New Structural Model for the Alkali-Induced Si(111)-(3 × 1) Reconstruction from First Principles

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A new structural model is proposed for the alkali-induced Si(111)-(3 × 1) reconstruction, based on a natural extension of the Si(111)-(2 × 1) π-bonded chain reconstruction. First-principles total-energy calculations for several alkali adsorbates show this model to be stable relative to previously proposed models. The calculated electronic dispersion is in quantitative agreement with photoemission data, and simulated scanning-tunneling microscopy images largely reproduce those of experiment.

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The Si(111) surface is unstable when cleaved, and reconstructs to a surface whose microscopic structure and electronic properties are strongly dependent on temperature. A reconstructed surface with 2 × 1 periodicity is stable at low temperature; this converts upon heating to an intermediate 5 × 5 structure and, finally, to the well-known 7 × 7 ground-state structure. All of these reconstructions have been well characterized experimentally and theoretically. The picture is complicated by the presence of adsorbates, however, for which the dependence on adsorbate species, coverage, and deposition schedule leads to a much richer phase diagram. For metal adsorbates in particular, the competition between Si-Si and Si-metal bonding may be quite subtle, leading to new phases not found on the clean surfaces [1].

One such phase is the metal-induced M/Si(111)-(3 × 1) reconstruction (where M = Li, Na, K, Ag), which has received considerable experimental attention over the past 15 years. This phase is typically prepared by the annealing of Si wafers in ultrahigh vacuum to generate the 7 × 7 surface, followed by metal deposition at substrate temperatures in the desorption regime; this leads to a 3 × 1 phase that remains stable at room temperature. The atomic geometry of this phase is controversial, and no existing structural model adequately accounts for all of the experimental data. In this Letter, a new structural model is proposed for the alkali-induced Si(111)-(3 × 1) phase, based on a natural extension of the well-established π-bonded chain reconstruction of clean Si(111)-(2 × 1). The stability of this new model is strongly supported by first-principles total-energy calculations, and it successfully accounts for most if not all of the available experimental data.

To set the stage, the results of various surface probes are first reviewed briefly. (1) LEED I-V curves for the M/Si(111)-(3 × 1) phase (abbreviated M:3 × 1) with M = Li, Na, and Ag are essentially identical [2]. This suggests a size-independent interaction of the adsorbate with the surface, and points, in particular, to a unique M:3 × 1 reconstruction for which the size of the adsorbate is relatively unimportant. (2) Oxygen uptake measurements indicate that the 7 × 7 $\rightarrow$ 3 × 1 conversion is accompanied by a strong reduction in the density of surface dangling bonds [3]. (3) Comparison of Auger data for Ag:3 × 1 and Ag:7 × 7 leads to the conclusion that the absolute metal coverage for this phase is Θ = 1/3 monolayer (ML) [4,5], consistent with the results of coaxial impact-collision ion scattering spectroscopy [6]. (4) Scanning-tunneling spectroscopy (STS) I-V curves for Na:3 × 1 show a clear energy gap of 0.7–0.8 eV, which closes only upon completion of a second Na layer. (5) Ultraviolet photoemission spectroscopy measurements on K:3 × 1 confirm the semiconducting electronic structure of this phase, and x-ray photoemission spectroscopy data are consistent with a saturation coverage of 1/3 ML [7]. Angle-resolved ultraviolet photoemission spectroscopy reveals surface states within 2 eV of the Fermi level, with dispersion along the $[1\bar{1}0]$ direction (parallel to the rows) in the range 0.3–0.5 eV. (6) Filled-state scanning-tunneling microscopy (STM) images for Li:3 × 1 [8], Ag:3 × 1 [8], and Na:3 × 1 [9] all show similar structure: double rows of maxima, resembling zigzag chains with the spacing of equilateral triangles, commensurate with the bulk-terminated surface. Empty-state images for Li:3 × 1 and Ag:3 × 1 are also similar, appearing as single narrow lines with small side spurs [8].

The first proposed structural models for the M:3 × 1 phase featured single rows of adsorbates at a coverage of Θ = 1/3 ML, with the adsorbate located at the top site [10] or a threefold site [11] of the bulk-terminated surface. Since the unreconstructed surface consists entirely of six-member rings of Si, this model has a surface layer which can be denoted simply as "...666666...." Fan and Ignatiev later proposed a simple missing-row model (denoted "...660660...") to account for the double rows observed in STM, without specifying the metal coverage or adsorption site [2]. Recently, several groups independently proposed a structure that is a variant of the Seiwatz chain [12], consisting of parallel π-bonded chains formed by five-member rings of Si, separated by empty channels (...500500...), with a top-site adsorbate saturating the surface dangling bond [5,7,13].

The new structural model proposed here can best be described as an extension of Pandey's π-bonded chain model [14], which is widely accepted as the atomic geometry of the clean Si(111)-(2 × 1) reconstruction. The 2 × 1 Pandey model consists of alternating seven-member and five-member rings (...757575...). The M:3 × 1 extension of this model, hereafter referred to as the "extended Pandey chain," simply inserts a six-member ring into this sequence (...765765...). One expects this geometry to be energetically favorable: the 2 × 1 π-bonded chain is known to be stable, and the addition of a six-member ring provides a single surface dangling bond to serve as an adsorption site, consistent with $\Theta = 1/3$ ML. The Seiwatz chain model, although also passivated, is expected to be energetically less favorable, because the five-member rings create a buckling surface stress that is unrelieved in the absence of seven-member rings. The bulk-terminated and missing-row models are expected to be still less stable, since simple valence-bond counting suggests surface dangling-bond densities of 2 and 4 per 3 × 1 cell, respectively.

The above arguments, although naive, in fact correctly predict the energy ordering given by first-principles total-energy calculations with full structural relaxation. The calculations were performed with the Corning electronic-structure code of Teter, Payne, and Allan [15], which solves the Kohn-Sham equations in the local-density approximation (LDA) with a plane wave basis, using norm-conserving pseudopotentials of Teter [16]. Six different structural models were considered: the four discussed above, plus substitutional versions of the extended Pandey and Seiwatz models in which the alkali substitutes for the surface silicon atom in the six-member ring. To investigate the possibility of adsorbate dependence, independent calculations were performed for Li, Na, K, and Rb adsorbates (the first three have been observed experimentally, while Rb has not yet been studied). For each of the structural models, supercells with inversion symmetry were formed from eight layers of bulk Si plus the reconstructed surface layer, with a vacuum layer equivalent to four Si layers. Several starting locations were explored for the adsorbates, each near—but not on—a high-symmetry site. In this way, barriers to adsorbate movement on the surface were circumvented, and a mirror plane normal to $[1\overline{1}0]$ was not built into the calculation, but rather emerged naturally. The kinetic-energy cutoff was 12 Ry, and four equidistant k points were used throughout [17]. Full structural relaxation was performed until the rms force was less than 0.05 eV/Å.

Typical fully optimized structures are shown in Fig. 1 for Li adsorbates, for all but the substitutional models (whose relaxed geometries are similar to their nonsubstitutional counterparts). In each case, only the geometry corresponding to the adsorption site with the lowest total energy is pictured. Since each model contains a different number of Si atoms, N, the relevant surface energy to compare across models is given by $E_s = [E_t(N) - NE_t^{\mathrm{bulk}}]/2$, where E_t^{bulk} is the total energy per atom of bulk Si, computed using the same lattice vectors, energy cutoff, and zone sampling as for the surface calculations, and the factor of 2 accounts for the two surfaces per unit cell. The relative surface energies are listed in Table I. As expected, for each of the four alkalis the extended Pandey chain is the lowest-energy model, followed by the Seiwatz chain model; the bulk-terminated surface, the missing-row models, and the substitutional models are substantially higher in energy.

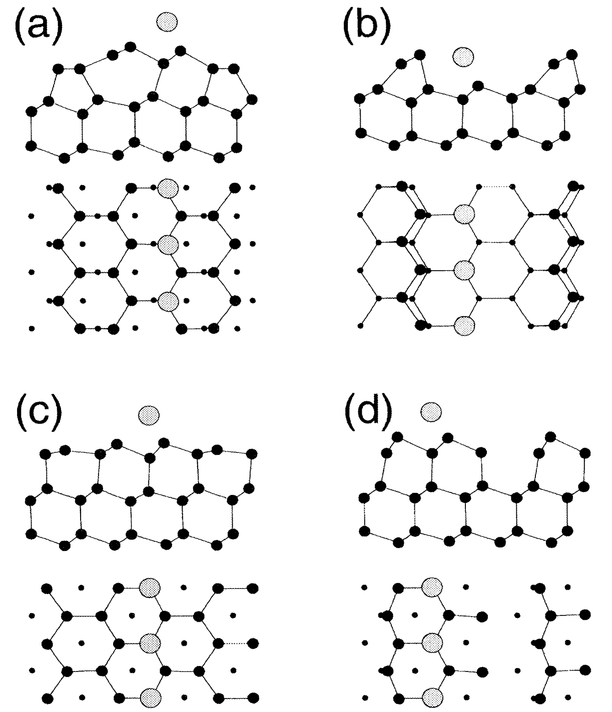

FIG. 1. Fully relaxed geometries for four of the six structural models considered: (a) extended Pandey chain, (b) Seiwatz chain, (c) bulk-terminated surface, and (d) simple missing row. The gray circles are Li adsorbates.

For the nonsubstitutional models considered here, the lowest-energy adsorption site is the T_4 (the threefold-coordinated site above a second-layer Si atom). This contradicts other proposed models [5,7,10,13], but is consistent with theoretical LDA studies of alkali adsorption on unreconstructed Si(111) [18]. Clearly, passivation by an alkali is not as simple as for hydrogen, where the adsorption does occur at the top site [19]. The adsorption at a threefold site also has a strong effect on the detailed arrangement of Si atoms, creating a puckering of the surface near the adsorbate. This effect is clearly evident in Fig. 1, and is particularly dramatic for the extended Pandey and Seiwatz models: indeed, when the adsorption is at the other available threefold site, the asymmetry in the π-bonded chain is opposite to that shown. This puckering strongly suggests that the alkali s electron is donated to empty Si surface states and that the resulting ionic attraction to the adsorbate ion causes the observed puckering.

TABLE I. Surface energies E_s (relative to the extended Pandey chain) and band gaps E_g for fully relaxed models of M/Si(111)-(3 × 1). Several of the relaxed structures for Li adsorbates are pictured in Fig. 1. All energies are in eV.

M	Reconstruction	Ring structure	E_s	E_g
Li	Extended Pandey chain	...765765...	0	0.36
Li	Seiwatz chain	...500500...	0.01	0.30
Li	Bulk terminated	...666666...	0.30	0
Li	Pandey substitutional	...705705...	1.35	0
Li	Simple missing row	...660660...	1.51	0
Li	Seiwatz substitutional	...500500...	1.58	0
Na	Extended Pandey chain	...765765...	0	0.39
Na	Seiwatz chain	...500500...	<0.01	0.26
K	Extended Pandey chain	...765765...	0	0.42
K	Seiwatz chain	...500500...	0.08	0.25
Rb	Extended Pandey chain	...765765...	0	0.37
Rb	Seiwatz chain	...500500...	0.10	0.25

Moreover, the binding of the adsorbate to the surface is sufficiently strong to overcome the ion-ion Coulomb repulsion: total-energy calculations on doubled cells (with 3 × 2 periodicity) in the Pandey geometry show no tendency for the alkalis to form zigzag chains.

Comparison of experimental and theoretical electronic band structures also favors the extended Pandey model. The energy gap for the Pandey model ranges from 0.36–0.42 eV (indirect) for the different alkalis; this is consistent with the measured STS values of 0.7–0.8 eV if one allows for the usual LDA gap underestimate. For the Seiwatz model the gap is ~30% smaller, ranging from 0.25–0.30 eV (direct, at Γ). Not surprisingly, the bulk-terminated surface, the missing-row model, and the substitutional models are all metallic. Figure 2 shows the surface-state dispersion for the extended Pandey model. One of the two occupied surface states disperses downward for wave vectors approaching the zone boundary, in good agreement with recent angle-resolved photoemission data on single-domain Li:3 × 1 [20].

Closely related to the surface electronic structure is the adsorbate-induced work-function change $\Delta\Phi(M)$. Experimentally, $\Delta\Phi(\text{Na}) = -1.0$ eV and $\Delta\Phi(\text{K}) = -1.4$ eV, relative to clean 7 × 7 [5]. Preliminary LDA calculations for the extended Pandey model give $\Delta\Phi(\text{Li}) \approx -1.0$ eV, relative to the zero-coverage 3 × 1 surface. While not directly comparable to the experimental data, this result is consistent with the small measured work-function change.

Although the geometry of the 3 × 1 extended Pandey chain is analogous to the 2 × 1 Pandey chain, there are important differences between the two. Ancilotto *et al.* [21] have used *ab initio* molecular dynamics to show that the ground-state geometry of the 2 × 1 π-bonded chain has a chain-atom asymmetry opposite to that of the 3 × 1 chain shown in Fig. 1(a); this "chain-low" configuration is in agreement with experiment. They also found that the "chain-high" configuration is a local minimum only 0.005 eV/surface-atom higher in energy. For M:3 × 1,

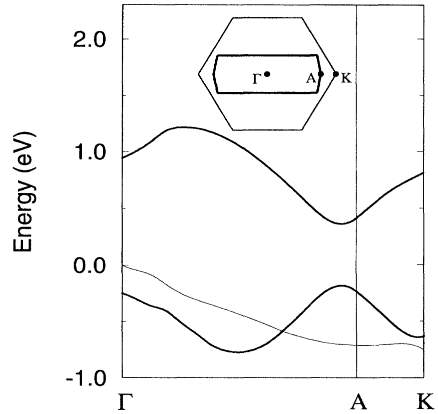

FIG. 2. Surface-state band structure for the fully relaxed extended Pandey chain with a Li adsorbate. Thick curves are states arising from Si atoms in the π-bonded chain; the thin curve arises from the surface Si atom in the sixfold ring. For other alkalis, the surface-state bands are very similar. Inset: surface Brillouin zones for 3 × 1 (thick outline) and 1 × 1 surfaces (thin outline).

the puckering effect of the adsorbate ion is at least partially responsible for reversing the energy ordering of the chain-high and chain-low configurations. This in turn has important consequences for determining which Si atoms are imaged in STM, as will be demonstrated below.

The availability of atomically resolved STM images of M:3 × 1 has both guided and hindered the construction of structural models for this phase. Jeon *et al.* attributed the double rows of bright spots in filled-state images of Na:3 × 1 to Na zigzag chains, and concluded on this basis that the saturation coverage was in fact 2/3 ML and that adsorption occurred without reconstruction of the underlying Si surface [9]. The narrow dark channels in filled-state images have suggested structural models with missing rows (the Seiwatz model and the simple missing-row model). The present work does not support this interpretation, however: The missing-row model has a total energy far too high to be a plausible candidate, while for the optimized Seiwatz model, the large difference in the height of the chain atoms ($\Delta z = 0.64$ Å for Li) makes it very unlikely that both atoms would be imaged at the same bias.

The key to understanding the filled-state STM images is to recognize that the observed double rows are *not* the signature of a π-bonded chain. As Stroscio and Feenstra have demonstrated, the 2 × 1 π-bonded chain leads to filled- and empty-state images which *both appear as single rows* of bright spots, 180° out of phase along the row direction [22]. Even if one naively regards the 3 × 1 double rows as a map of the Si atomic positions, the observed ratio of lateral to longitudinal spacing (approximately equilateral triangular) is incompatible with a π-bonded chain, for which the ideal bond angle is not 60°, but rather the tetrahedral angle, 109.47°. All of these difficulties are resolved by the extended Pandey model. In the geometry of Fig. 1(a) the two highest Si atoms (i) have a small height difference, $\Delta z = 0.28$ Å; (ii) are not both members of a π-bonded chain; and (iii) form a nearly equilateral bond angle of 61°.

Numerical simulations of STM images support this argument. Figure 3 shows contour maps of the local-state density, $\rho(r,\varepsilon) = \sum_{nk} |\psi_{nk}(r)|^2 \delta(\varepsilon - \varepsilon_{nk})$, integrated over states near ε_F, at a fixed height above the surface. The filled-state image clearly shows a double row of equilateral triangular spots, which arises from the occupied surface states associated with the two highest Si atoms (marked by arrows). The absence of any contribution from the adsorbate confirms the earlier hypothesis that the alkali s electron is donated to Si surface states. The simulated empty-state image appears as single rows of spots with small lateral protrusions, in agreement with the observed empty-state STM images [8]. Simulated images for the other alkalis are very similar, with only minor differences. In contrast, simulated images for the Seiwatz model show single rows of spots (reflecting the much larger surface-atom height difference), in sharp contradiction with all experimental STM data.

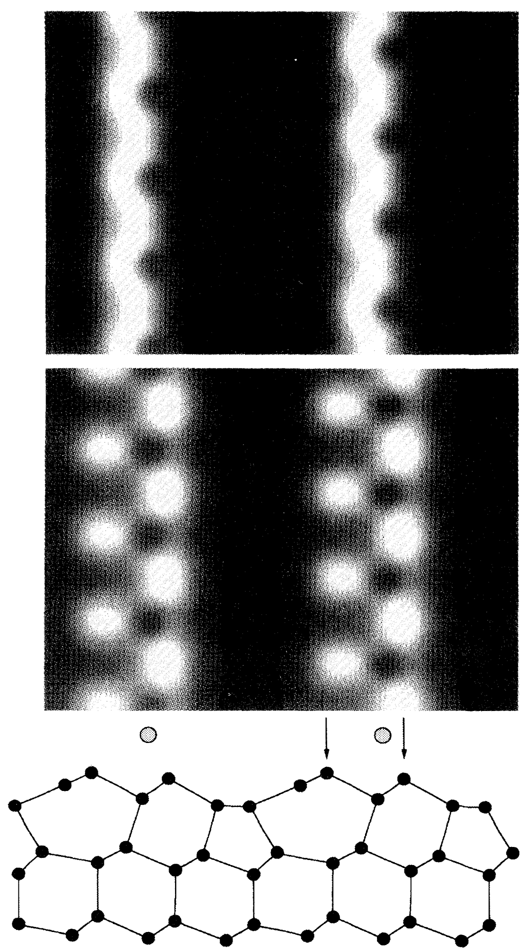

FIG. 3. Simulated STM images for Li/Si(111)-(3 × 1). The empty-state image (top) is simulated by integrating $\rho(r,\varepsilon)$ from ε_F to $\varepsilon_F + 1.0$ eV; for the filled-state image (bottom) the interval is from $\varepsilon_F - 2.0$ eV to ε_F. The registry with the atomic geometry is shown at bottom.

In summary, a new structural model has been introduced for the alkali-induced Si(111)-(3 × 1) reconstruction. This model, an "extended Pandey chain," has a lower total energy than any previously proposed model consistent with the experimentally determined coverage of 1/3 ML. The role of the adsorbate is primarily that of an electron donor and dangling-bond passifier. The ionically bound adsorbate strongly perturbs the surface geometry and electronic dispersion; all the alkali adsorbates considered here are found to behave in a very similar fashion, irrespective of their size. The calculated energy gap, surface-state dispersion, and simulated STM images are in excellent agreement with the experiment.

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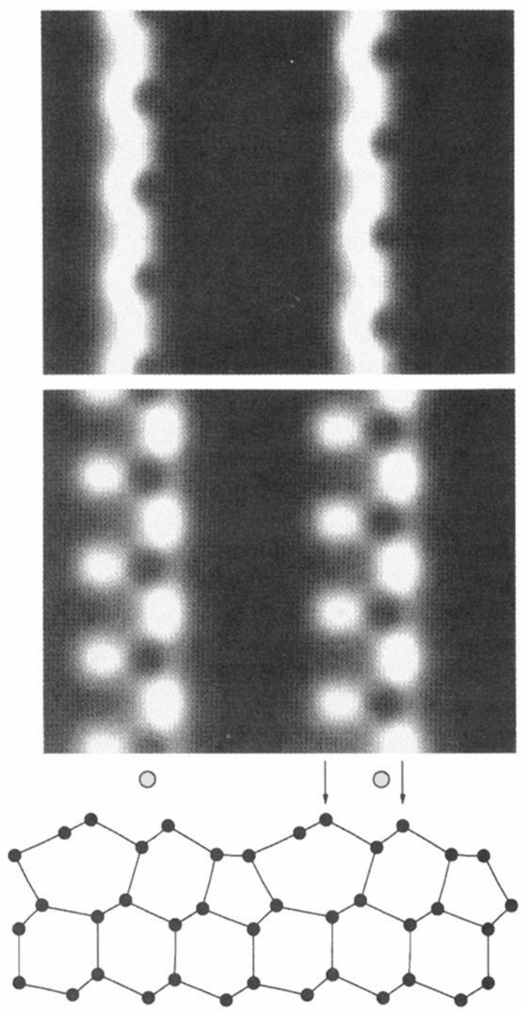

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