface-state band structure is in good agreement with the ARUPS measurement.[8] Moreover, the buckled MTL models is consistent with recent STM studies[11,13] reporting a mass transport in the phase transition from the clean (7×7) phase to the AM-covered (3×1) phase, since the number of Si atoms in the MTL model deviates considerably from the clean (7×7) phase.

The rest of the text is organized as follows. In Sec. II, we briefly describe the pseudopotential density-functional scheme. In Sec. III, we report the energetics, the equilibrium atomic structures, and the corresponding electronic structures for the Na- and K-adsorbed Si(111)-(3×1) surfaces. For the K-covered surface, the surface-state band structure is compared with the ARUPS data.[8] In Sec. IV, we discuss our results in comparison with the recent calculation[16] and STM data,[11,13] and, finally, we give a summary in Sec. V.

II. CALCULATIONAL METHOD

In our calculations, we use the norm-conserving separable pseudopotentials[17,18] together with the density-functional theory within local-density approximation (LDA).[19,20] Partial-core corrections are also included in the pseudopotentials of alkali atoms (Na and K).[21] We simulate the AM/Si(111) surface by a periodic slab geometry with a substrate of ten Si layers[22] (excluding the top-layer adatoms in the MTL model) and a vacuum layer equivalent to six Si layers. For potassium adsorption, additional vacuum layers equivalent to two Si layers are inserted in order to reflect the larger atomic size of potassium. For various adsorption sites, the AM and Si atoms up to the fifth layer are relaxed following the calculated forces until the remaining forces are all within 0.01 Ry/Å . We use a plane-wave basis with the energy cutoff of 10 Ry and take a uniform grid of six k points in an irreducible (3×1) surface Brillouin zone.[23]

III. RESULTS

A. Atomic structures

We discuss first the energetics and the equilibrium atomic structures of the Na-covered Si(111)-(3×1) surface. Since the number of Si atoms in the MTL model is different from the π-bonded chain and overlayer models, we calculate surface energies as $E_{\mathrm{surf}} = (E_{\mathrm{slab}} - NE_{\mathrm{Si,bulk}})/2$, where E_{slab} is the energy of the slab, $E_{\mathrm{Si,bulk}}$ is the energy per atom of bulk Si, N is the total number of Si atoms in the slab, and the factor 2 accounts for two surfaces in a slab. It is important to calculate both E_{slab} and $E_{\mathrm{Si,bulk}}$ on an equal basis for an accurate estimation of the surface energy. Here, $E_{\mathrm{Si,bulk}}$ is computed using the same parameters as those of surface slab calculations; that is, 10 Ry for the plane-wave cutoff energy and six irreducible k points for the (3×1) bulk supercell of 18 atomic layers. As shown in Table I, the threefold site[24] is much more stable for adsorption than the on-top site in all

TABLE I. Energetics of the Na adsorption on Si(111) -(3×1). All energies are given in eV/Na relative to that of the energy-minimized buckled MTL structure.

	Adsorption sites	
Structural models	Threefold (T_4)	On-top
MTL	0.00 (buckled)	1.06 (symmetric)
π-bonded chain	0.11	0.79
Overlayer	0.12	0.92

the structural models, and a *buckled* MTL structure is the most stable. In the case of the buckled MTL model, there are two kinds of T_4 adsorption sites: one (T_4) is that shown in Fig. 1, and the other (T_4') is the site shifted from the T_4 site by one third of the longer primitive vector. Our calculation shows that the T_4' site is higher in energy by 0.09 eV/Na.

We present the equilibrium atomic structures of the models in Fig. 2 and the corresponding atomic positions in Table II. The *buckled* MTL structure is characterized by a large buckling (about 0.63 Å) of the top-layer Si chain toward the Na chain adsorbed on a nearby threefold site, and the Si-Si bond length within the top-layer chain is 2.37 Å, slightly longer (0.8%) than the bulk bond length (2.35 Å). The previously proposed *symmetric* MTL structure is found to be stable only with the on-top Na adsorption, as shown in Fig. 2(b) (even in that case, there exists a small buckling of about 0.07 Å), but it is subject to the buckling reconstruction with a large energy gain of 1.06 eV (Table I). The physical origin of this buckling instability will be discussed later in connection with the calculated electronic structure. The equilibrium structures of the π-bonded chain and overlayer models shown in Fig. 2(c,d) are less stable (about 0.11 eV/Na) than that of the buckled MTL model. The characteristic buckling of the π-bonded chain is 0.58 Å, and the Si-Si bond length within the π-bonded chain is 2.30 Å, 2.1% shorter than the bulk bond length. The overlayer structure, which is similar to the π-bonded chain model in energetics (with energy difference of less than 0.01 eV), is characterized by a large atomic corrugation (about 0.76 Å) between the top-layer *bonded*
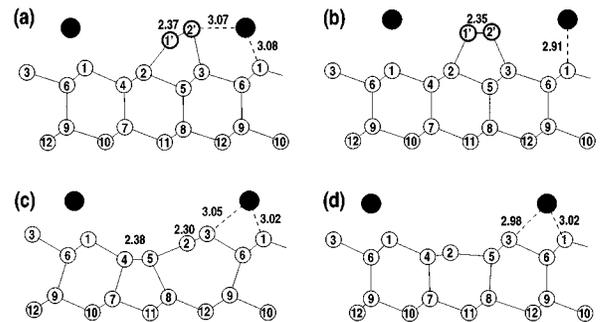
FIG. 2. Equilibrium adsorption geometries of Na/Si(111)-(3×1): (a) the buckled MTL (T_4 adsorption site), (b) the symmetric MTL (on-top adsorption site), (c) the π-bonded chain, and (d) the overlayer models. Filled and empty circles represent Na and Si atoms, respectively. The characteristic surface bond lengths are given in Å.

TABLE II. Coordinates of the equilibrium geometries for Na/Si(111)-(3×1) in Fig. 2. The coordinate axes and labeling of atoms are shown in Fig. 1 and Fig. 2. The Z direction is perpendicular to the surface with the reference at the slab center. All numbers are in Å.

Atom	Buckled MTL			π-bonded chain			Overlayer		
no.	X	Y	Z	X	Y	Z	X	Y	Z
Na	7.68	9.11	9.28	7.68	10.05	9.10	7.68	8.87	9.02
1′	1.92	4.81	8.53						
2′	3.84	6.05	9.15						
1	0.00	-0.05	7.01	0.00	0.86	6.90	0.00	-0.10	6.92
2	1.92	3.32	6.73	1.92	6.53	6.64	1.92	3.40	6.19
3	3.84	6.60	6.74	3.84	7.66	7.22	3.84	6.72	6.95
4	3.84	2.13	6.05	3.84	2.97	5.75	3.84	2.10	5.98
5	5.76	5.54	5.84	5.76	4.37	5.78	5.76	5.71	6.00
6	7.68	8.89	6.04	7.68	9.70	5.99	7.68	8.86	5.92
7	3.84	2.21	3.64	3.84	2.33	3.49	3.84	2.22	3.55
8	5.76	5.55	3.48	5.76	5.53	3.60	5.76	5.54	3.60
9	7.68	8.85	3.64	7.68	9.02	3.70	7.68	8.87	3.57
10	1.92	1.10	2.80	1.92	1.18	2.74	1.92	1.09	2.75
11	3.84	4.40	2.76	3.84	4.51	2.69	3.84	4.44	2.77
12	5.76	7.79	2.77	5.76	7.83	2.90	5.76	7.76	2.76

TABLE III. Coordinates of the equilibrium geometries for K/Si(111)-(3×1) in Fig. 3. The coordinate axes and labeling of atoms are shown in Fig. 1 and Fig. 3. The Z direction is perpendicular to the surface with the reference at the slab center. All numbers are in Å.

Atom	Buckled MTL			π-bonded chain			Overlayer		
no.	X	Y	Z	X	Y	Z	X	Y	Z
K	7.68	9.37	9.81	7.68	10.11	9.70	7.68	8.87	9.59
1′	1.92	4.79	8.57						
2′	3.84	6.03	9.20						
1	0.00	-0.05	7.01	0.00	0.93	6.90	0.00	-0.10	6.92
2	1.92	3.30	6.74	1.92	6.56	6.62	1.92	3.40	6.20
3	3.84	6.59	6.76	3.84	7.69	7.13	3.84	6.72	6.95
4	3.84	2.14	6.04	3.84	3.00	5.74	3.84	2.10	5.98
5	5.76	5.54	5.85	5.76	4.41	5.75	5.76	5.70	6.00
6	7.68	8.88	6.04	7.68	9.78	5.99	7.68	8.86	5.92
7	3.84	2.22	3.62	3.84	2.33	3.48	3.84	2.22	3.55
8	5.76	5.55	3.51	5.76	5.53	3.57	5.76	5.54	3.59
9	7.68	8.78	3.63	7.68	9.02	3.70	7.68	8.87	3.57
10	1.92	1.11	2.80	1.92	1.18	2.75	1.92	1.09	2.74
11	3.84	4.42	2.76	3.84	4.50	2.67	3.84	4.44	2.77
12	5.76	7.78	2.78	5.76	7.84	2.90	5.76	7.77	2.76

(directly bonded to AM) and *rest* (not directly bonded to AM) Si atoms. The details of the overlayer structure can be found in Ref. 12.

The atomic structures of the K/Si(111)-(3×1) surfaces shown in Fig. 3 and Table III are very similar to the Na-covered cases, except for the fact that the K-Si bond lengths

FIG. 3. Equilibrium adsorption geometries of K/Si(111)-(3×1): (a) the MTL, (b) the π-bonded chain, and (c) the overlayer models. Filled and empty circles represent K and Si atoms, respectively. Characteristic surface bond lengths are given in Å.

are on average about 0.41 Å longer than the Na-Si bond lengths. In fact, all of the atomic position changes from the Na adsorption to the K adsorption are less than 0.07 Å. In energetics, the relative stability of the buckled MTL structure is more enhanced to a 0.17 eV/K atom compared with 0.11 eV/Na for the Na-adsorbed surfaces. The π-bonded chain model is energetically comparable with the overlayer model with an energy difference less than 0.01 eV/K atom like the Na-adsorbed case. The nearly identical Si-substrate structures for Na and K can explain well the observed AM-insensitive LEED I-V curves.[2]

The reconstructions in the three models look very different, but there is a common structural feature that the AM adsorption induces a large atomic corrugation at surface by upward (downward) movement of the bonded (rest) Si atoms. With this similar bonding configuration, the three models have similar surface energies. Among them, the buckled-MTL structure is the most stable with non-negligible energy differences of 0.11 eV for Na adsorption and 0.17 eV for K adsorption.

B. Electronic structures

The band structure of the Na-covered buckled MTL geometry is shown in Fig. 4(a). There are three surface-state bands in the bulk gap: the lower two (S_1 and S_2) are fully occupied and the other (S_3) is empty. In band picture, therefore, this surface is a semiconductor with a band gap of 0.28 eV at the $\overline{\Gamma}$ point. However, the surface-state band gap (between S_2 and S_3), which may be more pertinent to the STM experiment, is about 0.50 eV. For a better understanding of the semiconducting nature, the charge characters of the representative surface states are shown in Fig. 5. It is clear that the state S_1 (S_3) originates from the dangling-bond state localized in the up (down) atom of the buckled Si chain and
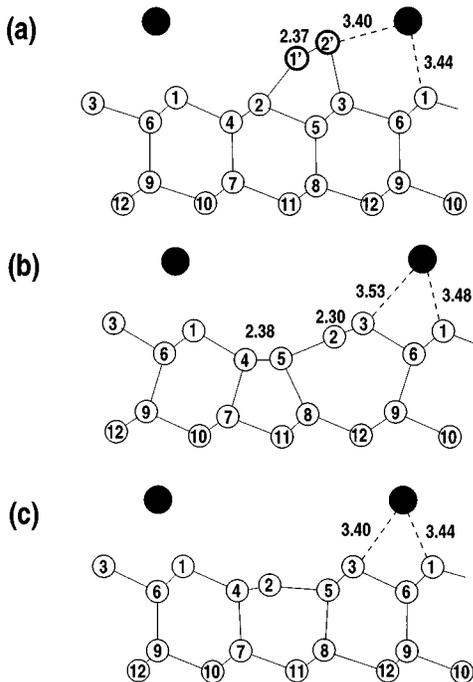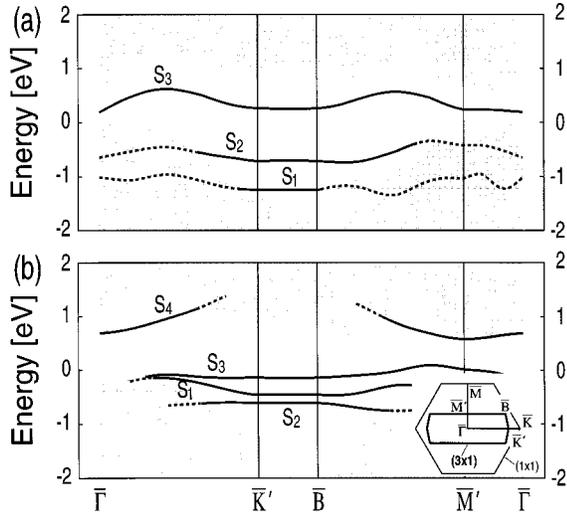
FIG. 4. Surface band structures of Na/Si(111)-(3×1): (a) the buckled MTL and (b) the symmetric MTL models. The inset in (b) shows the surface Brillouin zone for the (3×1) unit cell with that for the (1×1) unit cell as a reference. All energies are with respect to the valence band maximum at $\overline{\Gamma}$. Shaded areas are the projected bulk-band structure. Surface and resonance states are represented by solid and dashed lines.

the state S_2, from the subsurface Si atom bonding to Na. (The Na-derived surface state is hidden in the conduction band continuum.) That is, the two low-lying dangling-bond states (S_1 and S_2) on the bonded Si atoms are completely filled and the state on the rest (i.e., buckled-down) Si atom is empty. This removal of chemically active dangling-bond states is possibly the origin of the reported AM-induced chemical passivation for surface oxidation.[3]

In addition, the above observation of the occupied up-atom state (S_1) and empty down-atom state (S_3) strongly suggests that the large band separation is driven by the buckling of the Si chain, since it is well known that a buckling at covalent semiconductor surfaces tends to induce a large band separation by dehybridizing the dangling-bond states into the lower s (for the up atom) and higher p (for the down atom) orbitals. In order to quantify the effect of the buckling on electronic structure, we examine the band structure of the metastable *symmetric* MTL geometry in Fig. 4(b): there are three dangling-bond states (here, S_1, S_2, and S_3 are labeled to be matched in character to those of the buckled MTL case) and a Na-derived state (S_4). Strictly speaking, the symmetric
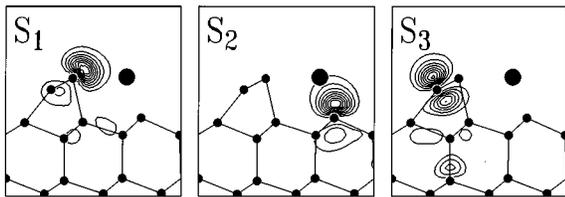
FIG. 5. Charge characters of the representative surface states S_1, S_2, and S_3 at $\overline{K}'$ in the Na-covered buckled MTL model [see Fig. 4(a)]. Larger (smaller) circles represent Na (Si) atoms. Contour spacings are 0.015 e/Å^3.
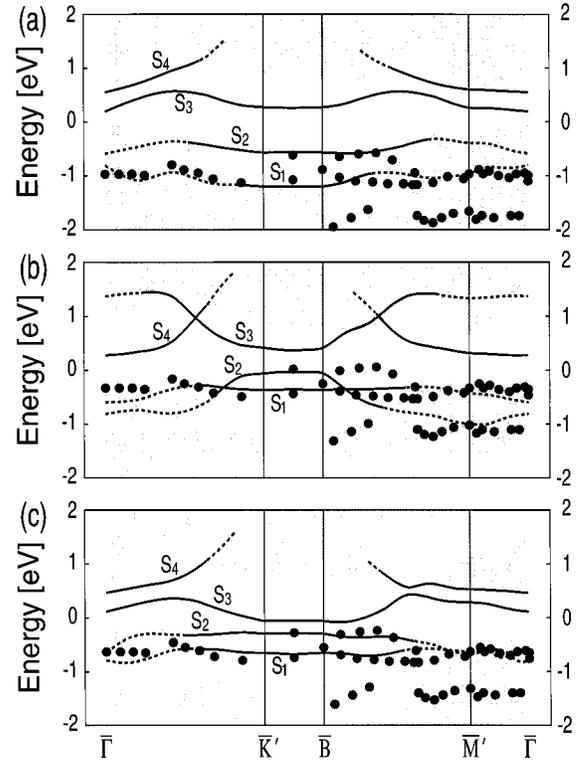
FIG. 6. Surface band structures of K/Si(111)-(3×1): (a) the MTL, (b) the π-bonded chain, and (c) the overlayer models. All energies are with respect to the valence band maximum at $\overline{\Gamma}$ point. Shaded areas are the projected bulk-band structure. Surface and resonance states are represented by solid and dashed lines. Filled circles in each figure represent the ARUPS data reported for the K-covered surface (Ref. 8).

MTL structure is a band metal, since the separation of the bands S_1 and S_3 (originating from the symmetric Si chain) is incomplete. As can be seen in Fig. 4, a major change induced by the buckling is a large separation of S_1 and S_3, which are initially originated from top-layer Si atoms. It is evident from this comparison that the semiconducting gap results from the top-layer buckling. The large electronic energy gain due to the gap opening, therefore, will be the major driving force for the buckled reconstruction in the MTL model. The interaction of the threefold-site Na with the *bonded* Si atoms is also important from the fact that the reverse buckling (height exchange of the up and down atoms) of the top-layer Si chain is energetically very unstable.

The band gaps for the π-bonded and overlayer models are 0.42 and 0.0 eV, respectively.[25] (Surface-state band gaps between S_2 and S_3 become 0.47 and 0.26 eV.) The calculated band gaps 0.28, 0.42, and 0.0 eV (or, a little larger 0.50, 0.47, and 0.26 eV for the surface-state band gaps) of the MTL, π-bonded chain, and overlayer models are somewhat smaller than the measured value of about 0.8 eV.[4] A direct comparison of band gaps between the present theory and experiments, however, is not so meaningful, since it is well known that LDA calculations tend to underestimate band gaps. Since ARUPS data are not yet available for the Na/Si(111)-(3×1) surface, in what follows we will compare the calculated dispersions and bandwidths of the surface states with the ARUPS data for the K/Si(111)-(3×1) surface.

TABLE IV. Surface-state bandwidths of models for K adsorption. All energies are in eV.

	S_1	S_2	S_3
MTL	0.40	0.30	0.39
π-bonded chain	0.30	0.97	1.09
Overlayer	0.23	0.35	0.24
Experiment [a]	0.47	0.48	.

[a]Reference 8.

We present in Fig. 6 the energy bands for the K-covered structures in comparison with the ARUPS measurement of Sakamoto *et al.*[8] and also give the characteristic surface-state bandwidths in Table IV. In the figure, for the best comparison with the calculated bands, we shift rigidly the experimental data[26,27] by -0.33, 0.24, and -0.05 eV for the MTL, π-bonded chain, and overlayer models, respectively. As shown in Fig. 6 and Table IV, the calculated dispersions and bandwidths of the occupied surface states for the MTL model agree best with the ARUPS data. With the surface bandwidths a little smaller than the experimental values, the overlayer model is also acceptable in view of the the comparison of the surface-band structure. In the case of the π-bonded chain model, however, there is noticeable disagreement in S_2 with the experiment: the calculated dispersion does not match the experimental one (especially, along $\bar{B}$-$\bar{M}'$) and its width of 0.97 eV is too large for the measured 0.48 eV. In conclusion, based both on the energetics and on the spectroscopic examination, we propose the buckled MTL structure as the ground-state structure of AM/Si(111)-(3×1).

IV. DISCUSSION

Unlike our conclusion in the previous section, Erwin[16] recently proposed the π-bonded chain model as the ground-state structure from the pseudopotential LDA total-energy calculations for the AM (Li, Na, K, and Rb) adsorbed Si(111)-(3×1) surface. But, his energetics argument does not appear very decisive, since the energy difference (between the MTL and π-bonded chain models), which ranges from 0.01–0.10 eV/AM according to adsorbates, is quite small (in particular, 0.01 eV for Li and Na adsorption). His primary argument in favor of the π-bonded chain model is that its simulated STM image shows a double row structure, in contrast to the case of the buckled MTL model, where only single rows of spots appear due to the large height difference between bonded Si atoms. We should address, however, that since the STM image is not a real topograph of a surface, but a local density of states,[28] it is indirect and can sometimes be misleading. For example, it is well known that the asymmetric dimer of Si(001)-(2×1) appears symmetric in room-temperature STM. The possibility, therefore, cannot be excluded that the double row can be obtained in the MTL model through surface-tip interaction[29] or thermal flipping of top-layer Si chains.[30,31]

Using a combination of core-level photoemission and STM, Paggel *et al.*[13] showed that the alkali metal-induced structural phase transition from Si(111)-(7×7) to Na/Si(111)-(3×1) proceeds exclusively through the step edges. The transition involves a mass transport[32] out of (7×7)-reconstructed domains for a conversion into the (3×1) domains. Since the number of Si atoms in the MTL model deviates much from that of the clean (7×7) phase while the π-bonded chain and overlayer models have the similar number of Si atoms to the (7×7) phase,[33] the observation reporting the mass transport supports the MTL model for the AM/Si(111)-(3×1) surfaces.

V. SUMMARY

In summary, we have proposed a *buckled* missing-top-layer structure as the ground-state atomic geometry for the Na- and K-covered Si(111)-(3×1) surfaces at the coverage of 1/3 ML, based both on the energetics and on the comparison of the calculated electronic structures with the recent ARUPS data. We have demonstrated that this model provides a consistent theoretical explanation of the measured structural, chemical, and electronic properties of the AM/Si(111)-(3×1) surfaces.

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[15] In fact, a variation of the π-bonded chain model where Na sub-

stitutes a surface Si atom was also proposed in Ref. 10, but this structure was found to be highly unstable in our calculation and so was ruled out in the present discussion.

[16] During the preparation of the manuscript, we saw another pseudopotential calculation for AM/Si(111)-(3×1) [S. C. Erwin, Phys. Rev. Lett. **75**, 1973 (1995)]. In the paper, they proposed the π-bonded chain model as the ground-state structure based on the energetics and the calculated electronic structures.

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[22] When we increase the size of the slab from 10 to 12 Si layers, we see that the change of the energy difference between the π-bonded and overlayer models is negligible (less than 0.01 eV).

[23] Our previous calculations (Ref. 12) using these parameters were found to produce converged structural and electronic properties of the Na/Si(111)-(3×1) surface. However, since Erwin made a different conclusion (Ref. 16) using the plane-wave cutoff energy of 12 Ry, we carry additional total-energy calculations by increasing from 10 Ry to 12 Ry, which show that our energetics does not change within 0.01 eV.

[24] There are two similar threefold sites at Si(111)-(1×1): the filled (T_4) and hollow (H_3) sites. We found in our work of Ref. 12 that T_4 and H_3 are equally stable for Na adsorption and have very similar bonding geometries and electronic structures. In the present study, therefore, we focus only on the T_4 site.

[25] Electronic structures of the π-bonded chain and overlayer models for the Na adsorption are not shown, since they are very similar to those for the K case, as will be shown shortly, except for the fact that the Na-induced surface band is about 1 eV higher in energy than the K-induced one.

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[33] The dimer-adatom-stacking fault (DAS) model [K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, Surf. Sci. **164**, 367 (1985)] has 12 atoms in the adatom layer, 42 atoms in the rest atom layer, and 48 atoms in the layer containing the stacking fault. Adding these figures is equal to 2×49+4, which means that the DAS model has an extra four (about 8% more) Si atoms in a (7×7) unit cell compared to the ideal structure containing the same number of Si atoms as the π-bonded and overlayer models. Because it has two more Si atoms in a unit cell (67% more), only the MTL model contains a much different number of Si atoms from the clean (7×7) phase.