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Si(111):Na: Structural and electronic properties from *ab initio* molecular dynamics

Isabelle Moullet,* Wanda Andreoni,† and Michele Parrinello
IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

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We present an *ab initio* molecular-dynamics (Car-Parrinello) study of Na adsorption on Si(111). For one-monolayer coverage the bulk-terminated surface does not reconstruct, in agreement with recent low-energy-electron-diffraction data. The equilibrium Na geometry largely confirms Northrup's predictions with an albeit partially ionic bonding. Energy bands are in excellent agreement with angle-resolved photoemission. Temperature effects and metastable configurations on the 1×1 and 2×1 phases are discussed. For half-monolayer coverage, the 1×1 structure is predicted to be unstable.

Alkali-metal adsorption on semiconductor surfaces is a subject of wide and growing interest[1] owing to the prototypical nature of the physical system and to the general technological interest in metal-semiconductor interfaces. One of the relevant issues is the suppression of the semiconducting properties of the surface and the advent of metallization in the substrate and/or in the metal layers, as well as its dependence on the metal coverage. In order to develop some understanding of this process, electronic and structural studies must be performed which require especially accurate experiments as well as theoretical techniques of proved predictive power. From the experimental side, in particular, photoelectron spectra have been measured for Si(111) with K,[2] Cs,[3,4] and more recently Na (Ref. 5) adsorbates. At the low coverage corresponding to the minimum of the work function (monolayer regime), Si(111):Na and Si(111):Cs appear to be semiconducting, while Si(111):K is metallic. Also, interestingly, low-energy-electron-diffraction data show that the silicon surface layers present a different structural pattern in the three cases.[2-5] In fact, starting with a 2×1 reconstructed clean silicon surface, this is observed to retain the same periodicity after adsorption of potassium, while it recovers the ideal pattern in the case of Na and transforms to a $\sqrt{3}\times\sqrt{3}$ periodicity when Cs is adsorbed.

Theoretically, the issue of the stability of the 2×1 reconstructed surface under alkali-metal chemisorption has been studied only partially, on the basis of static energy calculations.[6-8] In particular, for the case of K,[8] local-density-approximation- (LDA) pseudopotential energy calculations indicated that, for a coverage corresponding to half-monolayer, the ideal surface provides at least one more favorable configuration for the K atoms than the 2×1 reconstructed one. Moreover, in this case, the bonding between the metal and Si was predicted to be ionic, thus prompting a debate about the complex nature of this chemistry which clearly must depend on the specific metal, the specific surface, and the specific coverage.

Static calculations of Si(111):Na have also been performed for the ideal Si surface with the pseudopotential-LDA approach by Northrup[9] and more recently within the linear-muffin-tin-orbitals–LDA scheme by Ossicini, Arcangeli, and Bisi.[10] There are three high-symmetry positions available to the sodium atoms: the onefold-top site (OTS), the threefold-filled site (TFS), and the threefold-hollow site (THS). The calculations in Ref. 9 made with the silicon atoms kept on the bulk positions predict the THS as the energetically favored one. In Ref. 10 the nature of the Si—Na bond has been investigated for the THS and TFS geometries, however keeping the first Si-Na distance at a fixed value (5.12 a.u.). In both cases, the type of bonding turned out to be only partly ionic.

In this paper, we consider the system Si(111):Na and treat it with the Car-Parrinello method[11] which has recently been applied successfully to the study of the 2×1 reconstruction of Si(111).[12] In particular, starting from the clean ideal surface of silicon, a spontaneous transformation was observed to the 2×1 Pandey chain structure.[13] In the present work, we have attempted the same type of calculation and performed a dynamical simulated annealing search for the equilibrium structure. In contrast with the case of the clean surface, the presence of one monolayer of sodium [i.e., one Na per Si dangling bond, $\Theta=1$ (Ref. 14)] stabilizes the ideal structure in agreement with the experimental findings of Reihl *et al.*[5] Our calculations confirm Northrup's result for the equilibrium position of the sodium atoms but predict a larger Si-Na distance. The calculated energy band for the surface occupied states appears to be in excellent agreement with experimental data.[5] A partial study of the sodium adsorption on the 2×1 modification suggests that this is unfavored energetically. In particular, a configuration with the Na atoms near the THS would correspond to a local minimum, but is high in energy ($\simeq 0.5$ eV per Na atom). Preliminary results for the case of half-monolayer coverage ($\Theta=\frac{1}{2}$) suggest that the ideal structure is unstable and that a reconstruction process must occur, which looks more complex than the 1×1→2×1 transition.

The computational details are the same as in Ref. 12. The geometry used consists of a periodically repeated slab of one layer of sodium ($\Theta=1$ or $\frac{1}{2}$), eight layers of silicon, one layer of H atoms used to passivate the dangling bonds on the silicon atoms, and a vacuum region of ~15 a.u. The periodicity of our supercell is $\sqrt{3}\times4$, i.e., one commensurable with both the ideal and the 2×1 phases. The $k=0$ Bloch wave functions of this cell are expanded in plane waves with a cutoff of 8 Ry. Convergence with respect to the number of k points was tested in the same way as in Ref. 12, i.e., with static calculations performed on a smaller unit cell and for different meshes. The presence of a non-negligible dipole at the Na-Si interface has required an additional test for the width of the vacuum region. We have checked, for instance, that structural energy differences are unaffected by the increase from ~ 15 to ~ 21 a.u. Angular-momentum-dependent pseudopotentials describe the electron-ion interaction, with s nonlocality. In the case of Na, the pseudopotential used[15] was derived by including the nonlinear core correction in the exchange correlation functional.[16] The standard linear approximation is known to give a contraction of the atomic size for the alkali metals.[17,18] Parameters and tests of the Na and Si pseudopotentials are given in Refs. 18 and 19, respectively. The input data of the molecular dynamics runs are a time step of 1.4×10^{-1} psec and $\mu=500$ a.u.

We started our calculations with the Si atoms on the ideal positions of the (111) truncated bulk and the Na atoms on the OTS's. Both the Na atoms and six layers over eight of the silicon atoms were allowed to readjust. This has proven to provide a good approximation to the semi-infinite system in determining the structure and dynamics of the clean surface.[12] A simple steepest-descent relaxation resulted mainly in a significant shrinking of the first silicon interlayer separation (by ~ 0.16 a.u.), which corresponds to a decrease of the Si—Si bond lengths by ~ 0.1 a.u. We note that a similar bond-shortening effect (by ~ 0.15 a.u.) was obtained for the ideal uncovered Si(111) surface when constrained to remain in a 1×1 structure.[12] The compression of the first layer of the 1×1 structure is indeed a well-known effect[20] on the clean surface and in the case of substitutional chemisorption. We then let the atoms move freely under the action of the forces, and observed an increase of the kinetic energy. This was accompanied by a rapid readjustment of the atomic positions, with the Na atoms moving from the OTS's to the THS's. We also performed a separate simulated annealing search for the lowest-energy configuration and heated the system up to ≈ 800 K. By following the atomic trajectories, we noticed that the sodium atoms were diffusing over different positions (resembling the high-symmetry threefold ones), while the displacement of the silicon atoms was relatively limited, one order of magnitude smaller than that of sodium. This was a clear indication of the weak dependence of the structure of the substrate from the bonding with Na and also, at least within the time of our observation, of the stability of the ideal 1×1 phase in the case of full Na coverage. At high temperatures (700–800 K) the system was stable in configurations already close to the THS. The positional disorder was mainly confined to the sodium layer. Once quenched, an ordered arrangement of the sodium atoms was obtained at THS-like positions.

TABLE I. Characteristics of three configurations. N_{coord} is the first Si-Na coordination number, $d_{\mathrm{Si\text{-}Na}}$ is the bond length, d_z is the distance between Na layer and substrate, ΔE is the energy per Na atom relative to THS. Values in parentheses are from Ref. 9.

	N_{coord}	$d_{\mathrm{Si\text{-}Na}}$ (a.u.)	d_z (a.u.)	ΔE (eV)
THS	3	5.65 (5.1)	3.8 (2.9)	0 (0)
TFS	1,3	5.63, 5.83	4.05	0.06 (0.12)
OTS	1	5.37	5.37	0.50 (0.6)

We have further relaxed the THS and the TFS configurations. In both cases, we found that the relaxed structure presented a slight distortion of the silicon layers along the $[11\bar{2}]$ direction and that the undistorted geometry was higher in energy only by 0.007 eV per Na atom, i.e., almost degenerate within the accuracy of the calculations. Such a distortion was, however, an artifact of our choice of the supercell. Further static calculations made with a smaller unit cell and a larger k-point sampling (8 and 15 k points in the irreducible surface Brillouin zone) predicted the undistorted structures to be lower in energy but only by 0.007 eV per Na atom.

Table I contains a comparison of the geometrical parameters and energies of the OTS, TFS, and THS configurations, which we find to be a saddle point and local minima of the potential energy surface, respectively. Contrary to the case of substitutional adsorption (OTS), in both the THS and TFS configurations sodium adsorption induces a small expansion of the first interlayer distance (by 0.04 and 0.10 a.u., respectively). While the instability of the OTS configuration can be easily expected on simple geometrical grounds ($N_{\mathrm{coord}}=1$), it is difficult to identify the reason for the preference for the THS with respect to the TFS, since the energy balance is rather delicate as also indicated by the small energy difference. In fact, for instance, the TFS provides a larger average coordination, but (as a consequence) the average Si-Na distance increases (by ~ 0.1 a.u.). Also, on passing from TFS to THS, no change in the silicon substrate takes place, apart from a tiny elongation of the Si—Si bonds (0.02 a.u.).

The relative stability of the three configurations appears to be determined by the Na-Si interaction. In fact, the Na-Na distances are the same in the three cases (7.26 a.u.) and separate calculations keeping the silicon atoms at the positions of the bulk-terminated surface yield structural energy differences which are essentially unaltered with respect to the values in Table I. These calculations also show that the relaxation of the substrate induces only a tiny variation in the positions of the sodium atoms.

We have calculated the binding energy of the Si(111):Na system (THS) with respect to the equilibrium structure of the clean (2×1) surface[12] and the isolated sodium atoms treated in the local-spin-density approximation. Our value is ~ 2.1 eV. The contribution from the relaxation of the substrate amounts to only 0.02 eV.

In Table I we also compare our results with those of Northrup[9] which were obtained with a different type of slab and with unrelaxed Si structure. In our calculations, the energy difference between TFS and THS is smaller (by a factor of 2) and the Si-Na distance is ~ 0.55 a.u.

larger.[21] A further difference exists in the calculated binding energy. The value reported in Ref. 9, referred to the bulk-truncated surface, is 2.05 eV. In our scheme this is 2.5 eV.

We have investigated the nature of the Si—Na bond through an analysis of the electron density distribution. Figure 1 shows, in the case of the THS configuration, a planar projection of the difference density $\Delta\rho(\mathbf{r})$ calculated taking as reference the superposition of the charge densities of the clean surface with the silicon atoms in the positions of our equilibrium structure $\rho_{\text{Si}}(\mathbf{r})$ and of the sodium atoms $\rho_{\text{Na}}(\mathbf{r})$. As expected, it is mainly localized at the Si-Na interface, does not have a specific directional character, and manifests the presence of charge transfer from the sodium layer to the interface region. In order to obtain an estimate of the charge transfer and of its localization, we have calculated the average $\overline{\Delta\rho}(z)$ of the difference electron density over planes parallel to the surface and the integral

$$I=\int_{\text{vacuum}}^{z_{\text{Na}}}\overline{\Delta\rho}(z)dz\Big/\int_{\text{vacuum}}^{z_{\text{Na}}}\overline{\rho_{\text{Na}}}(z)dz\ , \qquad (1)$$

where z_{Na} is the position of the sodium layer. As can be seen in Fig. 2 the charge transfer is mostly confined to the first Si layer and $I \sim 25\%$. The same is true for the TFS configuration. Our findings are in agreement with the results of Ossicini, Arcangeli, and Bisi.[10] In the case of the OTS geometry, instead, the estimated value of I is lower (18%): this may also be viewed as a factor responsible for the destabilization of the OTS configuration.

In Fig. 3 we report the calculated energy bands along two symmetry directions of the 1×1 surface Brillouin zone and compare them with the angle-resolved photoemission data of Reihl *et al.*[5] The system is correctly predicted to be nonmetallic, with an energy gap of ≈ 1 eV at Γ. Also for the adsorbate-induced surface-state band the agreement is apparently very good. We notice a slightly larger dispersion in the experimental data. The nature of the surface states and their localization also deserves some comments, in particular as to their character and localization changes depending on the k point. For instance, at the M point the surface state appears to contribute to the Si—Na bond and is not simply confined to the sodium layer. In contrast, a state near the resonance (e.g., half-way along the ΓK direction) has a dominantly bulklike character as expected for resonant states.

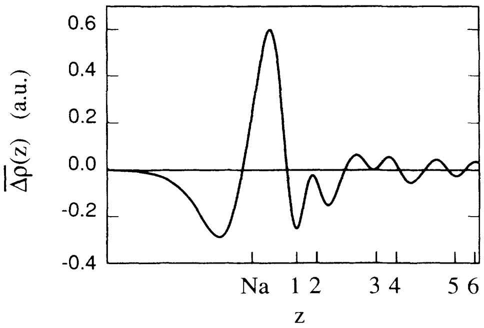

FIG. 2. Average of the difference electron density over planes parallel to the surface $\overline{\Delta\rho}(z)$. z_{Na} indicates the position of the sodium layer. Numbers from 1 to 6 indicate the positions of the first to the sixth silicon layers.

We have studied finite-temperature properties by equilibrating the system around 300 K and following its evolution for ~ 1 psec. Hence two facts were established: the stability of the 1×1 structure and the permanence of the sodium atoms around the THS positions. The limited length of the run and the small size of the system do not,

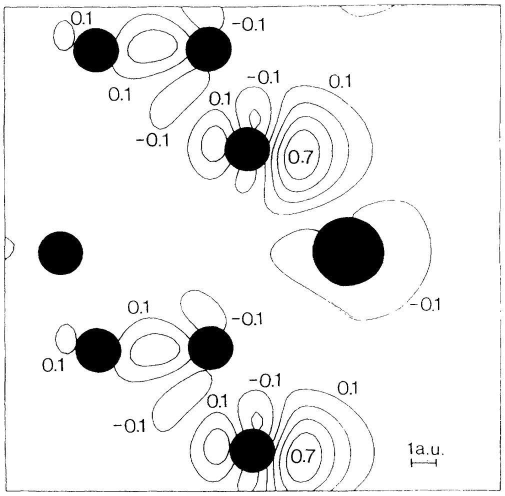

FIG. 1. Difference charge density projected on the plane defined by the [111] and [11$\bar{2}$] directions in the equilibrium structure. Units, $100e/(\text{a.u.})^3$.

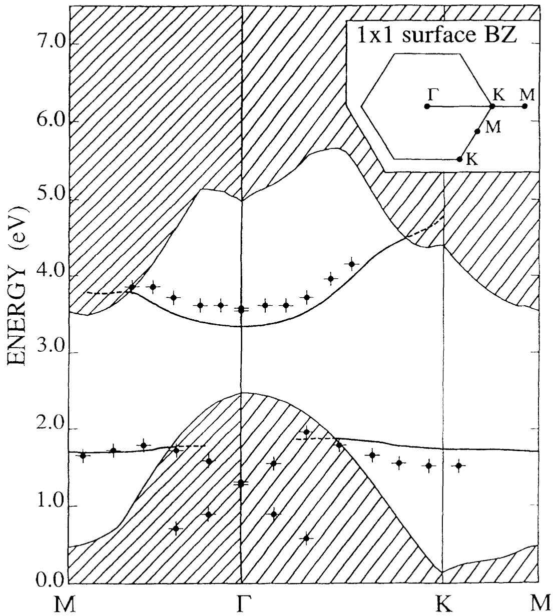

FIG. 3. Energy bands in the equilibrium configuration. Shaded areas, projected bulk bands. Bullets, experimental data from Ref. 5.

however, allow the unambiguous determination of other finite-T properties.

In order to investigate the possibility of a low-energy configuration of the adsorbate on the 2×1 reconstructed surface, we have considered the silicon atoms in the equilibrium positions determined in Ref. 12 and put the sodium atoms again on the THS's. Relaxation, followed by "free" dynamics, resulted in a configuration still similar but of lower symmetry. This is higher by 0.55 eV per Na atom than our lowest-energy structure on the 1×1 surface. Comparison with the lower-energy structures on the ideal surface indicates that this configuration on the 2×1 provides a rather unfavorable environment for the Na atoms: for the two nonequivalent Na atoms $N_{\text{coord}}=2$ and 4 respectively, with $d_{\text{Si-Na}}=5.88$ and 6.20 a.u. Also, our estimate of the charge transfer yields a value of $I\approx10\%$, i.e., significantly lower than the apparently optimal 25% value. The two nonequivalent Na atoms have a large buckling (2.1 a.u.). The silicon geometry in this case appears to be significantly affected, in that the buckling of the first two layers increases by a factor of ~2 with respect to the calculated clean surface. Also, the relaxation of the substrate increases the binding energy by 0.1 eV per Na atom (i.e., by 7%). We also notice that, in spite of the preserved presence of fivefold and sevenfold rings characteristic of the chain structure, important distortions occur in the silicon layers. These can be viewed as signs of metastability.

Preliminary calculations indicate that a high barrier exists between the 2×1 and the 1×1, which is hard to overcome in our simulation. In fact, by heating the 2×1 system up to ≈2000 K and cooling it down, we have observed a transformation to a disordered state which still resembles the 2×1 but is highly distorted. It is probable that our limiting factor is the time of observation.

Attempts to study the structural stability of the ideal surface at lower coverage ($\Theta=\frac{1}{2}$) indicate that this is not stable but instead that a profound change of the structure takes place. The limitation of our unit cell does not allow us to determine which reconstruction the adsorbate may induce, but certainly this is not commensurable with our cell, since it results only in a significant disordering of the substrate.

In conclusion, we have determined the equilibrium structure of the Si(111):Na surface at one-monolayer coverage, which in agreement with experiment turns out to have the 1×1 periodicity. In trying to resolve the debate about the nature of the chemical bonding, we find that it cannot be classified as either purely ionic or covalent, in view of the limited charge transfer and of the absence of directional character. The weak role of the substrate in determining the relative stability of different configurations is also established. Reconstruction is predicted for the case of half-monolayer coverage.

For a more complete understanding of the alkali-metal adsorption on Si(111), calculations on the other systems are necessary since, as observed experimentally, they stabilize different structures of the substrate. Our preliminary calculations for the case of one-monolayer coverage of K show that, in clear contrast with the present results for Na, the THS configuration on the 1×1 and the 2×1 surfaces are almost degenerate.[22]

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[*] Present address: Section Physique, Université de Lausanne, 1015 Lausanne, Switzerland.

[†] Corresponding author, electronic address: AND@ZURLVM1.

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