Realistic Tight-Binding Calculations of Surface States of Si and Ge (111)

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We give semiempirical tight-binding calculations of dangling- and back-bond surface bands and resonances for unreconstructed relaxed Si and Ge (111) surfaces. For Si at high-symmetry points these are in very good agreement with those of Appelbaum and Hamann. Comparison of the results with the energy-loss-spectroscopy data of Rowe and Ibach suggests that the observed back-bond resonances are associated primarily with minima in the back-bond surface bands.

The tight-binding (TB) method of treating the electronic structure of semiconductors is attractive because of its immediate connection with ideas of chemical bonding, but it has been replaced in realistic treatments of bulk valence and conduction bands by the pseudopotential method, which yields very accurate results with very few parameters.[1] Self-consistent results have been obtained for Si (111) 1×1 surfaces by combining a pseudopotential treatment along the surface with a cellular (numerical integration) approach normal to the surface.[2] These calculations, when made fully self-consistent,[2] can serve as a standard to determine the validity of more economical methods, including especially the intuitively appealing TB or atomic orbital (AO) method. We find that AO's can be made to yield results for both bulk valence and surface bands which are very similar to those of more rigorous fully self-consistent calculations, granted the inevitable uncertainties (of order 0.03 Å) in our knowledge of the coordinates of the surface atoms.

Our motivation for exploring the TB approach stemmed from the observation[2] that about 70% or more of the charge associated with surface states [either of the dangling-bond type, which lie between the valence and conduction bands and are labeled S_1 in energy-loss experiments,[3] or of the deeper back-bond (relaxation) type, labeled S_2 and S_3] is localized outside the second layer of atoms. This means that surface states are more like deep traps than they are like shallow impurity states, and it highlights the necessity of localizing the states to achieve self-consistency (including dynamical equilibrium of surface atom cores). With a nearest-neighbor Hückel model we have already shown[4] that qualitatively correct results can be obtained using AO's, including in the relaxed case the existence and correct binding energies of the S_2 and S_3 back-bonding states. However, that model did not yield quantitatively satisfactory results, especially for the bandwidth of the dangling-bond states.

To achieve quantitatively satisfactory results, we have made extensive studies of TB fits to the energy bands of Si and Ge, the results of which will be described in detail elsewhere.[5] The valence bands can be fitted very well, and the lowest conduction band fairly well, using only eight parameters: the s and p atomic energies, the four nearest-neighbor s-p overlap integrals, and the $(pp\sigma)_2$ and $(pp\pi)_2$ second-neighbor interactions. With this set the parameters vary regularly from $(ss\sigma)_1$ to $(sp\sigma)_1$ to $(pp\sigma)_1$ and satisfy the two-center approximation. They are overdetermined through a least-squares fitting procedure involving forty energy levels regularly spaced throughout the Brillouin zone. Our bulk energy bands fit the pseudopotential and/or experimental energy levels (where known) with an rms accuracy for the valence bands of 0.3 and 0.2 eV for Si and Ge, respectively, compared to typical band widths of 2–3 eV.

Having determined an accurate set of bulk parameters, we can immediately calculate surface states and surface resonances for semi-infinite lattices. To treat the effects of relaxation of the surface plane (contraction caused by strengthening of back bonds), we assume that each overlap parameter is altered according to

$$H_{kl}(R_{ij}) = H_{kl}(R_{ij}^{\,0})\exp[\beta(R_{ij}^{\,0} - R_{ij})]. \qquad (1)$$

In Eq. (1) the bulk parameters and bond lengths are represented by $H_{kl}(R_{ij}^{\,0})$ and $R_{ij}^{\,0}$, respectively. The exponential factor describes the enhancement of interactions caused by surface contraction.

The use of a common enhancement factor in Eq. (1) represents an oversimplification whose validity we now examine by comparing the results obtained from it with those of Appelbaum and Hamann (AH).[2] We consider Si (111) sur-

TABLE I. (111) Si and Ge relaxed surface-state energy levels, in eV.

$\vec{k}_s$	n	AH(Si)	TB(Si)	TB(Ge)
Γ	1	0.88	1.04	0.48
	2(2)	−1.95	−1.71	−1.78
	3	−12.87	−12.90	−12.84
J	1	0.04	0.17	0.07
	2	−3.55	−3.78	−3.89
	4	−10.67	−10.46	−10.73
K	1		0.11	0.28
	2		−5.65	−5.64
	3		−8.35	−8.94
	4		−9.60	−10.02

faces with a surface contraction[2] of 0.33 Å and let $\beta = 3.50(a/4)^{-1}$, where a is the cubic-lattice constant. For practical purposes we have one leading parameter, $\beta\delta R_{12}$, where R_{12} is the separation of nearest-neighbor atoms in the first and second layers; because of the inherent uncertainties in δR_{12} (which must be comparable to or greater than the uncertainties in theoretical calculations[6] of bulk bond lengths), the adjustable character of both calculations is comparable.

Our results for $\vec{k}_s$ (the surface wave vector) at Γ (zone center), J (edge center), and K (corner) for Si (111) are listed in Table I, where they are compared with those of AH.[2] The back-bonding bands themselves are shown in Fig. 1. By comparing, at each $\vec{k}_s$, the surface-state energies with the energies of bulk states with wave vector $\vec{k} = \vec{k}_s + \vec{k}_n$, where $\vec{k}_n$ is normal to the (111) surface, we establish whether a given state is a true surface state or only a surface resonance. Large portions of the back-bonding bands are seen to be resonant, but for the purposes of, e.g., electron-energy-loss experiments[3] the resonant states may contribute to the observed spectra almost as well as the true surface states.

Calculations have also been done for Ge (111) 1 × 1, assuming the same contraction of the surface plane (0.33 Å) and the same value of β. The results for the back-bonding bands are almost the same as for Si, but there are differences in the dangling-bond bands which are shown in Fig. 2. These differences arise primarily from the difference between the bulk conduction bands of Si and Ge.

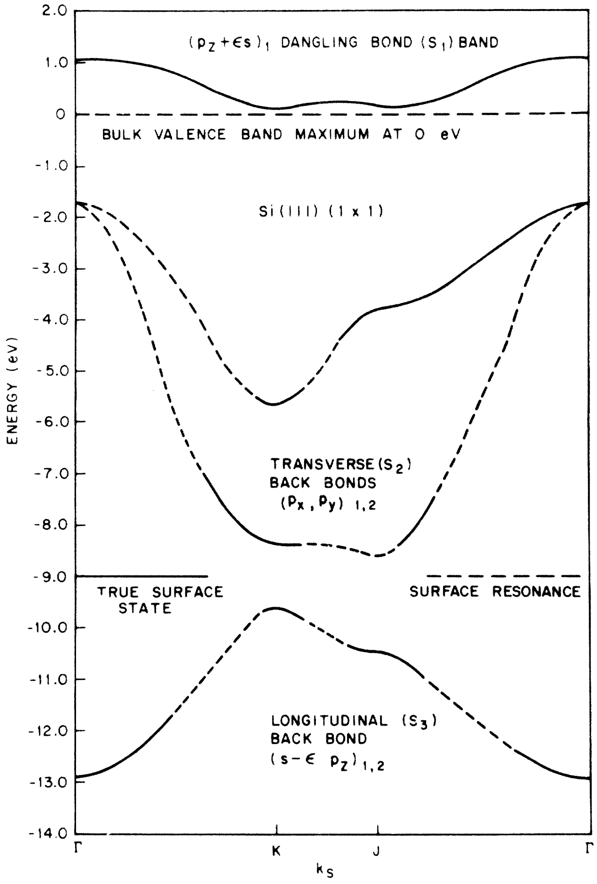

FIG. 1. Dangling- and back-bond surface bands and resonances for a relaxed Si (111) surface.

The absolute position of the AH dangling-bond bands relative to the bulk valence-band maximum is quite sensitive to the degree of self-consistency of their potential in the region just outside the first atomic plane. Our model (based on "neutral-atom" energy levels, which is *not* equivalent to a superposition of neutral-atom pseudopotentials) reproduces the AH position for Si within about 0.15 eV. Even more impressive are our results

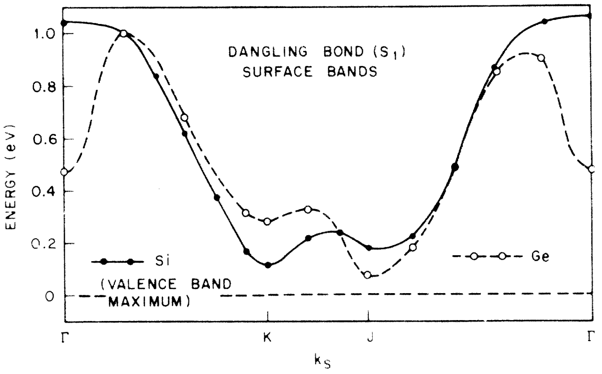

FIG. 2. Comparison of dangling-bond surface bands of Si and Ge relaxed (111) surfaces.

for the bandwidth of the dangling-bond band. AH give this width as 0.84 eV, while we find a width of 0.87 eV.

Because of the σ symmetry of the S_1 and S_3 surface bands, compared to the π symmetry of the S_2 bands, in an energy-loss experiment[3] one would expect the final states of electrons excited from the S_1 and S_3 bands to have similar energies, although different final-state energies would be possible for electrons excited from the S_2 bands. Moreover, the initial energies should be dominated by either the step-function discontinuities associated with maxima and minima or saddle-point logarithmic peaks. For the back bonds the maxima and saddle points arise primarily from surface resonances, which we may regard as surface states broadened by autoionization into the parent bulk bands of similar planar symmetry. The step-function discontinuities associated with minima, on the other hand, lie below their parent bulk bands and so should be less broadened and therefore observable in energy-loss spectroscopy (ELS).[3] The minima for the back-bond bands occur at -5.6, -8.6, and -12.9 eV. The first and last of these energies correspond to the S_2 and S_3 resonance transition energies[3] if we assume a common final state near $+2.0$ eV. The second energy would give rise to a resonance near 10.6 eV which would not be separated from the surface plasmon resonance at 11 eV. However, on the (7×7) surface the observed loss peak at 11 eV is unusually broad, and this may be taken as evidence for its composite character.

We have also obtained results (Table II) for Si and Ge (100) relaxed 1×1 surfaces. Because of double bonding, the contraction of the surface plane is assumed to be 0.45 Å and the relaxed parameters are taken from (1) with β unchanged from (111). Because the reconstructed 2×1 surfaces are thought[7] to have 50% vacancies, comparison with experiment is tentative. The upper dangling-bond surface band is a p_y or p_z state localized on surface atoms, the second one $p_x+\epsilon s$. It seems likely that the broad and weak ELS resonance[3] from 6 to 10 eV is associated with band 3, which arises from p_z or p_y states localized on atoms in the second layer. The $s+\epsilon p_x$ back-bond surface bands lie lower in energy on (100) than on (111), and in the ELS data the corresponding losses are broader and extend to higher energies [from 13 to 16 eV for (100) compared to 13 to 15 eV for (111)]. This is in good agreement with the portions of the bandwidths of the surface bands for each surface which lie below the bulk bands.

TABLE II. (100) Si and Ge relaxed surface-state energy levels, in eV.

$\vec{k}_s$	n	Si	Ge
Γ	1	1.91	1.77
	2	0.47	0.28
	3	−5.39	−5.50
	4	−13.53	−13.31
J	1	1.54	1.64
	2	−0.64	−1.02
	3	−8.14	−8.36
	4	−11.88	−11.88
K	1	−0.66	−0.12
	2	−0.83	−1.09
	3	−9.94	−10.23
	4	−10.89	−10.92

More detailed comparisons of the effects of surface states and resonances on, e.g., photoemission spectra[8] require inclusion of the effects of surface reconstruction.[7,9] Calculations for reconstructed surfaces will be reported elsewhere.

Added note.—The distinction between surface resonances and true surface states has been made by comparing, at a given $\vec{k}_s$, the energy of an apparently exponentially decaying state with the range of energies spanned by bulk states.[10] The significance of the resonant states is demonstrated by calculations (to be published) which show that the analytic singularities in the two-dimensional density of states associated with the (combined) resonant and true surface bands shown in Fig. 1 are reproduced in the atomic density of states of the surface atom.

Our interpretation of the S_2 and S_3 features observed in ELS has been strengthened by recent measurements by ELS of unoccupied surface-state spectra on Ge (111) 2×1 by J. E. Rowe (to be published). When combined with earlier optical data,[11] Rowe's spectra suggest significant exciton enhancement (peaking up) of the step-function thresholds.

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Two-Dimensional Molecular Diffusion: An NMR Study of the Intercalation Complex $TaS_2:NH_3$

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Anomalous behavior of the proton spin-lattice and spin-spin relaxation times in the intercalation complex $TaS_2:NH_3$ is shown to result from the two-dimensional aspects of the motion of the intercalated ammonia molecules.

Interest has been generated by the observation that atoms or molecules can be intercalated into layered transition-metal dichalcogenides.[1] The structure of the intercalation complex $TaS_2:NH_3$ is shown schematically in Fig. 1. The host material, the $2H$ polytype of TaS_2,[1] forms a layered structure, the basic layer unit consisting of a hexagonal sheet of Ta atoms sandwiched between similar sheets of sulfur. Adjacent units are held together weakly, with the interlayer Ta-Ta distance being 6 Å. When NH_3 molecules enter between the TaS_2 layers the interlayer Ta-Ta distance increases to 9 Å. In the presence of excess ammonia, the molecules almost completely fill the interlayer region, presumably forming a hexagonal array. For complete filling there is one NH_3 molecule per TaS_2. Intercalation modifies the host properties, changing the character of the conduction electrons and greatly enhancing the electronic anisotropy.[1] Indeed, interest in the intercalation complexes of the layered dichalcogenides results largely from the quasi-two-dimensional character of the conduction bands and the modification of the superconducting properties of the dichalcogenides by intercalation. Intercalation also affects the guest molecules, and we are using NMR to study the chemistry of the guest-host interaction and the dynamics of these molecules. Previous wide-line NMR observations indicate rapid molecular motion at 300 K,[2] that is confined to two dimensions by the TaS_2 layers. The present transient NMR data unambiguously exhibit the two-dimensional character of this motion. We believe this is the first quantitative microscopic study of such effects.

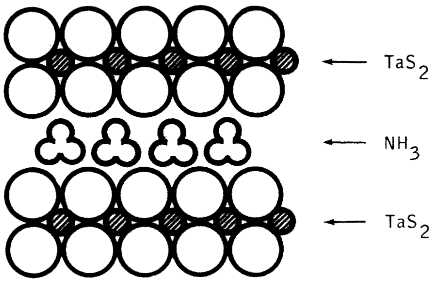

FIG. 1. Schematic representation of the intercalation complex $TaS_2:NH_3$.

The intercalation complexes are formed by exposing $2H$-TaS_2 powder to high-purity NH_3 vapor generated by a reservoir of dry liquid ammonia at room temperature. The TaS_2 swells rapidly. After one day the ammonia reservoir is frozen with liquid nitrogen and the sample is quickly sealed. The composition of the sample was determined by elemental analysis to be $TaS_2(NH_3)_{1.00 \pm 0.05}$. Proton spin-lattice ($T_1$) and spin-spin ($T_2$) relaxation times were measured at 300 K for frequencies from 4.5 to 85 MHz. The magnetization recovery after saturation was exponential and the uncertainties in T_1 were ± 5%. Data for samples of $TaS_2:N^{14}H_3$ and $TaS_2:N^{15}H_3$ are shown in Fig. 2(a). The values of $1/T_1$ are the same for both samples and decrease with increasing frequency, the total change being greater than 40%.[3] The T_2's were measured by the Carr-Pur-