

CHEMICAL PSEUDOPOTENTIAL THEORY
OF SURFACE RECONSTRUCTION

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Chemical pseudopotential idea is applied to discuss reconstructions at semiconductor surfaces. The surface energy is minimized in the bond description from first principles. Simple models for two surfaces of silicon lead to a reconstruction in agreement with current pictures.

I. Introduction

Since Harrison's bond theory[1] of determining surface reconstructions at semiconductor surfaces from energy principles, several theories[2-5] have been presented which aim at accounting for every detail of LEED and photoemission spectra. These theories involve either a couple of force constant parameters or a few scaling functions for interaction. The current microscopic theory[3-5] is capable of predicting the reconstruction only after a complete surface band structure is calculated as a function of the atomic displacements in the surface region, which requires a huge amount of numerical calculation. The resulting reconstruction, on the other hand, does not appeal to chemical bond intuition as Harrison's qualitative theory[1].

The chemical pseudopotential(CPP) method[6] is characterized by complementary aspects. It is based on first principles and requires no external parameters or scaling rules. It is a local theory that fits to the chemical bond concept. In addition self-consistency is in principle built in. The CPP method has been successfully applied to the bulk band structure[7,8], the bulk moduli[9] and the imperfections[10,11] of covalent semiconductors. The electronic structure of ideal and relaxed (but not reconstructed) silicon surfaces was discussed by Casula, Ossicini, and Seloni[12] in this method.

We apply the CPP method to the problem of determining surface reconstruction in its simplest version. Our numerical calculations on the well-known silicon surfaces show that the method is conveniently applicable and represents a natural extension of Harrison's original discussion.

II. Bond Energies in the CPP Representation

An expression for the energy of a covalent bond in the bulk (undistorted) crystal was derived by Bullett[9] in the CPP formalism. The breakdown of symmetry in the bonds near the surface requires a modification, which can be done in an approximate way by still considering a bond $|\phi_{ab}\rangle$ of the form $\alpha(|\phi_a^b\rangle + |\phi_b^a\rangle)$ which is built from a hybrid $|\phi_a^b\rangle$ of energy ϵ_a^0 , located on atom A and directed toward atom

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B and a similar one on atom B, but now $|\phi_a^b\rangle$ and $|\phi_b^a\rangle$ are no more equivalent and have different atomic energies because atoms A and B are in different environment. Following the notation of Bullett[9], the bond energy is given by

$$\begin{aligned} \epsilon_{ab} = & (1/2) (\epsilon_a^0 + \epsilon_b^0) \\ & + \frac{V_{aa} + V_{bb} + V_{ab} + V_{ba} - \sum_{a,\text{core } b} S_{a,\text{core } b} V_{\text{core } b,a} - \sum_{b,\text{core } a} S_{b,\text{core } a} V_{\text{core } a,b}}{2(1+S_{ab})} \\ & - \alpha \left(\sum_d S_{ab,bd} V_{bd,a} + \sum_c S_{ab,ac} V_{ac,b} \right) \quad [\alpha^{-2} = 2(1+S_{ab})] \end{aligned} \quad (1)$$

in terms of the overlap S and the matrix element V of the change in atomic potential caused by the presence of a neighbor atom. In eq. (1) both S and V are evaluated between hybrids and bonds but they are also expressible as linear combinations of matrix elements between atomic orbitals. We have evaluated these using Herman-Skillman's program and their values at the bulk interatomic distance are listed in Table I. Their variation with interatomic distance is shown in Fig.1. It should be noted that the core(2s,2p)-valence(3s,3p) matrix elements are as large as or larger than the valence-valence ones and are strongly distance-dependent. This leads to a large repulsion (core orthogonalization[9], the core terms in eq.(1)) and their variation contributes very importantly to surface reconstruction.

Table I Potential matrix elements V and overlap integrals S for n.n. Si atoms at their bulk separation calculated with Herman-Skillman atomic functions and potentials: Note the nonhermiticity of V

ℓ	m	$V^{\ell m}$ (eV)	$S^{\ell m}$
valence-valence			
3s	-3s	-1.31	.251
3s	-3p σ	-3.40	.397
3p σ	-3s	-0.95	.397
3p σ	-3p σ	-1.71	.291
3p π	-3p π	-0.81	.275
core-valence			
2s	-3s	-4.185	.030
2s	-3p σ	-12.146	.084
2p σ	-3s	-2.167	.017
2p σ	-3p σ	-3.065	.030
2p π	-3p π	-1.111	.011

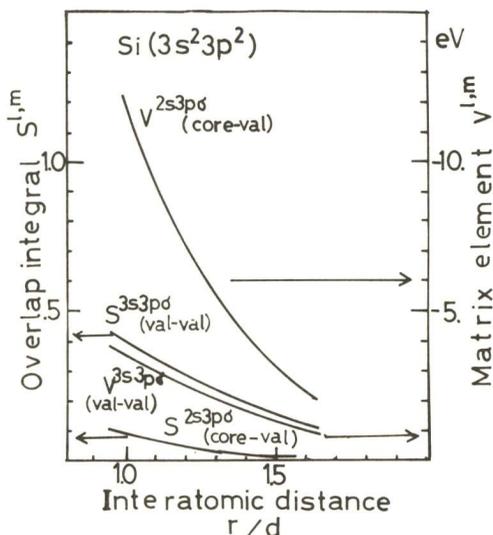


Fig.1 Variation of representative overlap integrals S and potential matrix elements V with interatomic distance

III. Energy Minimization

We consider simplest models for two well-studied surfaces of Si and examine how our method works. In all cases only the motion of the first layer atoms along a symmetry axis is considered.

For the Si(111) 2×1 reconstruction we assume a simple ionic model as shown in Fig.2(a), where alternate rows of surface atoms are subjected to vertical displacements u_1 and u_2 , with accompanying charge

transfer δZ from the lowered atom L to the raised atom R. The change in energy per surface unit cell by this reconstruction is

$$\begin{aligned} \delta E(u_1, u_2, \delta Z) &= 4\delta\epsilon_{a,r}(u_1, u_2) + 2\delta\epsilon_{a,r}(u_1, u_2) + 4\delta\epsilon_{a,l}(u_1, u_2) + 2\delta\epsilon_{a,l}(u_1, u_2) \\ &+ 2\delta\epsilon_{a\bar{a}}(u_1, u_2) + 2\delta\epsilon_{a,\bar{a}}(u_1, u_2) \\ &+ (1+\delta Z)[\epsilon^{DB}(u_1) + U\delta Z] + (1-\delta Z)[\epsilon^{DB}(u_2) - U\delta Z] - U(\delta Z)^2 - 2\epsilon^{DB}(0) \\ &- 2\alpha(\delta Z)^2 \\ &+ (6 + \frac{3}{2}\delta Z)\epsilon^{ES}(u_1) + (6 - \frac{3}{2}\delta Z)\epsilon^{ES}(u_2) - 12\epsilon^{ES}(0) \end{aligned} \quad (2)$$

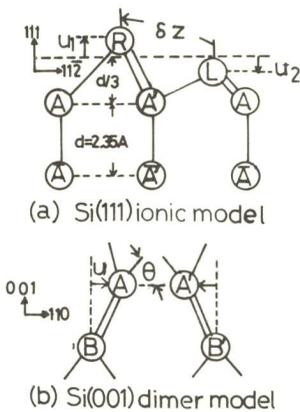


Fig.2 Reconstruction models for Si surfaces

where, on the right, the first line represents the energy change in the bonds between the first and the second layer, the second line the similar quantity for the second and the third layer, the third line the change in the surface dangling bonds, the fourth line accounts for the Madelung energy resulting from the surface ionization and the last line is the change in electrostatic energy between the first and the second layer. The intra-atomic Coulomb repulsion U is estimated to be $\sim 7\text{eV}$ from the calculated free atom ionization energies and the Madelung energy α is $\sim 0.7\text{eV}$ for the surface lattice. After eliminating δZ from the minimum condition

$$\delta Z = \frac{\epsilon^{DB}(u_2) - \epsilon^{DB}(u_1) + \frac{3}{2}[\epsilon^{ES}(u_2) - \epsilon^{ES}(u_1)]}{2(U - 2\alpha)} \quad (3)$$

the energy δE can be determined for a given configuration; all bond and electrostatic energies are calculated numerically as functions of u_1 and u_2 . The energy δE reaches a minimum of -2.38eV at $u_1 = 0.20d$, $u_2 = -0.18d$ and $\delta Z = 0.38$ electrons, where $d = \text{bulk n.n. distance } 2.35\text{\AA}$. At this configuration, the charge transfer, the change of core orthogonalization by reconstruction, and the distortion of surface dangling bonds contribute almost equally to lowering energy, and their sum overcomes the enhancement in the back bond energy. The electrostatic energy does lower the energy but its contribution is not important.

In a similar method we have examined a dimer (covalent) model [13] for the same surface, in which alternate rows of surface atoms undergo a displacement u toward each other within the plane and the vertical dangling bonds rotate to form covalent bonds. The amount of this rotation is determined by orthogonalizing the surface bond to the three back bonds, so that the problem involves a single variable u . We find that the total energy increases with u and no minimum is attained; the increase in the three distorted back bond energy is too great to be overcome by the bond forming energy.

On the (001) surface of silicon, on the other hand, the surface atom has two back bonds and two dangling bonds, so that the direction θ of one of its dangling bonds and the atom's parallel displacement u can be taken as independent variables of the 2×1 dimer model. This

reconstruction is illustrated in Fig.2(b). The change of total energy per surface unit cell is

$$\delta E(u, \theta) = 2\delta\epsilon_{aa}(u, \theta) + 2\delta\epsilon_{DB}(u, \theta) + 8\delta\epsilon_{ab}(u, \theta) + 8\delta\epsilon_{ab}^{ES}(u) + 2\delta\epsilon_{aa}^{ES}(u) \quad (4)$$

for this model, where the first term represents the energy of the new bond created at the surface and the other terms give similar quantities as before. The total energy is again minimized with respect to u and θ . A minimum of -0.57eV per dimer is reached at $u=0.18d$ and $\cos\theta=0.7$.

IV. Discussion

Table II compares the displacements of surface atoms employed by several authors, which shows the values are still far from being conclusive. One of the advantages of our method is its freedom from accumulation errors in energy evaluation, which are inherent in most band type calculations. Our model is extremely primitive, yet its predictions are not inconsistent with current pictures of surface reconstruction derived from diverse sources.

Table II Displacements in A of the first layer atoms in the (2x1) reconstruction at the (111) and (001) surfaces of silicon, either assumed or determined: Some of the works involve displacements other than these. The primed and unprimed displacements correspond to the two inequivalent atoms in the surface unit cell, and z and z' are perpendicular to the surface.

(111)	Authors			z	z'
	present			0.47	-0.42
	Taloni and Haneman (2x2) [14]			0.18	-0.11
	Pandey and Phillips[15]			0.35	-0.29
	Schlüter, Chelikowsky, Louie and Cohen[16]			0.18	-0.11
	Appelbaum and Hamann[17]			0.16	-0.35
	Harrison[1]			0.78	-0.78
	Chadi[3]			0.31	-0.44
(001)	Authors	x	x'	z	z'
	present	0.42	-0.42	0	0
	Appelbaum and Hamann[2]	0.69	-0.69	0.09	0.09
	Chadi[5]	0.46	-1.08	0.04	-0.44

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