Adsorption geometry and saturation coverage of Na on the Si(100)-(2×1) surface: First-principles calculations

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(Received 19 June 1991)

We have performed first-principles total-energy calculations for Na on the Si(100)-(2×1) surface at different coverages. At half-monolayer Na coverage [one Na atom per Si(100)-(2×1) unit cell], the most favorable adsorption site of Na is found to be the valley bridge site. At one-monolayer Na coverage [two Na atoms per Si(100)-(2×1) unit cell], the Na atoms occupy both the valley bridge sites and the pedestal sites. The one-monolayer-coverage models have substantially lower surface energies than the half-monolayer-coverage models, indicating that the saturation coverage should be one monolayer. We also found that the surface is metallic at half-monolayer Na coverage and semiconducting at one-monolayer coverage.

I. INTRODUCTION

Clean Si(100) surface has a well-known (2×1) reconstruction, in which the surface atoms are dimerized.[1] The dimerization is preserved upon the adsorption of alkali-metal atoms, and a (2×1) unit cell is usually found at saturation coverage. The alkali metal on the Si(100) system has attracted a fair amount of attention, because it can serve as a prototypical system for studying the metallization of semiconductor surfaces. Despite an abundance of experimental[2–11] and theoretical[12–17] efforts, a consensus is still lacking about many basic issues such as the equilibrium geometries, absorption sites, saturation coverage, and the nature of the metal-semiconductor bonding. The purpose of our study is to calculate the electronic and structural properties of alkali metal on Si(100) by accurate first-principles total-energy calculations, using Na on Si(100) as the prototype.

The geometry of the dimerized Si(100) substrate and the positions of various plausible absorption sites are illustrated schematically in Fig. 1. We have adopted the nomenclature of the surface sites that has been used extensively by other authors.[9,13,16] We will also use half (and one) monolayer coverage to indicate one (and two) Na adatoms per surface Si dimer.

Most of the earlier studies assumed that the alkali atoms reside on the *H* (pedestal) site.[2] Local density-functional calculations by Ciraci and Batra[13] reached the same conclusion. However, the cluster calculations of Ling, Freeman, and Delley[16] found the *B* site to be the most favorable site of adsorption. Scanning tunneling microscopy,[8] on the other hand, found Li and K atoms to adsorb at the atop site and stabilize buckled dimers at low coverages. The nature of the alkali-metal–Si bond is also controversial. Some authors concluded that the bonding is ionic, with the alkali atoms donating almost all the electrons to the Si surface,[13] while others[12] concluded that there is almost no charge transfer between the alkali metal and Si substrate. The metal–Si bond length found by various authors also varies substantially, from considerably smaller than the sum of the covalent radii[13] to equal to or even larger than the sum of covalent radii.[14,16] Most earlier studies found the saturation coverage to be half a monolayer while some recent experiments[4,11] put the coverage at one monolayer. K on Si(100) surface was reported to be semiconducting[3] by one group and metallic[6] by another. Na/Si(100) was found to be semiconducting.[10]

II. METHOD

The calculations are performed within the framework of the local density-functional formalism.[18] The Wigner interpolation formula[19] was used for the local exchange-correlation potential and norm-conserving pseudopotentials[20] are used. The calculations are fully self-consistent with eigenvalues and charge densities obtained on a uniform grid of 18 **k** points in the two-dimensional irreducible Brillouin zone. We employed a plane-wave basis set,

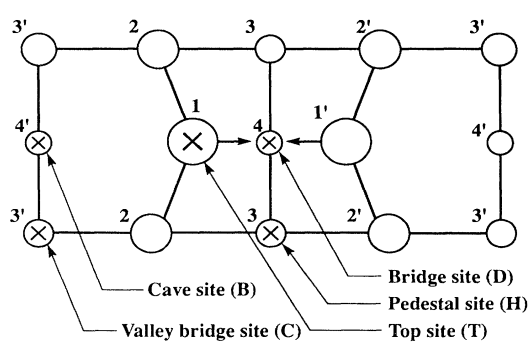

FIG. 1. Schematic top view of Na/Si(100), with the crosses marking various adsorption sites for the alkali atoms. The circles indicate the Si atoms, with the smaller size circles deeper into the bulk. The numbers mark the Si atoms in the *n*th layer. The Si atoms marked by *n* and *n'* are inequivalent if the dimer is asymmetrical.

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with kinetic-energy cutoff up to 10.5 Ry, corresponding to 2200–2400 plane waves in the unit cell. A "supercell" geometry is used and the unit cell consists of ten atomic layers (20 Si atoms), with a vacuum region equivalent in the thickness to six layers of Si separating the repeated slabs. We consider both half- and one-monolayer Na coverage models, which have one and two Na atoms on each surface in the (2×1) unit cell, respectively. Most of the plausible adsorption sites are considered. The forces are calculated with the Hellmann-Feynman theorem,[21] and all the atoms are relaxed until equilibrium is reached within the symmetry constraints of each model.

III. RESULTS

We will first present results about the preferred Na adsorption sites for half- and one-monolayer (ML) Na coverage, and then the energetics are compared to determine the equilibrium saturation coverage. For half-monolayer Na coverage, we have considered five absorption sites, the *B*, *C*, *H*, *D*, and *T* sites as depicted in Fig. 1. For the more open absorption sites such as the cave (*B*) and valley bridge (*C*) sites, we also considered the possibility of the Na atoms residing in subsurface positions. However, we found that the subsurface positions of Na are unstable, and the forces on the Na atoms eventually push them out to the equilibrium positions outside the Si layers. Exploratory calculations were done with a smaller plane-wave cutoff of 4.5 Ry, and the fully relaxed configurations for Na atoms at the *T* and *D* sites are energetically very unfavorable compared with *C*, *B*, and *H* sites. Thus, these two sites are rejected, and we proceeded with high-convergence calculations for Na atoms at the *C*, *B*, and *H* sites. The fully relaxed configurations with Na atoms at these three sites remain close in energy, with $E(C)<E(B)<E(H)$. Thus the *C* site is the preferred Na absorption site at $\frac{1}{2}$-ML coverage. The structural parameters for the minimum-energy configuration with Na at the *C* sites are listed in Table I. We note that the surface energy of the *C* and *B* sites differs only by 0.03 eV per surface Si atom. In view of the small energy differences, we have repeated the calculation with the Hedin-Lundqvist[22] form of local exchange correlation, and the same energy ordering $[E(C)<E(B)<E(H)]$ is obtained. An earlier calculation[17] found the *H* site to be the lowest in energy for Na on Si(100). To trace the origin of the discrepancy between the two calculations, we tried to see if we can reproduce some of the results in Ref. 17. We checked the case of Na on the ideal (unreconstructed) Si(100) surface using the same plane-wave energy cutoff as in Ref. 17 and found that our energy diagram is very similar to that shown in Fig. 3 of Ref. 17, except that the equilibrium bond length for various sites are slightly longer in our case. So, we believe that the discrepancy between our results and those of Ref. 17 comes mainly from the fact that we have employed a larger basis, and possibly also because we have conducted a more thorough search in the configuration space of atomic positions. In any case, it is fair to say that the difference is small, since both calculations concluded that the *H*, *B*, and *C* sites are all very close in energy. Since there is an odd number of electrons per (2×1) unit cell at half-monolayer Na coverage, all the half coverage models are metallic. The Si surface remains dimerized in the presence of $\frac{1}{2}$ ML of Na for all the absorption sites we have considered, and the dimers are symmetrical except for the case of Na on the atop (*T*) site.

TABLE I. The structural parameters in Cartesian coordinates of the top five Si layers and the Na adatoms for Na occupying the *C* site (half ML coverage) in units of Å.

Atom number			
N	*X*	*Y*	*Z*
1 Na	3.874	0.000	6.384
1 Si	−1.236	−1.937	5.408
2 Si	1.236	−1.937	5.408
3 Si	−1.794	0.000	4.114
4 Si	1.794	0.000	4.114
5 Si	3.874	0.000	2.573
6 Si	0.000	0.000	2.891
7 Si	3.874	−1.937	1.258
8 Si	0.000	−1.937	1.478
9 Si	−1.999	−1.937	0.000
10 Si	1.999	−1.937	0.000

We now come to the case of 1-ML Na coverage, which has two Na atoms per (2×1) surface unit cell. We considered various plausible combinations of sites such as *H-C*, *H-B*, *B-C*, *B-D*, *C-D*, and *H-D*, as well as other possibilities with the Na atoms at intermediate positions between the *C* and *H* sites, and also the *T* and *B* sites. Exploratory calculations with a lower cutoff of 4.5 Ry indicated that the relaxed configurations with Na atoms at *H-C* and *H-B* sites have lower energies than other combinations. We then proceeded with higher convergence (10.5 Ry) calculations for these two combinations and found that the fully relaxed *H-C* sites model has the lowest energy. The structural parameters for the *H-C* sites model are listed in Table II. At the ground-state *H-C* site configuration, the Si(100) surface remains dimerized in the presence of 1 ML of adsorbed Na. The Si dimers are symmetrical and have a distance of 2.64 Å, which is longer than the calculated distance of 2.29 Å in asymmetrical dimers of the clean Si(100) surface. Hence, alkali-metal adsorption reduces, but does not destroy the dimerization on the Si(100) surface. The Na—Si bond lengths are 2.93 Å at the *H* site and 3.10 Å at the *C* site. Using a Si covalent bond length of 1.18 Å, the corresponding Na "radii" would then be 1.75 and 1.92 Å, respectively, both of which are close to the Na metallic radius of 1.83 Å. Even for the case of $\frac{1}{2}$-ML coverage, the calculated Na—Si bond length at the *C* and the *H* sites are 3.08 and 2.95 Å, respectively, again close to sum of the covalent radius of the Si and the metallic radius of Na. This is consistent with the results of recent low-energy electron diffraction (LEED) (Ref. 9) and surface-extended x-ray-absorption fine-structure[5] experiments, and does not support a strongly ionic bonding picture. We found the Na/Si(100) surface to be semiconducting at

TABLE II. The structural parameters in Cartesian coordinates of the top five Si layers and the Na adatoms for the H-C model in units of Å.

Atom number			
N	X	Y	Z
1 Na	0.000	0.000	7.222
2 Na	3.874	0.000	6.390
1 Si	−1.320	−1.937	5.465
2 Si	1.320	−1.937	5.465
3 Si	−1.790	0.000	4.099
4 Si	1.790	0.000	4.099
5 Si	3.874	0.000	2.866
6 Si	0.000	0.000	2.568
7 Si	3.874	−1.937	1.469
8 Si	0.000	−1.937	1.253
9 Si	−1.999	−1.937	0.000
10 Si	1.999	−1.937	0.000

the lowest energy configuration of the H-C site model, consistent with recent angle-resolved photoemission studies.[10]

A consensus has not been reached for the saturation coverage of Na on Si(100). To resolve this issue, we calculated the surface energy of Na on Si(100) for both $\frac{1}{2}$- and 1-ML coverage, defined as

$$E_s(\Theta)=\tfrac{1}{4}\times[E(\text{slab})-N_{\text{Si}}E_{\text{Si(bulk)}}-4\Theta E_{\text{Na(bulk)}}] \ ,$$

where $E_s(\Theta)$ is the surface energy per surface Si atom, and the Na coverage is half (one) ML when $\Theta=0.5$ (1.0). In the above expression, E(slab) is total energy of slab, N_{Si} is the number of Si atoms in the surface "supercell," $E_{\text{Si(bulk)}}$ and $E_{\text{Na(bulk)}}$ are the bulk energies of Si and Na, respectively. There are factors of 4 because there are four surface sites in the slab (which has two surfaces) in the (2×1) unit cell. The surface energies of half Na ML and one Na ML models are compared with the surface energy of the fully relaxed clean Si(100) surface with asymmetrical dimers in Fig. 2. We note that the system has lower surface energies when covered with Na, and since we have defined the surface energy with respect to the bulk energies, Na should "wet" Si(100) as observed experimentally. Moreover, the surface energies for the 1-ML model are unambiguously lower than half ML models, suggesting the saturation coverage should be one, rather than $\frac{1}{2}$ ML. Recent ion scattering experiment,[11] combined with LEED and Auger-electron spectroscopy, determined the saturation coverage to be 0.97 ± 0.05 ML for Cs and 0.98 ± 0.05 ML for K on Si(100). Since Na is smaller in size than K and Cs, it is reasonable that the Na saturation coverage on Si(100) is also 1 ML.

A recent dynamical LEED analysis[9] favored the H site if the analysis is restricted to half ML Na coverage, but an equally small R factor is obtained for the H-C model if the Na coverage is assumed to be 1 ML. Detailed structural parameters are not quoted for the H-C model, but the heights of Na atoms above the Si surface are determined to be 1.90 Å at the H site and 0.95 Å at the C site, which are quite close to our theoretical values of

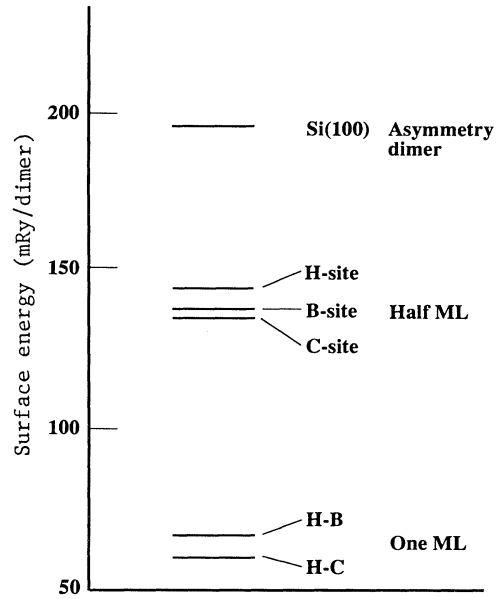

FIG. 2. Schematic surface energy diagram. Note that surface energy is lowest at 1-ML Na coverage.

1.76 Å (H) and 0.93 Å (C). Since the vertical heights of the Na atoms at the H and C sites are rather different, one may choose to regard the Na layer as a double layer.[4] In fact, the double layer model for K/Si(100) suggested by Abukawa and Kono[4] based on x-ray photoelectron diffraction is essentially the same as the H-C site model we found for Na/Si(100).

IV. SUMMARY

We have performed first-principles total-energy and force calculations to determine the electronic and structural properties of the Na/Si(100) system. The energetically favored adsorption site for half ML Na coverage is the C (valley bridge) site, while both the H (pedestal) and C (valley bridge) sites are occupied at 1-ML Na coverage. The Na—Si bond lengths are found to be close to the sum of the covalent radius of Si and the metallic radius of Na, and thus support the notion of covalent bonding at the high-coverage regime. Surface energy calculations suggest that the Na coverage should be 1 ML, rather than half ML, at equilibrium and the surface is semiconducting at 1-ML Na coverage. We note in passing that we found several metastable structures at 1 ML in which the Si dimers are asymmetrical and the surface is metallic. Although these configurations are not energetically favorable at 1-ML Na coverage, they may be relevant at low-coverage situations.

ACKNOWLEDGMENTS

Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. This work was supported by the National Science Foundation under Grant No. DMR-8819379, and in part by the Director of Energy Research, Office of Basic Energy Sciences.

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