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# Atomic and electronic structure of the Na/Si(001)-(2×1) surface

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We have obtained energy-minimized atomic and the resultant electronic structures for Na adsorbed on Si(001)-(2×1) at two different coverages. The passage through a 2×3 structure before reaching the 2×1 structure at a monolayer coverage is explained based on these results. At a monolayer coverage the calculated structure is puckered in accord with recent experiments. The observed reentrant behavior to an insulating state at the monolayer coverage of alkali metals also follows naturally from these calculations. We also find that up to this coverage, the reversal to ideal surface structure is energetically unfavorable and this is to be contrasted with Si(111)-(2×1). An explanation is offered for differing values of charge transfer quoted in the literature.

The nature of metallization of Si(001)-(2×1) surface by alkali metals, proposed[1] by Ciraci and Batra (CB) in 1986, has led to a flurry of activity both experimentally[2–10] and theoretically.[11–15] Early experiments[16] had indicated that it is not possible to grow ordered layers beyond one half of one monolayer coverage. Incidentally, one half of one monolayer is $\theta=1$ in our definition, where $\theta$ is the number of alkali atoms per 2×1 surface unit cell. This is equivalent to $3.39\times10^{14}$ adsorbates/cm$^2$. More recently,[3,5] ordered overlayers beyond this coverage have been successfully grown. However, the newer experimental data are still in mutual conflict[3,5,8] regarding the saturation coverage. CB (Ref. 17) later extended the calculations to higher coverages of K and presented preliminary results confirming their earlier picture of ionic bonding.

There have been several important new developments in this field. Angular resolved photoemission experiments by Enta, Kinoshita, Suzuki, and Koho[5] have shown that when the Si(001)-(2×1) surface is dosed to "saturation" coverage of K, the resulting system is an insulator. From their Auger electron spectroscopy (AES) measurements, they[5] draw the conclusion that the saturation coverage corresponds to $\theta=2$. No characteristic breaks, normally associated with a layer by layer growth, were observed by them. Oellig and Miranda,[3] on the other hand, reported at least four breaks in the Si *LMM* AES intensity. However, after the completion of second K layer, the growth of the third and fourth K layer did not change the work function. This is contrary to the results by Enta *et al*,[5] who find that the saturation of $\Delta\phi$ and AES intensity coincide with each other. Abukawa and Kono[8] have proposed a model, based on a kinematical analysis of the x-ray photoelectron diffraction patterns of K $2p$ core-level experiments, for $\theta=2$ coverage. Finally, a new 2×3 low-energy-electron diffraction spectroscopy (LEED) structure has been reported[10] at low coverages. We also mention that no value of the charge transfer from alkali metal to Si surface is yet commonly accepted. The actual adsorption sites at various coverages are still largely unknown.[3]

In this Rapid Communication, we present atomic and electronic structures for the alkali metal adsorption on Si(001)-(2×1) at two coverages, $\theta=1$, 2, which have bearings on all of the above issues. We conclude from our calculations that at the lower coverage, the quasihexagonal site proposed by Levine[18] and a long bridge site along the dimerization direction are equally favorable in energy. Thus, both sites can be occupied at room temperature. At the monolayer coverage ($\theta=2$), our calculations predict simultaneous occupation of both these sites. The structure we find is puckered in accord with recent experiments.[8] However, the cave site, tentatively proposed by experiment,[8] is found to be unfavorable. The LEED observation[10] of a 2×3 structure at low coverages can be satisfactorily explained in terms of near equal probability of occupancy of the two sites. These calculations are also able to explain the reentrant behavior to an insulating state observed by Enta *et al.*[5]

Our calculations are based on an extensive set of *ab initio* total energy; electronic structure and force calculations performed within the repeating slab geometry. We use the standard self-consistent field (SCF) pseudopotential method in the momentum space representation.[19] The particular alkali metal we have chosen is sodium; the results for K are expected to be similar. In our previous work,[1] we used potassium as a prototype for alkali metals. There is some suggestion[7] that the particular form of the ionic pseudopotential[20] we used may lead to a low value for the K-Si bond length. It is hoped that Na ionic pseudopotential may not suffer from this drawback to the same extent due to a somewhat smaller core size.

The structural models used in our calculations are displayed in Fig. 1. We considered three types of adsorption sites in detail at the 2×1 surface at $\theta=1$. The hollow site[18] $H(4,2,1)$ above the third layer of Si is quasihexagonal. The numbers in parenthesis give the number of Si neighbors in the first three Si layers around the adsorption site. In the long bridge site, $B(2,4,2)$, the adsorbate is located above a fourth-layer Si atom and connects the rows of dimers. The cave site, $C(4,\hat{2},2)$, has adsorbate above the third layer of Si but due to reconstruction this is a more open site than $H(4,2,1)$. Also as can be seen in Fig. 1, the second-layer Si atoms are in fact closer to the adsorbate than the first-layer Si atoms. This is indicated by placing a caret above two. These sites are simply labeled as $H$, $B$, and $C$ in Fig. 1. Other possible sites were ruled

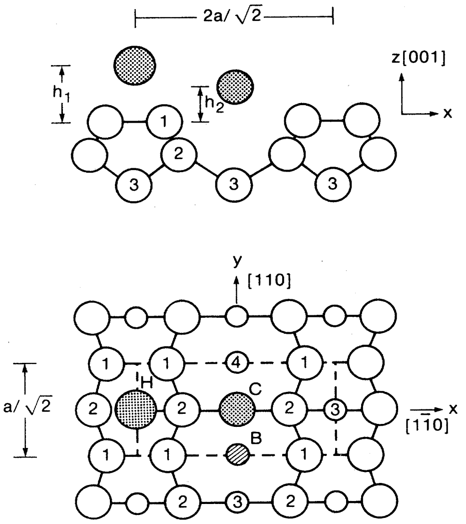

FIG. 1. Side and top views describing the positions of adsorbed sodium atoms on the Si(001)-(2×1) surface. Shaded and empty circles denote Na and Si atoms, respectively. Numerals in the circles indicate Si atomic layers. Important sites in the unit cell have been labeled by *H*, *B*, and *C*.

out either from preliminary energy calculations or on physical grounds.

Our analysis of the energetics for the optimum binding structure at $\theta = 1$ is presented in Table I. *H* site is marginally more stable in energy than *B* site. The potential energy curve, as a function of the vertical height *h*, at *B* site is rather flat. The energy changed by only 0.007 eV when *h* was changed by 0.5 a.u. This is due to the fact that a large change in *h* produces only a minor change in the nearest-neighbor Si-Na distance *d*. An important point is that *d* is nearly the same for *H* and *B* adsorption sites which leads to similar adsorption energies. Also from Table I, we note that our results for energy differences and bond lengths seem to be well converged. Only *B* site shows some sensitivity for reasons stated above and becomes slightly more favorable (~0.01 eV/cell) than *H* site. We conclude that at room temperature both *H* and *B* sites shall be occupied, governed only by the kinetics considerations. Furthermore, since *B* site is almost buried in the surface, little change in work function will occur if only *B* sites were occupied. The occupancy of *C* site is found to be unfavorable. Also from the last columns it is clear that reverting to an ideal surface at this coverage is energetically highly unfavorable. Although the adsorption on the ideal surface is actually more favorable, the loss in energy due to dimer breaking (~1.6 eV) is not offset by the additional bonding due to adsorption at the ideal surface. This is to be contrasted[21] with Si(111)-(2×1) where the energy loss due to breaking weak Π-bonding reconstruction is well compensated for by the additional adsorption energy on ideal Si(111).

TABLE I. Calculated relative energies (in eV) measured with respect to *H* site for various adsorption sites for Na at $\theta = 1$ on Si(001)-(2×1) and ideal (*I*) Si(001) surfaces. The optimized vertical heights *h* and nearest-neighbor Si-Na interatomic distances *d* are given in Å. Positive values for $\Delta E$ correspond to energetically less favorable configurations. The Bloch states were represented by a basis set of ~550 plane waves corresponding to $|\mathbf{k}+\mathbf{G}|^2 < 4.5$ Ry. The numbers in parentheses are for calculations performed with ~1000 plane waves, $|\mathbf{k}+\mathbf{G}|^2 < 6.5$ Ry.

| Sites | *H* | *B* | *C* | *I*(*H*) | *I*(*B*) |
|---|---|---|---|---|---|
| $\Delta E$ | 0.0 | 0.03(−0.01) | 0.14(0.14) | 0.89 | 1.32 |
| *h* | 1.27(1.32) | −0.16(−0.29) | 0.64(0.58) | 0.79 | 1.80 |
| *d* | 2.60(2.62) | 2.64(2.66) | 2.83(2.79) | 2.83 | 2.63 |

At $\theta = 2$, a plausible structure involves occupying *H* and *B* sites simultaneously. An alternative involves occupying *H* and *C* sites simultaneously. Simultaneous occupation of *B* and *C* sites can be ruled out on physical grounds. The *H*-*C* structure has been tentatively proposed[8,17] but is energetically unfavorable, according to our results summarized in Table II. We also establish that reverting to the ideal surface is energetically unfavorable even at a monolayer coverage. The low-energy structure according to our calculation is a puckered one for which $\Delta h \simeq 0.9$ Å. The puckering leads to a reduction in the ion-ion repulsion energy. It may be thought of as a dilayer[22] of alkali metal. A puckered structure at monolayer coverage of K on Si(001)-(2×1) has been proposed[8] with $\Delta h \simeq 1.1$ Å. Our results confirm the puckering but suggest that the site is *H*/*B* rather than *H*/*C*. The vertical heights we find are $h_1 = 1.4$ and $h_2 = 0.5$ Å. Both these values are larger than the corresponding heights at $\theta = 1$. This is in accord with the known results[23] that with increasing coverage there is an outward relaxation of the overlayer. At low coverages ($\theta = 2/3$) a 2×3 structure[10] can arise because an adsorbate in *H* site blocks off four surface sites. Then the next alkali atom can adsorb in *B* site, but must skip the adjacent unit cell. This gives rise to a 2×3 structure at $\theta = 2/3$. At monolayer coverage all *H* and *B* sites can be filled and we again recover a 2×1 structure. The ordered structures[10] 2×1, 2×3, and 2×1, are thus readily explained by the energetics presented in Tables I and II.

Our calculated electronic structures at the two coverages, shown in Fig. 2, give a band picture rather similar to that for the clean Si(001)-(2×1) surface. Recall that Si(001)-(2×1) has two surface dangling bands, $D_1$ and $D_2$, in the bulk forbidden energy gap which can accommo-

TABLE II. Calculated relative energies (in eV) measured with respect to *H*/*B* site for various adsorption sites for Na on Si(001)-(2×1) and ideal (*I*) Si(001) surfaces at $\theta = 2$. The symbol *H*/*B*, for example, defines adsorption sites for two Na atoms; one in *H* and the other in *B* site. Their optimized vertical heights (in Å) are $h_1$ and $h_2$, respectively.

| Sites | *H*/*B* | *H*/*C* | *I*(*H*/*H*) | *I*(*H*/*B*) |
|---|---|---|---|---|
| $\Delta E$ | 0.0 | 0.1 | 0.2 | 0.6 |
| $h_1$ | 1.4 | 1.4 | 0.7 | 0.6 |
| $h_2$ | 0.5 | 0.7 | 0.7 | 1.7 |

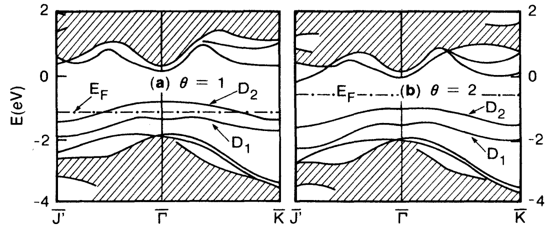

FIG. 2. Calculated energy band structure of Na-covered Si(001)-(2×1) surface at (a) $\theta=1$ and (b) $\theta=2$. The zero of energy is arbitrarily set at the lowest unoccupied level at $\bar{\Gamma}$. The adsorbates are in $H$ and $H/B$ sites.

date up to four electrons but actually hold only two. The reconstructed clean surface is thus insulating in nature. A single alkali adsorbate atom per unit cell partly fills the $D_2$ band leading to a metallic state. If two adsorbate atoms are present, the 2×1 unit cell would have just enough electrons to fully occupy $D_1$ and $D_2$ bands leading once again to a semiconducting[5] surface at $\theta=2$. This picture is confirmed by our calculations. An important point is that the alkali overlayers do not introduce any new bands in this energy region although some modifications of the intrinsic bands are obviously noted. The reentrant behavior to the insulating state[5] as a function of coverage thus follows naturally from our calculations. The transfer of Na(3$s$) electron into Si levels is also consistent with the atomic term values since $\epsilon_{\mathrm{Si}}(3p)=-0.48$ and $\epsilon_{\mathrm{Na}}(3s)=-0.38$ Ry.

The origin of the above metal-insulator transition is traced to the ionic interaction between the alkali metal and Si, and to the presence of active surface states on the Si surface. This can be best seen from the spatial distribution of the alkali-metal charge upon adsorption in $H$ and $H/B$ sites. In Fig. 3(a) the difference valence charge density plot $\Delta\rho(\mathbf{r})=\rho_{\theta=1}(\mathbf{r})-\rho_{\theta=0}(\mathbf{r})$ in a vertical (110) plane passing through the dimer bond is shown. The partial filling of the dangling-bond states by the Na(3$s$) electron is fairly obvious. Some depletion of charge is noted from the region between first and second layers in favor of accumulation between the Na and Si surface layer. The corresponding plot at $\theta=2$ is shown in Fig. 3(b). The valence electrons of the adsorbed atoms are again essentially accommodated in the dangling surface state bands. However, a small amount of charge does accumulate between alkali metals and the second-layer Si atoms. This suggests some covalency in an otherwise ionic bond. Also from the charge distribution one can sense an onset of interaction between alkali atoms. Of course, this interaction is weak and in view of the gap between $D_2$ and the conduction band, one concludes that the alkali overlayer is not metallized up to the monolayer coverage. One should keep in mind that the intra-atomic Coulomb repulsion (Hubbard $U$) may become effective when both $D_1$ and $D_2$ are fully occupied. This may alter the electronic structure somewhat, but is beyond the scope of present calculations.

There has been much discussion in the literature[1-15] about the amount of charge transfer, $\Delta Q$, from alkali metals to Si. Values ranging from 0 to ~1 have been quoted for the K-Si system. Oellig and co-workers[3,4] have obtained $\Delta Q\simeq0.3$. This value is extracted from their experimental data on the change in work function using the Helmholtz formula as well as an empirical tight-binding calculation. Based on the charge density analysis and the charge allocation obtained from their pseudofunction calculations, Kasowski and Tsai[11] have given $\Delta Q\simeq0$. Tsukada *et al.*[15] have concluded, from Mulliken population analysis as well as a space partitioning scheme, that $\Delta Q\simeq0.1$. A more sophisticated analysis[12] of the charge transfer, based on a constrained space orbital variation, led to $\Delta Q\simeq0.9$.

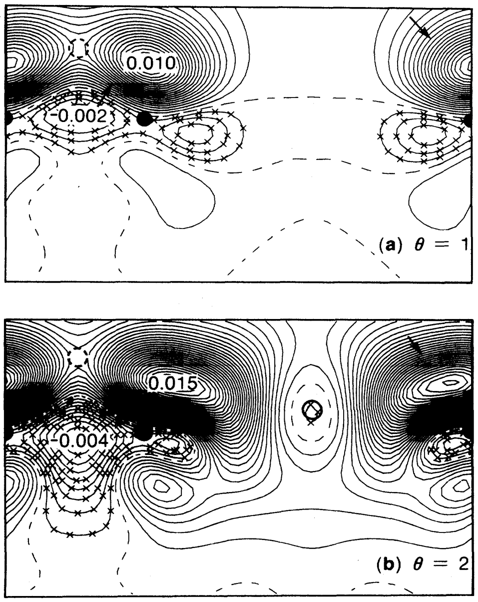

FIG. 3. Contour plots of the charge-density difference between Na-covered and clean Si(001)-(2×1) surface in the vertical (110) plane, (a) $\theta=1$, (b) $\theta=2$. The contour spacings are $5\times10^{-3}$ e/a.u.[3] Dotted lines give zero-density contours; depletion region is given by contours with crosses. Positions of Si and Na atoms are indicated by filled and open circles, respectively. The dotted circle shows that Na is not in this plane. Small arrows give the direction of increasing charge-density contours.

An examination of the spatial distribution of the charge density in Fig. 3 offers an explanation for these widely different computed values. The alkali charge is obviously localized in the region between alkali overlayer and Si surface layer whether or not the charge is in Si dangling bonds. It is also clear that Na and Si cores are situated rather close to each other. The problem then arises in assigning the charge in a unique fashion to a particular center. Any sensible partitioning of the space would project $\Delta Q\sim0.1-0.4$. A similar value shall be obtained from an analysis based on Helmholtz expression which at $\theta=1$ is $\Delta Q\simeq\Delta\phi(\mathrm{eV})/6r_{\perp}(\mathrm{\AA})$. Here, $r_{\perp}$ is the normal dipole length. If we take it equal to $h$ from Table I for $H$ site, then for $\Delta\phi=3$ eV, one gets $\Delta Q\simeq0.4$. However, this ignores the fact that the spatial distribution of the charge density is quite asymmetric as can be seen from Fig. 3(a). The "center" of the excess charge in the normal direction does not coincide with the Si core. This essentially means that $r_\perp$ entering in the Helmholtz formula is less than $h$. A simple estimate then gives $r_\perp \simeq 0.6$ Å and, hence, $\Delta Q \simeq 0.8$. Thus, one has to be careful in supplying an appropriate value for the separation between positive and negative "centers." For these reasons, several different values for the charge transfer exist in the literature.

In closing, we state that our calculations have led to the conclusion that the two Na atoms per unit cell prefer to be in a puckered structure in accord with recent experimental observations.[8] The surface dangling bond bands (somewhat modified due to the adsorbates) continue to exist up to $\theta = 2$. Since these bands are completely filled for $\theta = 2$, one gets an insulating surface at this metal coverage in accord with the experimental findings.[5] Whether the multilayer of alkali metals can grow on Si(001), or the adsorption saturates at $\theta = 2$, remains an unresolved experimental[3,5,8] issue.

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[1] S. Ciraci and I. P. Batra, Phys. Rev. Lett. **56**, 877 (1986); Phys. Rev. B **37**, 2955 (1988).

[2] For a nice review, see P. Soukiassian and T. Kendelewicz, in *Proceedings of the NATO Advanced Research Workshop on Metallization and Metal-Semiconductor Interfaces, Garching, 1988,* edited by I. P. Batra (Plenum, New York, 1988), p. 465.

[3] E. M. Oellig and R. Miranda, Surf. Sci. **177**, L947 (1986); E. G. Michel, M. C. Asensio, and R. Miranda, in Ref. 2, p. 381.

[4] E. M. Oellig, E. G. Michel, M. C. Asensio, R. Miranda, J. C. Duran, A. Munoz, and F. Flores, Europhys. Lett. **5**, 727 (1988); J. E. Ortega, E. M. Oellig, J. Ferron, and R. Miranda, Phys. Rev. B **36**, L6213 (1987).

[5] Y. Enta, T. Kinoshita, S. Suzuki, and S. Kono, Phys. Rev. B **36**, 9801 (1987).

[6] I. P. Batra, J. M. Nicholls, and B. Reihl, J. Vac. Sci. Technol. A **5**, 898 (1987).

[7] T. Kendelewicz, P. Soukiassian, R. S. List, J. C. Woicik, P. Pianetta, I. Lindau, and W. E. Spicer, Phys. Rev. B **37**, 7115 (1988).

[8] T. Abukawa and S. Kono, Phys. Rev. B **37**, 9097 (1988).

[9] Y. Murata, H. Tochihara, and M. Kubota, in Ref. 2, p. 367; H. Tochihara, M. Kubota, M. Miyao, and Y. Murata, Surf. Sci. **158**, 497 (1985).

[10] G. S. Glander and M. B. Webb, Bull. Am. Phys. Soc. **33**, 570 (1988); Surf. Sci. (to be published).

[11] R. V. Kasowski and M. H. Tsai, Phys. Rev. Lett. **60**, 546 (1988); see response to this comment by S. Ciraci and I. P. Batra, Phys. Rev. Lett. **60**, 547 (1988).

[12] P. S. Bagus and I. P. Batra, Surf. Sci. **206**, L895 (1988); I. P. Batra and P. S. Bagus, J. Vac. Sci. Technol. A **6**, 600 (1988).

[13] Y. Ling, A. J. Freeman, and B. Delley, Phys. Rev. B (to be published).

[14] I. P. Batra, Prog. Surf. Sci. **25**, 175 (1987).

[15] M. Tsukada, N. Shima, Z. Zhu, H. Ishida, and K. Terakura, in Ref. 2, p. 351; H. Ishida, N. Shima, and M. Tsukada, Phys. Rev. B **32**, 6236 (1985).

[16] H. Tochihara, Surf. Sci. **126**, 523 (1983).

[17] S. Ciraci and I. P. Batra, in Ref. 2, p. 335; I. P. Batra, J. Chim. Phys. (to be published).

[18] J. D. Levine, Surf. Sci. **34**, 90 (1973).

[19] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

[20] C. B. Bachelet, D. R. Hamann, and M. Schluter, Phys. Rev. B **26**, 419 (1982).

[21] I. P. Batra and S. Ciraci, Phys. Rev. B **37**, 8432 (1988); S. Ciraci and I. P. Batra, Phys. Rev. Lett. **58**, 1982 (1987).

[22] A. U. MacRae, K. Muller, J. J. Lander, J. Morrison, and J. C. Phillips, Phys. Rev. Lett. **22**, 1048 (1969).

[23] I. P. Batra and S. Ciraci, Phys. Rev. B **33**, 4312 (1986); G. M. Lamble, R. S. Brooks, D. A. King, and D. Norman, Phys. Rev. Lett. **61**, 1112 (1988).