UC-404
LBL-25628 c.1

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

Presented at the 19th International Conference on the Physics of Semiconductors, Warsaw, Poland, August 13–20, 1988

First Principles Theory of Semiconductor Surface State Energies

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July 1988

For Reference

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Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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First Principles Theory of Semiconductor Surface State Energies

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The quasiparticle surface state energies are evaluated for semiconductor surfaces using a self energy approach which incorporates many-body effects due to the electron-electron interaction. Quantitative results are presented for the prototypical Si(111):As and Ge(111):As surfaces and compared to angle resolved photoemission data as well as scanning tunneling spectroscopy measurements showing excellent agreement. Consequences for calculations based on the local density approximation are discussed.

Theoretical treatment of semiconductor surface state energies has either been empirically based or carried out within the framework of the local density functional (LDA) approach. The latter does not require empirical input, but suffers from the band gap problem well known in the case of bulk semiconductors: the minimum gap is underestimated by 30-100% in comparison to the measured optical absorption edge. For bulk semiconductors, a self energy approach including the many-body aspect of the electron-electron interaction has proved quite successful in giving accurate quasiparticle energies and band gaps [1]. Here we briefly describe a self energy approach for the surface case. This work complements structural studies of surface reconstruction based on total energy minimization using the LDA [2]. The atomic coordinates and self consistent charge density so obtained are used as input to the present calculation of the excitation energies. This provides the crucial link between structural studies and the extensive spectroscopic characterization of surfaces.

Briefly (for details, see [3]), the calculations are carried out using a repeated slab geometry. The equilibrium relaxation of the surface layer and corresponding ground state charge density are obtained from self consistent LDA pseudopotential calculations. The quasiparticle energies are given by [4]

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$$\left(T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right)\psi(\mathbf{r}) + \int d\mathbf{r}'\Sigma(\mathbf{r}, \mathbf{r}'; E^{qp})\psi(\mathbf{r}') = E^{qp}\psi(\mathbf{r}),$$

where the terms correspond to the kinetic energy, external potential due to the ion cores, the average electrostatic potential and the electron self energy operator respectively. The latter contains the effect of exchange and dynamical correlations. The electron self energy operator is expanded to first order in the screened Coulomb interaction (the GW approximation) [4]:

$$\Sigma(\mathbf{r}, \mathbf{r}'; E) = \frac{i}{2\pi}\int d\omega\, e^{-i\delta\omega} G(\mathbf{r}, \mathbf{r}'; E-\omega) W(\mathbf{r}, \mathbf{r}'; \omega).$$

The full crystalline Green's function G and dynamically screened Coulomb interaction W enter. Our approach is to make the best possible approximations for G and W separately, calculate Σ and then obtain the quasiparticle energies. Inclusion of local fields in the screened Coulomb interaction is crucial: the off-diagonal elements of the dielectric matrix in Fourier space distinguish the screening properties of the bulk region from the vacuum region as well as the variations from bonding to interstitial regions.

Proper addition of a monolayer of As to the Si(111) and Ge(111) surfaces yields a near ideal surface geometry [5]. The As atoms have been shown to substitute for the last layer of host atoms [5,6] stabilizing an unreconstructed surface because of the fully occupied As lone pair orbital. The 1×1 surface periodicity and extensive experimental characterization make these surfaces excellent prototypes for the present self energy approach.

The relaxed position of the As atoms has been calculated and agrees well with X-ray standing wave data [6]. Using this geometry, the electron self energy operator is evaluated to yield the quasiparticle energies for the surface states. Uncertainties in numerical convergence give a precision of 0.1 eV for the occupied surface states and 0.2 eV for the empty surface states.

The results for the Ge(111):As surface are presented in Fig. 1. The LDA energies are also shown. The salient features are the occupied As lone pair resonance/state and a well defined empty surface state split off from the continuum near $\bar{\Gamma}$. Relative to the LDA energies, the lone pair band is broader and the gap to the empty surface state is increased. Similar results pertain for the Si(111):As surface with the empty state in the projected gap. The position and dispersion of the lone pair band has been measured using angular resolved photoemission [5]. This data is compared to the calculated quasiparticle energies for Ge(111):As in Fig. 2 showing excellent agreement. Table I, with data at selected symmetry points, further illustrates the agreement.

The present calculations predict the position of the empty surface state near $\bar{\Gamma}$. This state has symmetry taken from the L_{1c} bulk conduction band states (antibonding states with a mixture of s and p_z character). Optical transitions between the lone pair band and the empty state at $\bar{\Gamma}$ are dipole allowed for light polarized perpendicular to the surface. The surface gap has

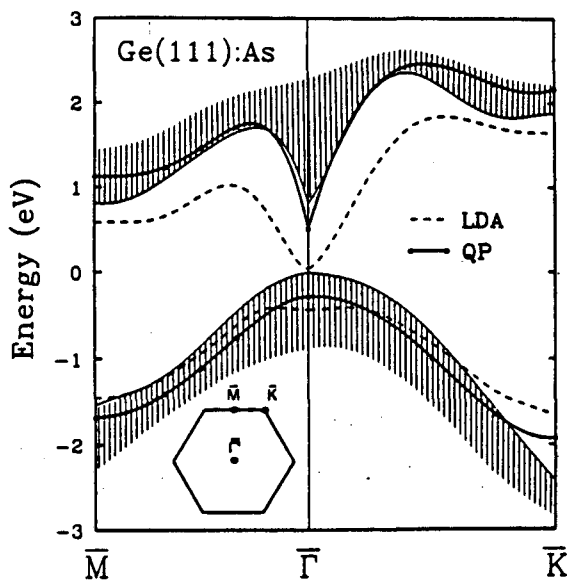

Figure 1. Comparison of the quasiparticle surface state band energies to those derived from the LDA. The quasiparticle bulk projected band structure is shown.

	LDA	QP	Expt
Si(111):As			
$\bar{\Gamma}$	-0.31	-0.39	-0.39
$\bar{M}$	-1.23	-1.44	-1.44
$\bar{K}$	-1.45	-1.71	-1.75
$\bar{\Gamma}\rightarrow\bar{K}$	1.14	1.31	1.36
$E_g(\bar{\Gamma}\rightarrow\bar{\Gamma})$	1.31	2.22	1.9
Ge(111):As			
$\bar{\Gamma}$	-0.43	-0.28	-0.44
$\bar{M}$	-1.45	-1.68	-1.81
$\bar{K}$	-1.61	-1.92	-2.06
$\bar{\Gamma}\rightarrow\bar{K}$	1.18	1.64	1.62
$E_g(\bar{\Gamma}\rightarrow\bar{\Gamma})$	0.47	0.79	0.8

Table I. Selected results for the occupied surface state energies relative to the valence band edge, the surface band dispersion and the surface state gap at $\bar{\Gamma}$ in comparison to the LDA and experiment (angle resolved photoemission from Ref. 5 and the gap from Ref. 7).

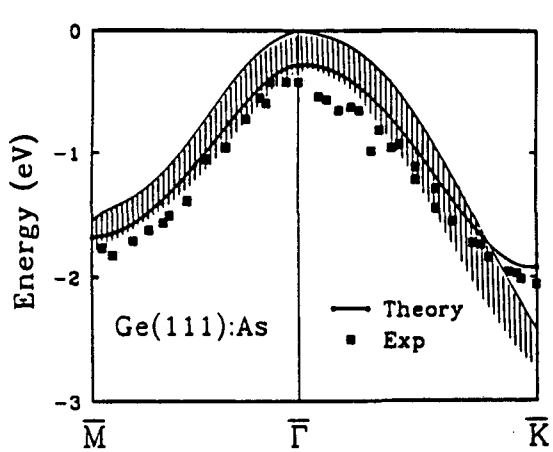

Figure 2. Comparison of the quasiparticle surface-state energies to data from angular resolved photoemission (Ref. 5).

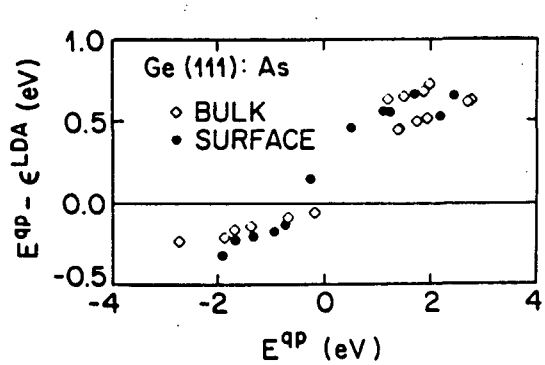

Figure 3. The difference between the quasiparticle energy and the LDA eigenvalues are shown as a function of energy for states near the gap.

been measured using scanning tunneling spectroscopy for both surfaces [7]. The data shows features which we associate with the onset of the lone pair band and the empty surface state predicted here. The measured gap is in good agreement with the present calculations, as shown in Table I.

Given the common use of LDA calculations to interpret surface spectroscopic data, one would hope to have a simple prescription for correcting the LDA eigenvalues. Unfortunately, a simple rigid shift of the empty surface states relative to the valence band edge is inadequate. This is illustrated for the case of Ge(111):As in Fig. 3. The correction is distinct for the occupied surface states in comparison to the bulk states. It interpolates through the gap for the surface states near $\bar{\Gamma}$. This is correlated with mixed character for these states. They derive weight from the bulk valence and conduction bands. Any model for correcting LDA surface state energies must account for this.

This work was supported in part by National Science Foundation Grant No. DMR8319024 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098. A grant of CRAY time at the NSF San Diego Super Computer Center is gratefully acknowledged.

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