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Instability and (2×1) reconstruction of Si(001) and (111) surfaces: a simple approach*

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Recently, the present author introduced a simple qualitative theory of the instability and reconstruction of surfaces of solids exhibiting a certain covalent component of bonding. This theory is now applied to the (2×1) Si(001) and (111) surfaces, with a possible extension to analogous surfaces of germanium and GaAs(001). It is proposed that Shockley surface states from the vicinity of the Fermi energy play a key role in the electron–phonon coupling.

Key words: Surface reconstruction — Surface states — Electron–phonon coupling — Silicon surfaces — Simple model

1. Introduction

The Si(001) (2×1) surface is a good example with which to illustrate the applicability of the pairing picture of reconstruction; this is mainly due to the existence of Shockley surface states (SS), which are non-bonding with respect to the bulk [1]. These states can intervene in several pairing mechanisms, the physics of which are quite different [2, 3]. For example, the pairing of dangling bonds can range from the typical chemical pairing to that mediated by an arbitrary boson field (i.e. caused by the exchange of e.g. phonons, excitons, plasmons or paramagnons, the last case also constituting a sort of Heitler-London-Heisenberg coupling [2, 3]).

Being typical of unsaturated bonds, a pair of SS on an ideal Si(001) (1×1) surface (which carries two broken bonds per atom) may be rehybridized [1, 4–7] to expose favourably directed lobes of one of the SS (bridge bond, *b*) to their counterparts on the neighbouring atoms in the surface plane, while the remaining

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

SS (dangling bond, d) projects along the perpendicular to the surface [8]. The properties of the b-states are the main reason why the existence of SS have long been considered to be the principal argument in support of the chemical (covalent) pairing mechanism of Si(001) surface reconstruction. Naturally, the electron-phonon interactions between SS from the vicinity of the Fermi energy (E_F) and lattice vibrations are crucial here, since they determine which deformation mode evolves after the surface formation. This point of view was recently used to investigate the instability and reconstruction of the W(001) surface [9]. As will be shown below, both b- and d-states take an active part in this pairing.

The chemical bond is a local real-space effect, while the electron-phonon coupling operates in the k-space. Local effects can be introduced, however, by calculating the electron-phonon matrix elements locally [9]. With the same simplifying assumptions as in [9], the change in the electronic band energy caused by a deformation ν perturbing the surface structure can be written (up to the 2nd order) in the form

$$\delta E_{\mathrm{band}} = \sum_r \delta \varepsilon_r = -\sum_{r,s} |\langle r|w_\nu|s\rangle|^2 \nu^2/(\varepsilon_s - \varepsilon_r), \tag{1}$$

where $|r\rangle$, $|s\rangle$, ε_r, ε_s are the wave functions and energies of occupied (r) and empty (s) electronic states of the unreconstructed system respectively, and w_ν is the first derivate of the one-electron Hamiltonian with respect to ν. Our main task is to find the properties of the matrix elements $\nu_{rs} = \langle r|w_\nu|s\rangle$ for different deformation modes (a more explicit form of ν_{rs} is given below), and this will be carried out in a simple qualitative way based only on symmetry arguments. We stress that exact quantitative statements lie outside the scope of the present paper, which, as we believe, can provide some elementary qualitative understanding of delicate surface stability problems.

Owing to the similarity of the surface energy bands [1, 4–9, 12, 18], our results also apply to the reconstruction of the Ge(001), Ge(111) and GaAs(001) surfaces [12, 25–27]. Since the last is the polar surface of an ionic system, special electrostatic arguments can support the buckling reconstruction.

2. Results and discussion

2.1. Si(001) *surface*

As already mentioned, two broken bonds (sp^3 hybrids $|1\rangle$ and $|2\rangle$) reside on each atom of this surface. Their mutual (intra-atomic) interaction causes a rehybridization [1, 4–8] $\varphi_b \sim |1\rangle - |2\rangle \sim p_x$, $\varphi_d \sim |1\rangle + |2\rangle \sim s + p_z$ (see Fig. 1 for the orientation of the x, y axes) and a separation in energy. Without this rehybridization, the two broken bonds would be degenerate in energy, which suggests a Jahn–Teller-like distortion of the C_{2v} symmetry. Contrary to early calculations [4, 5], recent results suggest that the upper b-SS band might be partly occupied (M. Tomášek, A. N. Sorokin, V. D. Kudrin, unpublished results (1971); see also e.g. [10, 11]—the exact position of E_F varies in different calculations). In view of established experimental and theoretical results, we shall consider two deformation modes of the surface layer, the dimerization ($\nu = \xi$) and the buckling mode ($\nu = \eta$),

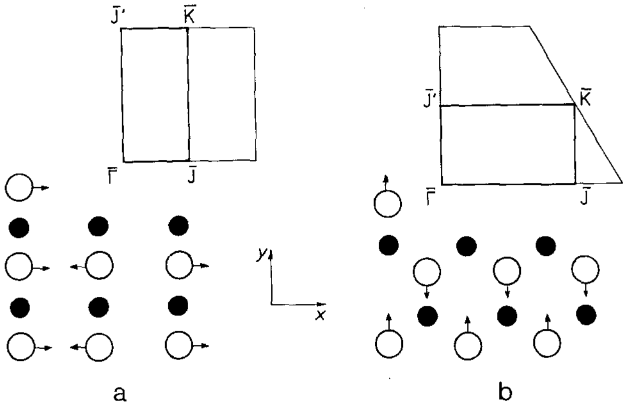

Fig. 1. The (2×1) deformation modes for **a** (001) and **b** (111) surface of Si. Large empty circles (○) denote surface atoms and small full circles (●) denote subsurface atoms. For the (2×1) structure, the inset shows the part of the surface Brillouin zone (SBZ) lying in the first quadrant, together with the corresponding part of the SBZ of the ideal (1×1) structure (thin line)

both with the wave vector $Q = \pi/a\ (1,0)$:

$$\xi = e_x \bar{\xi} \cos QR, \qquad \eta = e_z \bar{\eta} \cos QR.$$

For further reasoning it will be useful to fold [2, 3, 10] the SS bands of the ideal surface into a new reconstructed (2×1) surface Brillouin zone (SBZ) (Fig. 1); Fig. 2 shows the result for the SBZ high-symmetry directions. The interaction caused by a distortion of wave vector Q couples the "folded" branches (denoted by an asterisk in Fig. 2) to the "unfolded" ones. The principal interaction matrix elements for this coupling are $\xi_{bb}, \xi_{dd}, \xi_{bd}, \eta_{bb}, \eta_{dd}$ and η_{bd}, where e.g. $\nu_{bb} = \langle\varphi_b(k+Q)|w_\nu|\varphi_b(k)\rangle = \sum_j \langle\varphi_b(R)|w_\nu|\varphi_b(R-R_j)\rangle \cdot \exp ikR_j$, where w_ν is the "deformation" potential caused by ν, and $\varphi_b(k)$ is the surface Bloch function based on the hybrid φ_b. Fortunately, pronounced local properties of the orbitals

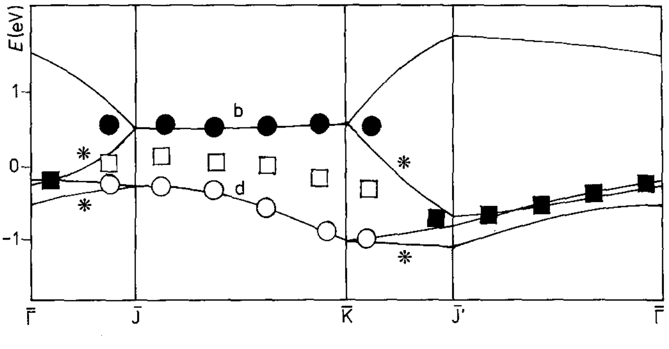

Fig. 2. Bridge (b) and dangling (d) surface state bands of Si(001) (1×1), folded into the (2×1) surface Brillouin zone (schematic). Along $\bar{J}-\bar{K}$, the bands are doubly degenerate. The importance of particular electron-phonon matrix elements in various regions of the SBZ is depicted (ξ_{dd} –○, ξ_{bb} –●, ξ_{bd} –■, η_{bd} –□); see the text for details

Table 1. k-dependence of electron-phonon matrix elements of the Si(001) (2×1) surface (ξ and η are the dimerization and buckling distortions respectively, and a is the lattice constant)

ξ_{bb}	ξ_{dd}	ξ_{bd}	η_{bb}	η_{dd}	η_{bd}
$\sin k_x a$	$\sin k_x a$	$\cos k_x a$	0	0	$\sin k_x a$

$\varphi_{b,d}$ (the only ones to be considered), together with the assumption of a strong electron-phonon coupling [9], make it possible to include just the matrix elements between nearest-neighbour surface atoms which differ by the translation vector $(a, 0)$.[1] By exploiting reflections σ_x, $\tilde{\sigma}_x$ in the mirror planes passing (i) through an arbitrary surface atom and (ii) just between two surface atoms, one finds several restrictions on ν_{rs}. (The essential symmetry properties employed read: $-\sigma_x\xi = \tilde{\sigma}_x\xi = \xi$, $\sigma_x\eta = -\tilde{\sigma}_x\eta = \eta$, $\sigma_x\varphi_d = \varphi_d$, $\sigma_x\varphi_b = -\varphi_b$.) First, it easily follows that $\eta_{bb} = \eta_{dd} = 0$ holds, and second, explicit dependence of the non-zero matrix elements ν_{rs} on k can be obtained (Table 1). As seen from this table, particular matrix elements are important in different regions of the SBZ, the strongest interactions being displayed in Fig. 2. Let us discuss the effect of various matrix elements in the two main situations that emerge from Fig. 2. First, near $\bar{\Gamma}$, $\bar{J}'$ and along $\bar{\Gamma}-\bar{J}'$, ξ_{bd} ($\cos k_x a$ dependence) is responsible for the coupling between the two SS lying close in energy. This coupling leads to a downward shift in energy of one of these SS and a partial depopulation of the other SS (which is the result of its upward shift). Second and certainly more important for the energy stabilization, ξ_{bb} and ξ_{dd} ($\sin k_x a$ dependence) cause a splitting of the b- and d-SS which both were originally doubly degenerate along the $\bar{J}-\bar{K}$ direction. Let us follow the evolution of the energy bands with increasing distortion ξ (cf. also Fig. 16 of [12]). At the beginning, the splitting is particularly large for b-SS ($|\xi_{bb}| \gg |\xi_{dd}|$—a consequence of the very favourable mutual position of the respective hybrids, enabling large overlap and a strong bond); however for sufficiently large but realistic distortions ξ, the b- and d-SS come so close together that an avoided crossing occurs. Due to large splitting in b-SS accompanied by partial population of the latter, the stabilization of the band energy (i.e. the negative contribution to it) is large for such ξ. This agrees with the generally accepted opinion that dimerization is by far the largest distortion on the Si(001) surface.

When b- and d-SS along $\bar{J}-\bar{K}$ approach each other, the chance for the buckling η to operate increases; this happens because η_{bd} also exhibits the $\sin k_x a$ dependence. (Theoretical calculations show [13] that for vanishing ξ, the Si(001) surface is stable with respect to η.) For the experimental values of the distortion ξ, b- and d-SS strongly interact [10, 12], and the perturbation theory based on the ideal (1×1) surface as a zero approximation fails to work. Hence, one is limited to the above qualitative arguments. Nevertheless, it is possible to show that in

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[1] The strength of the electron-phonon coupling has an important effect on the localization properties of the wave function [2, 9]. This sort of localization follows, e.g., from Sects. 3 and 5 in the first item of [2] if Eq. (10) of that paper is replaced by the electron-phonon coupling matrix element $(\langle r|w_\nu|s\rangle\nu$ in the present notation). Naturally, Eq. (9) then represents the usual pseudo Jahn-Teller secular equation

the neighbourhood of the ideal (1×1) geometry ($\xi=0$, $\eta=0$), the chance for the buckling to appear grows with increasing ξ. This follows from a perturbation expansion for the change of the total energy with respect to the ξ, η distortions that is analogous to that of the Landau 2nd order phase transition theory [14]:

$$\delta E = A\xi^2 + B\eta^2 + C\xi^4 + D\eta^4 + E\xi^2\eta^2 + \cdots . \tag{3}$$

Theoretical calculations [13] suggest that B is positive but small. We now sketch arguments that show that the elecron-phonon interaction causes E to have a negative sign, thus making the coupling between ξ and η energetically favourable. This fact will follow from the part of the 4th order contribution $\delta E^{(4)}$ containing the term $\xi^2\eta^2$. By supposing that in various parts of SBZ it is sufficient to consider only the interactions shown in Fig. 2 and, furthermore, that $|\xi_{bb}| \gg |\xi_{dd}|$ holds near $\bar{J}-\bar{K}$, the remainder of the complicated expression [15] for the $\delta E^{(4)}\ \xi^2\eta^2$ term is the sum of the negative contributions

$$-|\eta_{bd}|^2|\xi_{bb}|^2/(\varepsilon_{b_1}-\varepsilon_d)^2(\varepsilon_{b_2}-\varepsilon_d). \tag{4}$$

Equation (3) shows that for $\xi=\xi_0$, the coupling between ξ and η results in the renormalization of B, yielding a new coefficient $(B+E\xi_0^2)$ at η^2. For values $\xi_0^2 > -B/E$, which make the new coefficient negative, this mechanism leads to the destabilization of the surface with respect to η; similar coupling effects are well known in the theory of phase transitions [14].

Neither experiment nor theory give a definitive picture of the Si(001) (2×1) reconstruction yet [13, 16, 17]. Three situations can be envisaged: a) the $\xi-\eta$ coupling is weak and only one minimum of the total energy at $\xi \neq 0$, $\eta=0$ exists (symmetric dimer), b) one has a single minimum at $\xi \neq 0$, $\eta \neq 0$ (asymmetric dimer), c) there are two minima, the first related to the symmetric and the second to the asymmetric dimer, one situation being metastable. Both phases can coexist as observed recently in the experiments of Tromp et al. [17].

2.2. Si(111) *surface*

For this case there is one sp^3-like dangling bond per atom projecting along the perpendicular to the Si(111) surface and the single band is half-filled [1, 6, 18, 19]. The most promising reconstruction model at present is the π-bonded chain model of Pandey [20], in which the surface and subsurface atoms are displaced in the $[2\bar{1}\bar{1}]$ direction (parallel to the y axis in Fig. 1b) to give the (2×1) geometry ($Q=2\pi/3a(2\bar{1}\bar{1})$). This model again represents a certain kind of dimerization. One can imagine the reconstruction of the surface layer as the deformation shown by arrows in Fig. 1b. Contrary to reconstructions of metal surfaces, the deformations are large in the Pandey model, which leads to the formation of quasi-independent parallel zigzag chains [20]. Consequently, it is not surprising that subsurface layers are also involved in the reconstruction. It is to be stressed that the present approach does not pretend to be able to obtain the final equilibrium configuration of the crystal surface, but merely to show the kind of continuous deformations with respect to which the surface layer can be unstable, and in which surface states from E_F can play a dominant role.

Calculation of ν_{rs} [9] for the above displacements involves a single dangling bond on each surface atom (the interaction with nearest neighbouring subsurface atoms being neglected, a simplification which may not be easily justified). The resulting matrix elements exhibit a cos α (sin $\beta/2$) k-dependence, where $\alpha(\beta)$ is the coordinate along the $\bar{\Gamma}-\bar{J}(\bar{\Gamma}-\bar{J}')$ direction of the SBZ of the (2×1) structure (see Fig. 1b), which acquires the value π at the point $\bar{J}(\bar{J}')$. Hence, ν_{rs} is large in the considerable neighbourhood of the point $\bar{J}'$. The induced splitting of SS in this region (cf. Fig. 8a of [20]) points to an efficient (pseudo)-Jahn-Teller coupling in the Pandey model.

With Si(111), the present electron-phonon mechanism does not predict any buckling to occur because the corresponding matrix elements are zero, as was found for Si(001) and in [9]; see, however, [22]. If one admits that buckling can occur, i.e., that up and down displacements of alternating atoms of the zigzag chains perpendicular to the surface are possible, one immediately finds that an energy gap is also opened along the $\bar{J}-\bar{K}$ direction [23]. Such an SS band splitting leads to the existence of an ionic superstructure on the surface which, as is well known, simple LCAO models strongly exaggerate. The inclusion of electronic correlation supresses this artefact [13]. Accurate large-scale total energy calculations are needed to decide which of the two possible situations, namely the asymmetric or symmetric dimer model, is more favourable for the Si(111) surface from the energetic point of view; however that is not the purpose of the present simple approach.

It is interesting to notice the similarity between experimentally observed surface state structure of Si(111) (2×1) and Si(110) (5×1), the latter also probably exhibiting quasi-independent zigzag chains [24].

3. Conclusions

The reconstruction of the Si(001) (2×1) structure does not seem to follow the buckling mechanism, which has been shown [13] to arise from an artefact of the LCAO method. The actual reconstruction is caused mainly by a special kind of saturation of surface bridge and dangling bonds, and this results in a pronounced in-plane dimerization (symmetric dimer); however, the coupling of the dangling bonds with the buckling distortion might be energetically favourable and lead to the asymmetric dimer. One of these two surface structures might be metastable, thus explaining recent experiments [17]. For Si(111), the above (largely) oversimplified approach agrees with the Pandey π-bonded chain model.

Post script. A recent comparison of theoretical calculations and experimental results [28] favours the asymmetric model of the Si(001) (2×1) reconstruction. The authors of the scanning tunneling spectroscopic study [29] suspect, nevertheless, that the presence of a high concentration of defects or vacancies might be responsible for the appearance and stabilization of the buckling.

Recently, the Si(011) (2×1) reconstruction has been dealt with in [30] and a simple unifying approach to the (2×1) reconstruction of three typical silicon surfaces can be found in [31] and in the second item of [3].

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References and notes

1. Tomášek M, Koutecký J (1969) Int J Quantum Chem 3:249-267
2. Tomášek M (1967) Physica 36:420-430; (1968) Physica 39:21-24; (1968) Phys Lett A 26:374-375; (1969) Int J Quantum Chem 3S:849
3. Tomášek M (1985) In: Kollar J, Kroó N, Menyhárd N, Siklós T (eds) Phonon Physics, Proceedings, 2nd Int Conf Phonon Physics, Budapest 1985 World Scientific, Singapore pp 673-676, and J Phys France, to appear
4. Koutecký J (1962) Czech J Phys B 12:184/190
5. Tomášek M (1966) Czech J Phys B 16:828-836
6. Appelbaum JA, Hamann DR (1976) Revs Mod Phys 48: 479-496
7. Appelbaum JA, Baraff GA, Hamann DR (1977) Phys Rev B15:2408-2412; there are more interesting papers on the subject in this volume
8. Pollman J, Krüger P, Mazur A, Wolfgarten G (1985) Surf Sci 152/153:977-994
9. Tomášek M, Pick Š (1984) Surf Sci 140:L279-L284; (1985) Physica 132 B:79-86; (1985) Czech J Phys B 35:768-781; TCM Technical report, Cavendish laboratory, Cambridge University, January 15 (1985) pp 1-36
10. Pollman J, Mazur A, Schmeits M (1983) Physica 117/118 B:771-773
11. Wolfgarten G, Krüger P, Pollmann J (1985) Solid State Commun 54:839-842
12. Larsen PK, van der Veen JF, Mazur A, Pollman J, Neave JH, Joyce BA (1982) Phys Rev B 26:3222-3237
13. Pandey KC (1985) In: Chadi JD, Harrison WA (eds) Proceedings, 17th Int Conf Phys Semicond, San Francisco 1984, Springer, New York Heidelberg Berlin, pp 55-58
14. Bruce AD, Cowley RA (1987) Structural phase transitions. Taylor & Francis, London
15. Kato T (1966) Perturbation theory for linear operators. Springer, Berlin Göttingen Heidelberg New York. The non-zero contribution corresponds to the term $-T^{(1)}ST^{(1)}ST^{(1)}ST^{(1)}P$ in Eq. (2.33), 2, § 2 of Kato's book
16. Mazur A, Pollman J (1982) Phys Rev B 26:7086-7089
17. Tromp RM, Hamers RJ, Demuth JE (1985) Phys Rev Lett 55: 1303-1306
18. Tomášek M, Kudrin VD (1971) Doklady AN SSSR 1312-1313; English translation: Soviet Physics-Doklady (1972) 16:863-865
19. Ivanov I, Mazur A, Pollman (1980) Surface Sci 92:365-384
20. Pandey KC (1983) Physica 117/118 B:761-766
21. Uhrberg RIG, Hansson GV, Nicholls JM, Flodström SA (1982) Surf Sci 117:394-404; (1982) Phys Rev Lett 48:1032-1035
22. Feder R, Mönch W (1984) Solid State Commun 50:311-313
23. Olmstead MA, Chadi DJ (1986) Phys Rev B 33:8402-8409
24. Mårtensson P, Hansson GV, Chiaradia P (1985) Phys Rev B 31:2581-2583
25. Kevan SD (1985) Phys Rev B 32:2344-2350
26. Hansson GV, Uhrberg RIG, Nicholls JM (1983) Surf Sci 132:31-39
27. Himpsel FJ (1983) Physica 117/118 B:767-770
28. Pollmann J, Krüger P, Mazur A (1987) J Vac Sci Technol B5: 945-952
29. Hamers RJ, Tromp RM, Demuth JE (1986) Phys Rev B34:5343-5357
30. Tomášek M, Pick Š, (1988) J phys France 49:99-102
31. Tomášek M (1988) In: Koukal J (ed) Surface physics, Proceedings, 4th Int Symp Surf Phys, Bechyně 1987. Academia and Elsevier, Amsterdam