Applied Surface Science 56–58 (1992) 15–19
North-Holland

applied
surface science

Self-consistent study of the electronic and structural properties of the clean Si(001)(2 × 1) surface

Jarosław Dąbrowski [1] and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, D-1000 Berlin 33, Germany

Received 6 May 1991; accepted for publication 17 May 1991

We report a systematic study of density-functional theory calculations for the reconstructed Si(100)(2 × 1) surface. We find that *converged* calculations favor buckled dimers ($\theta \approx 15°$) over symmetric ones. The symmetric (non-buckled) character of dimers observed in scanning tunneling microscope images is explained as a result of a buckling vibration (flipping) between $\theta = +15°$ and $-15°$. The calculated surface band structure is compared to experimental photoemission data: whereas the dispersion of the occupied surface state is in good agreement with that of the measured band, the calculated indirect band gap is clearly too small. The latter is a typical result of DFT ground state calculations.

The unreconstructed (001) surface of Si (see fig. 1a) has two dangling orbitals per surface atom, each of them being filled with one electron. It is well established (see e.g. refs. [1–3]) that the energy of this surface is lowered if the surface atoms form dimers (see fig. 1b), so that only one bond per atom remains unsaturated. This reconstruction, first proposed in 1957 by Schiller and Farnsworth [4], gives rise to a (2 × 1) surface structure. The details of the dimer geometry (e.g. if the dimers are buckled or not), as well as the corresponding electronic structure of the reconstructed surface are still under debate. Whereas photoemission [5–8] and scanning tunneling microscope (STM) *spectroscopy* [3] show that the surface is non-metallic, which hints at buckled dimers [9–11] (see fig. 1c), the corresponding STM *surface-topography* shows symmetric (non-buckled) dimers [1–3]. The reconstruction of the clean Si(001) surface has been extensively studied

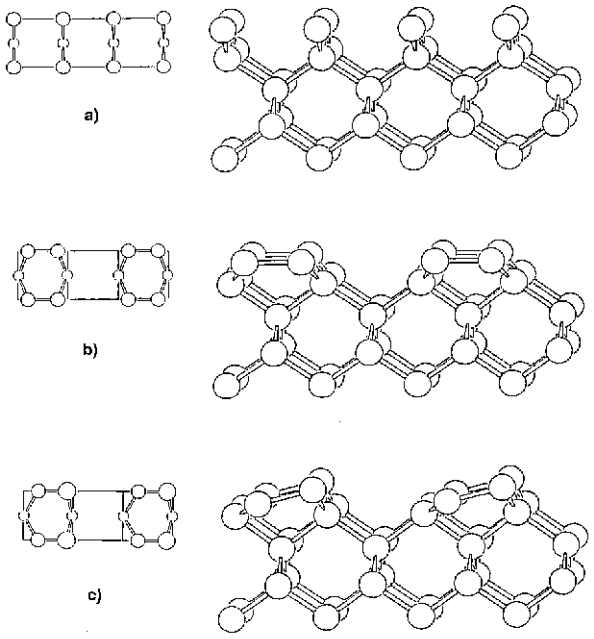

Fig. 1. Atomic arrangement of the Si(001) surface: (a) (1×1) bulk-terminated, (b) (2×1) symmetric dimers, (c) (2×1) buckled dimers. Top view on the left, side view on the right.

[1] Permanent address: Instytut Fizyki PAN, Al. Lotnikow 32, PL-02-668 Warszawa, Poland.

theoretically [9–21]. These different theoretical investigations also arrived at conflicting results, giving sometimes the symmetric [12–16] and sometimes the buckled [9–11,17,18] dimers as the ground state.

To clarify this issue we performed self-consistent density-functional theory (DFT) calculations for the reconstructed Si(001)(2 × 1) surface. The exchange-correlation functional was treated in the local-density approximation (LDA) [22]. We used fully separable, norm-conserving, ab-initio pseudopotentials of the Kleinman–Bylander form [23,24], and a super-cell geometry. The Kohn–Sham equation was solved using a plane-wave basis and applying a Car–Parrinello like technique [25]. We find that *converged* DFT-LDA calculations favor buckled dimers over symmetric ones. In this paper we discuss the influence of various numerical approximations on the calculated lowest-energy configuration. Further, we explain the symmetric (non-buckled) character of dimers observed by STM [1–3], and compare the calculated surface band structure to experimental photoemission data [5–7].

We begin with a description of the convergency criteria. In a super-cell geometry the surface is modelled by a slab of a finite number of atomic layers. This slab is repeated periodically in the direction of the surface normal. For the vacuum region between slabs we took a thickness of 15 bohr, which is sufficient for the through-vacuum surface–surface interaction to be negligible. The main calculations were done with slabs built of 10 atomic layers. Three layers on both sides of the slab were relaxed until all forces were smaller than $F_0 = 5 \times 10^{-4}$ hartree/bohr. The cut-off energy for the plane-wave basis set was $E_{\text{cut}} = 8$ Ry, and the electron density was built from 8 special $\boldsymbol{k}_{\parallel}$ points from the irreducible part of the surface Brillouin zone (BZ). For comparison several calculations have been performed for 6-, 8-, 10-, and 12-layer slabs and the effect of relaxation of two, three and four atomic layers has been checked as well. We used the theoretical lattice constant $a_0 = 10.16$ bohr of a crystal bulk calculation.

In order to investigate the quality of the BZ integration we consider the following sets of $\boldsymbol{k}_{\parallel}$ points, which we denote by a number $N_{\boldsymbol{k}_{\parallel}}$, and which are defined as follows: If for example $N_{\boldsymbol{k}_{\parallel}}$ is 6, the $\boldsymbol{k}_{\parallel}$ point set is given by $\boldsymbol{k}_{\parallel} = (\frac{1}{4}, \frac{1}{4})$ of the BZ of a (6 × 6) surface unit cell. It then follows, if the translational invariance of the surface is (1 × 1), that $N_{\boldsymbol{k}_{\parallel}} = 6$ defines $6 \times 6 = 36$ $\boldsymbol{k}_{\parallel}$ points of the irreducible part of the true *first* BZ. We tested the convergence of forces for a (1 × 1) bulk-terminated, 8-layer slab, and varied $N_{\boldsymbol{k}_{\parallel}}$ between 2 and 7. The sets $N_{\boldsymbol{k}_{\parallel}} = 6$ and $N_{\boldsymbol{k}_{\parallel}} = 7$ give the same (converged) results, while the forces for sets $N_{\boldsymbol{k}_{\parallel}} = 3$, 4, and 5 differ from the converged values by less than F_0. The $N_{\boldsymbol{k}_{\parallel}} = 2$ set gives worse results. The forces show little dependence on the slab thickness: the forces on the surface layers of 8-, 10-, and 12-layer slabs are equal within the accuracy of F_0.

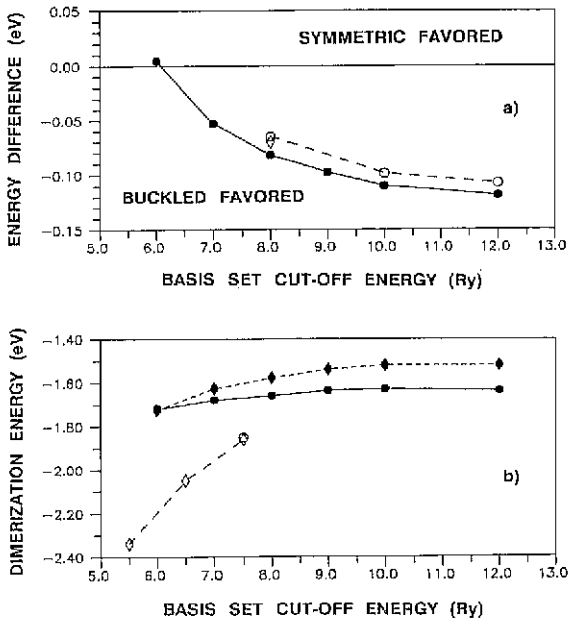

Fig. 2. (a) Energy difference per dimers between buckled and symmetric dimers as a function of the basis-set cut-off energy E_{cut}. Different sets of $\boldsymbol{k}_{\parallel}$ points are indicated: $N_{\boldsymbol{k}_{\parallel}} = 2$ with diamonds, $N_{\boldsymbol{k}_{\parallel}} = 4$ with full dots, and $N_{\boldsymbol{k}_{\parallel}} = 6$ with open dots. (b) Dimerization energy as a function of the basis set cut-off energy. Circles correspond to buckled dimers, diamonds correspond to symmetric dimers. Full symbols refer to this work with $N_{\boldsymbol{k}_{\parallel}} = 4$, while open symbols are results of Batra [16].

Fig. 2a shows the energy difference (per dimer) between buckled and symmetric dimers as a func-

tion of the basis-set cut-off energy. Results for the $N_{k_\parallel} = 2$, 4, and 6 sets of $k_\parallel$ points are shown. The geometry is taken from a calculation where three surface layers on both sides of a 10-layer slab were relaxed with $E_{cut} = 8$ Ry and $N_{k_\parallel} = 4$. The relaxation of atoms at all points in fig. 2a is not crucial for the picture, as we verified at cut-off energies of 6 and 12 Ry. Moreover, we found that the relaxation of the fourth layer is not important for the total-energy differences, and the total-energy differences for 6-layer slabs with only two layers relaxed, and for 8-layer slabs with three layers relaxed are very similar as well. We thus conclude that buckled dimers are favored over symmetric dimers, and that our $E_{cut} = 8$ Ry basis, together with the $N_{k_\parallel} = 4$ $k_\parallel$ set ensures accurate calculations. Fig. 2a also shows how the predicted lowest-energy configuration depends on the quality of the basis set, while the size of the $k_\parallel$ point set is less important: even the small $N_{k_\parallel} = 2$ set (2 $k_\parallel$ points for the (2 × 1) structure) yields good results. We like to recall that our tests only apply to $(\frac{1}{4}, \frac{1}{4})$-derived $k_\parallel$ sets. Γ-derived sets may converge slower.

The calculations of Batra [16] yielded symmetric dimers as the lowest-energy configuration. Because in ref. [16] the symmetric dimers have been studied with three different cut-off energies, we can directly compare these results to ours. This is done in fig. 2b, which gives the cut-off-energy dependence of the dimerization energy, i.e. the energy gained per dimer by relaxing the bulk-terminated surface from the (1 × 1) to the (2 × 1) structure (compare fig. 1a to 1b and 1c). Fig. 2b illustrates the importance of the basis-set quality and that the results of ref. [16] are not converged.

There is an apparent disagreement between the buckling of dimers, indicated by the surface electronic structure, and the symmetric character of dimers observed by STM images. In fig. 3 we show the calculated total-energy as a function of the dimer buckling angle. The total-energy surface has equivalent minima at buckling angles $\theta = \pm 15°$ ($\theta = 0°$ corresponds to the symmetric dimer). These two minima are separated by a barrier of about 0.1 eV. The calculations also show that different dimers are rather weakly coupled: total energies of two neighboring dimers

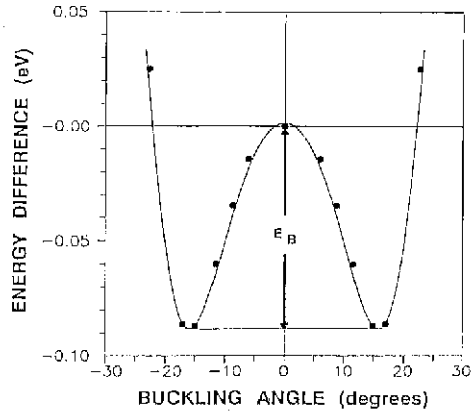

Fig. 3. Total energy of buckled dimers versus buckling angle θ, calculated with a $E_{cut} = 8$ Ry basis and the $N_{k_\parallel} = 4$ $k_\parallel$ set (see text).

buckled in the opposite and in the same direction (2 × 2 and 2 × 1 ordering) are almost the same (see also refs. [9,26,27]).

It takes about 10 ms to obtain a room-temperature STM picture of a dimer [3]. From fig. 3 we estimate that at room temperature a dimer flips about 10^9 times between $\theta = +15°$ and $-15°$ during the measurement time. We therefore conclude that the symmetric character of dimers, as observed in STM images, is due to such oscillations. The calculated surface topography of the electron-density surface built of either empty or occupied surface states of oscillating dimers are in good agreement with STM images of tip → sample and sample → tip currents, respectively. We also note that in accordance with ref. [21] we find that charging of dimers by adding one electron per dimer decreases the energy gained due to buckling and reduces the buckling angle θ. It is however not obvious to us if an electron emitted from the STM tip stays sufficiently long in the dimer orbital so that the charging effect will unbuckle the geometry.

The calculated surface bands (DFT-LDA eigenvalues) of buckled ($\theta = 15°$) and symmetric ($\theta = 0°$) dimers are shown in fig. 4. The occupied band of buckled dimers fits well to photoemission data [5,6]. Also the calculated gap at Γ ($E_\Gamma = 0.9$ eV) agrees well with the photoemission and inverse photoemission data [7]. However, the calcu-

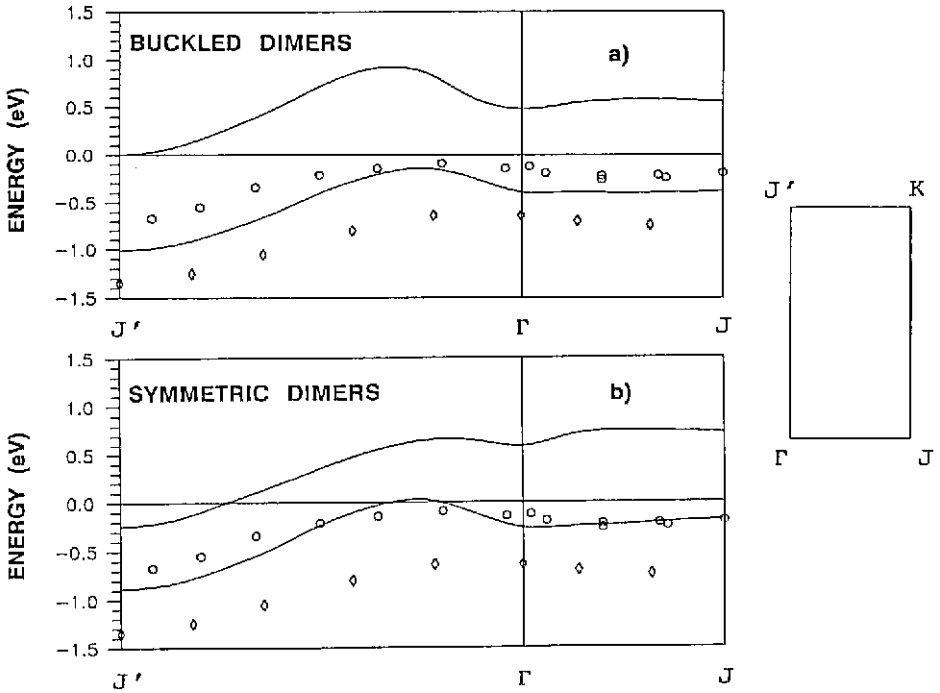

Fig. 4. Surface energy bands for (a) buckled ($\theta = 15°$) and (b) symmetric ($\theta = 0°$) dimers, calculated with the $E_{cut} = 8$ Ry basis and the $N_{k_\parallel} = 5$ $k_\parallel$ set (see text). Energies are given with respect to the Fermi level. Experimental photoemission data are indicated with circles [5] and diamonds [6].

lated indirect gap ($E_{ind} = 0.1$ eV), taken between the maximum of the lower and the minimum of the upper band in fig. 4 is smaller than the experimental estimate, which is $E_{ind}^{exp} \geq 0.7$ eV [7,8]. The calculated value for E_{ind} depends sensitively on the buckling angle θ: It increases by 0.3 eV when θ is increased from 15° to 23°. Consequently symmetric dimers would form a metallic surface with $E_{ind} = -0.3$ eV and $E_\Gamma = 0.9$ eV.

In summary, we performed a systematic theoretical study of the dimerization of the clean Si(001) surface. The results show that *converged* self-consistent DFT-LDA calculations favor buckled dimers (buckling angle $\theta \approx 15°$) over symmetric dimers ($\theta = 0°$). The energy difference between these two configurations is about 0.1 eV. The electronic structure of buckled dimers compares well with that deduced from photoemission experiments, however, the calculated indirect gap is too small. This is likely a consequence of the DFT-LDA approach which describes the electronic ground state, but not excitations. We find that different dimers are rather weakly coupled and thermal flipping of buckled dimers between $\theta = +15°$ and $-15°$ implies that in STM the dimers appear symmetric.

References

[1] R.M. Tromp, R.J. Hamers and J.E. Demuth, Phys. Rev. Lett. 55 (1985) 1303.
[2] R.J. Hamers, R.M. Tromp and J.E. Demuth, Phys. Rev. B 34 (1986) 5343.
[3] R.J. Hamers and U.K. Köhler, J. Vac. Sci. Technol. A 7 (1989) 2854.
[4] R.E. Schiller and H.E. Farnsworth, J. Chem. Phys. 30 (1957) 917.
[5] R.I.G. Uhrberg, G.V. Hansson, J.M. Nicholls and S.A. Flodström, Phys. Rev. B 24 (1981) 4684.
[6] R.D. Bringans, R.I.G. Uhrberg, M.A. Olmstead and R.Z. Bachrach, Phys. Rev. B 34 (1986) 7447.
[7] F.J. Himpsel and Th. Fauster, J. Vac. Sci. Technol. A 2 (1984) 815.

[8] P. Mårtensson, A. Cricenti and G.V. Hansson, Phys. Rev. B 33 (1986) 8855.
[9] D.J. Chadi, Phys. Rev. Lett. 43 (1979) 43.
[10] J. Ihm, M.L. Cohen and D.J. Chadi, Phys. Rev. B 21 (1980) 4592.
[11] K. Kobayashi, T. Terakura and S. Blügel, Tech. Rep. ISSP, Ser. A No. 2366 (1990).
[12] K.C. Pandey, in: Proc. 17th ICPS, Eds. D.J. Chadi and W.A. Harrison (Springer, Berlin, 1984) p. 55.
[13] M.C. Payne, N. Roberts, R.J. Needs, M. Needels and J.D. Joannopoulos, Surf. Sci. 211/212 (1989) 1.
[14] E. Artacho and F. Yndurain, Phys. Rev. Lett. 62 (1989) 2491.
[15] S. Ihara, S.L. Ho, T. Uda and M. Hirao, Phys. Rev. Lett. 65 (1990) 1909.
[16] I.P. Batra, Phys. Rev. B 41 (1990) 5048.
[17] M.T. Yin and M.L. Cohen, Phys. Rev. B 24 (1981) 2303.
[18] A. Mazur and J. Pollmann, Phys. Rev. B 26 (1982) 7086; J. Pollmann, P. Krüger and A. Mazur, J. Vac. Sci. Technol. B 5 (1987) 945.
[19] S. Ohnishi and M. Tsukada, Solid State Commun. 71 (1989) 391.
[20] P.C. Weakliem, G.W. Smith and E.A. Carter, Surf. Sci. Lett. 232 (1990) L219.
[21] P. Badziag, W.S. Verwoerd and M.A. Van Hove, Phys. Rev. B 43 (1991) 2058.
[22] D.M. Ceperley and B.I. Alder, Phys. Rev. Lett. 45 (1980) 566;
P. Perdew and A. Zunger, Phys. Rev. B 23 (1981) 5048.
[23] L. Kleinman and D.M. Bylander, Phys. Rev. Lett. 48 (1982) 1425.
[24] X. Gonze, P. Käckell and M. Scheffler, Phys. Rev. B 41 (1990) 12264;
X. Gonze, R. Stumpf and M. Scheffler, Phys. Rev. B (1991), in press.
[25] R. Car and M. Parrinello, Phys. Rev. Lett. 55 (1985) 2471.
[26] J. Ihm, D.H. Lee, J.D. Joannopoulos and J.J. Xiong, Phys. Rev. Lett. 51 (1983) 1872.
[27] A. Saxena, E.T. Gawlinski and J.D. Gunton, Surf. Sci. 160 (1985) 618.