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Electronic structure and bonding of Si{100} surfaces

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By arguments based on chemical-bond theory we have concluded that the structure of the {100} surfaces of Si involves asymmetrical pairs of a tricovalent $Si^-(s^2p^3)$ atom and a tricovalent $Si^+(sp^2)$ atom, with ideal bond angles 90° and 120°, respectively. With the minimizing of the sum of the squares of the deviations of the bond angles of these atoms and the atoms in the layer below from the ideal values (109.47° for the tetracovalent atoms in the layer below) the positional coordinates are assigned values close to those reported by Chadi and in rough agreement with experiment. The treatment leads also to a decision among alternative superstructures.

I. INTRODUCTION

In the {100} surface of silicon the surface atoms are in approximately a square array with edge 3.840 Å, with each atom attached by two single bonds to atoms in the layer below, the planes formed by these bonds being parallel throughout the surface. It was suggested by Schlier and coworkers[1-4] that the low-energy-electron-diffraction pattern indicates that adjacent rows of surface atoms are bent toward one another. Green and Seiwatz[5,6] then proposed a simple explanation of this bending: It could bring pairs of silicon atoms to within the normal Si–Si single-bond distance, 2.352 Å, from one another, permitting each of these atoms to form a third bond, thus approaching but not reaching the normal valence, 4. They pointed out that the stabilizing effect of the additional covalent bond for each Si_2 pair could overcome the strain energy of bending the bonds from their normal directions (tetrahedral, bond angles 109.47°). Thirteen years later Applebaum, Baraff, and Hamann[7-9] showed that the bond-angle strain energy could be reduced by small displacements in several lower layers of atoms. An important refinement was then made by Chadi[10] by calculations, in part empirical, involving minimization of the energy of the electron-ion system, with electron transfer permitted from one atom of a pair to the other. In the Chadi (the asymmetrical dimer) structure the two atoms of a pair swing toward one another to form a single covalent bond, but with different displacements, one by 0.46 Å and the other by 1.16 Å.

During the past couple of years the validity of the asymmetrical dimer model has come into question.[11,12] The most serious objection was the disagreement between angle-resolved ultraviolet photoemission spectroscopy measurements[13,14] of surface-state dispersion curves and theoretical calculations[15] of these curves based upon conventional models of the electronic structure with the asymmetrical dimer geometry. In addition, these theoretical calculations[15] on the electronic structure of the asymmetric dimer employing a fully self-consistent pseudopotential approach yielded a band considerably higher in energy than the measured band and a bandwidth twice as large as the measured bandwidth. The density of states resulting from these calculations also showed only poor agreement with that obtained from ultraviolet photoemission spectroscopy.[16] Finally, using a cluster model Redondo and Goddard[17] showed that, while closed-shell Hartree-Fock calculations lead to an asymmetric dimer description of the surface, the inclusion of electron correlation yields a symmetric dimer description of the ground state approximately 1.0 eV below the minimum for the Chadi structure.

The Chadi structure is given support by two recent theoretical studies of surface-state dispersion curves in relation to angle-resolved photoemission measurements.[18,19] Furthermore, the asymmetrical dimer geometry is favored by a dynamical low-energy-electron-diffraction analysis,[20] surface photovoltage and work-function measurements,[21] core-level spectroscopic results,[22] and ion-backscattering data.[23,24] Finally, an improved total-energy calculation[25] favors the asymmetrical dimer model.

Neither Green and Seiwatz nor Chadi discussed in detail the electronic structure of tricovalent silicon. We have found that the consideration of this question leads in a simple way to the derivation of a {100} surface structure essentially identical with that proposed by Chadi.[10]

II. TRICOVALENT SILICON

Neutral atoms of silicon and its congeners C, Ge, Sn, and Pb are either bicovalent, with an outer unshared pair of electrons, or tetracovalent, with tetracovalence predominant for C and Si and bicovalence predominant for Sn and Pb. The ions with either an added electron or a missing electron are tricovalent, as was pointed out by Goddard and McGill.[26]

Tin is a congener of silicon. The Sn_2 group in the compound R_2SnSnR_2 with R the unicovalent radical $[(CH_3)_3Si]_2HC$ has been shown by x-ray analysis of the crystal[27] to have an unusual structure, in that the tin-tin bond length is only a little less than the single-bond value, whereas a double bond would be expected to be formed, and the three ligands about each tin atom are pyramidally located, whereas with a double bond the structure would be planar. It has recently been pointed out[28] that a reasonable interpretation of this structure is that an electron is transferred from one Sn atom to the other, permitting each to be tricovalent, with electronic configurations sp^2 for Sn^+ and s^2p^3 for Sn^-, the latter having an unshared electron pair occupying an orbital with essentially s character and bond orbitals with mainly p character. The unshared electron pair resonates between the two tin atoms, making them equivalent. This structure requires $s \rightarrow p$ promotion of only one electron, with electron transfer, whereas the formation of a double bond requires this promotion for both atoms. Consideration of the ratio of promotion energy to bond energy and of the tendency to form both bicovalent and tetracovalent componds indicates that such a structure might well be found for compounds of Ge and Sn, but probably not for C and Si (predominantly tetracovalent) or for Pb (predominantly bicovalent). Support for this conclusion is provided by the results of quantum-mechanical calculations[29] for the molecules C_2H_4, Si_2H_4, and Ge_2H_4. The curve of the energy of ethylene as a function of the angle α between the CC axis and the CH_2 plane of each monomer unit has a well-defined minimum when the angle α is zero, the curve being well approximated by a parabola. For digermene, however, there is a maximum at $\alpha = 0°$, with minima at $\alpha = \pm 40°$, suggesting that the molecule has the singly bonded structure with a resonating unshared electron pair, as proposed for R_2SnSnR_2. The energy curve for disilene has a flat bottom over the range $\alpha = -20°$ to $+20°$, suggesting that the unusual structure makes a significant contribution when α deviates from 0°.

It might accordingly be concluded that the resonating-unshared-electron-pair structure might occur for pairs of Si atoms if conditions were such as to make the structure with a double bond unstable. This situation exists for silicon atoms on the {100} face of a silicon crystal. Each of these atoms is attached by single bonds to two atoms in the layer below the surface layer. By bending these bonds a pair of the surface atoms could approach one another, their interatomic distance decreasing from 3.84 to 2.35 Å, the single-bond value (or even to 2.14 Å, the double-bond value, but the strain energy associated with the large deviation from planarity of the two atoms and their six ligands would make the double-bonded structure unstable). There is accordingly the possibility that electron transfer would occur, with production of a single bond between the paired atoms.

III. DERIVATION OF THE STRUCTURE

Earlier considerations[28] indicate that the resonance frequency of the unshared electron pair for Si_2 is not so great as for Sn_2, and that in Si_2 one structure, $Si^-{-}Si^+$, might dominate over the other, $Si^+{-}Si^-$, leading to a resultant negative charge on the first silicon atom. A simple derivation of the structure can be carried out by assuming complete electron transfer as a first approximation. The first silicon atom, with an unshared $3s^2$ electron pair, forms three covalent bonds with its three $3p$ orbitals (with a little s character), the ideal value of the bond angles being 90°. The other silicon atom, with a positive charge, forms three sp^2 bonds, with the ideal value 120° for the bond angles. The two silicon atoms of a pair move toward one another to decrease the distance between them from 3.84 Å to the single-bond value 2.35 Å, each also keeping at this distance from two atoms in the layer below.

The approach of the two atoms to the single-bond distance by bending the bonds to the atoms in the layer below introduces bond-angle strain for these atoms as well as for the pair on the surface. We may make a simple calculation of the amount of strain by taking it as proportional to the sum of the squares of the deviations for the bond angles from the ideal values, which are 90° for Si^- with s^2p^3 configuration and essentially p bonds, 120° for $Si^+(sp^2)$, and 109.47° for the sp^3 atoms in the layer below. (In order not to complicate the calculation by introducing somewhat uncertain refinements we have not considered the effects of small amounts of d character of the bond orbitals and of the restriction of some of the bond angles to the tetrahedral value.) For a repeating unit of the two tricovalent surface atoms and two tetracovalent atoms in the layer below there are 18 bond angles, 4 of which are restricted to the tetrahedral value with our assumption that only the surface atoms are displaced from their ideal positions, and another 2 have values determined by the superstructure, the arrangement of the pairs relative to one another. For the other 12 angles the minimum of the sum of the squares of the differences between the value of the angle and its ideal value is found to occur for the displacements $\Delta x' = 0.55$ Å, $\Delta z' = -0.12$ Å, $\Delta x'' = -0.95$ Å, and $\Delta z'' = -0.39$ Å for the atoms Si′ and Si″ of the surface pair. These values are not far from Chadi's values $\Delta x' = 0.46$ Å, $\Delta z' = +0.04$ Å, $\Delta x'' = -1.08$ Å, and $\Delta z'' = -0.44$ Å.[10]

The strain energy for the symmetrical structure is 20% greater than that for the unsymmetrical structure, largely because the four angles 108.5° on Si′ and Si″ are far from the ideal values 90° for Si^- and 120° for Si^+.

IV. SUPERSTRUCTURES

Six reasonable superstructures are shown in Fig. 1, with the pairs equivalent in each. A selection among them can be made by considering the electrostatic energy and the contribution to the strain energy of the bonds connecting atoms Si^- and Si^+ with corresponding atoms in adjacent pairs. This contribution is zero for the structures 2×1 and 4×1,

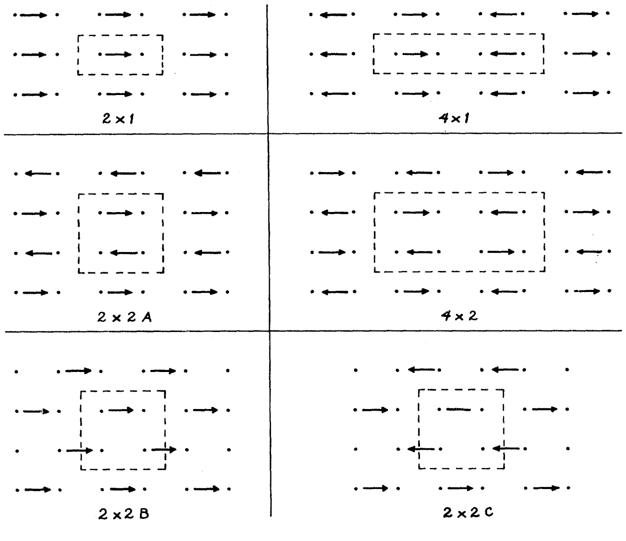

FIG. 1. Six reasonable superstructures for the Si{100} surface. The dots represent the unrelaxed surface atoms and the arrows the dipoles created by the formation of the asymmetrical dimer, with the atoms having positive charge at the arrow end of the dipole.

for which the pairs have the same orientation in vertical columns. The 4×1 structure may be ruled out, however, because of the electrostatically unfavorable distribution of Si^- and Si^+.

The bond-angle strain is only slightly greater for the structures 2×2 *A* and 4×2, by 3.0 deg^2 added to a total of 2457.2 deg^2 for the other 12 angles. The electrostatic energy favors 2×2 *A*, in that all four of the adjacent $\mathrm{Si}^- \rightarrow \mathrm{Si}^+$ dipoles have the stabilizing orientation, as compared with two stabilizing and two destabilizing for 2×1 and 4×2 and all four destabilizing for 4×1. Structures 2×2 *B* and 2×2 *C* are ruled out by very large bond-angle strain, at least 15% greater than that for the other structures.

V. CONCLUSION

The foregoing discussion shows that Chadi's structure for the surface atoms on the {100} face of silicon can be described as involving pairs of atoms that achieve tricovalence by the transfer of an electron from one atom to the other. Our simple calculation shows that the two atoms of a surface pair are bent toward one another by different amounts. Minimizing the sum of the squares of the differences between the values of 12 bond angles formed by the Si^-–Si^+ pair and the atoms in the layer below from the ideal values 90° for $\mathrm{Si}^-(sp^3)$, 120° for $\mathrm{Si}^+(sp^2)$, and 109.47° for $\mathrm{Si}(sp^3)$ places Si^- 1.24 Å above the layer below and Si^+ 0.97 Å above this layer. The electric charges on Si^- and Si^+ are probably reduced somewhat by the partial ionic character of the bonds formed by these atoms and by some resonance of the unshared electron pair from Si^- to Si^+, but not so much as to approximate Chadi's values ± 0.36. Consideration of the electrostatic energy and the bond-angle strain energy leads to the conclusion that the most stable superstructures are 2×2 *A*, 2×1, and 4×2. The experimental evidence favors the 2×1 structure, but evidence for 2×2 and 4×2 structures has been reported.[20,30–33]

The present work indicates that it is possible for all three of these superstructures to coexist on the Si{100} surface.

The angle-resolved photoelectron spectroscopy results of Himpsel, Heimann, Chiang, and Eastman[22] on the Si{100} surface support the notion of a dimer with oppositely charged Si atoms inasmuch as these results exhibit surface features near +0.4 eV and near −0.3 eV relative to the bulk Si(2*p*) levels. Based on their findings, Himpsel *et al.* rule out symmetrical pairing models. Moreover, the similarities in the angle-resolved photoemission spectroscopy spectra of the Si{100}, Ge{100},[34] and GaAs{100} (Ref. 35) surfaces suggest that all three surfaces have similar structures. Positively charged Ga atoms and negatively charged As atoms are surely expected on the latter surface.

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