Energy Dependence of the Single-Particle Self-Energy Correction for Ge and Si

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The energy dependence of the self-energy correction $\Delta(E)$ to local-density-functional pseudopotential theory has been determined for Si and Ge from -15 to 16 eV above the Fermi energy E_F, and compared to recent calculations. The real part of $\Delta(E)$ was determined from the shift, relative to calculations, of detailed x-ray bremsstrahlung isochromat spectra, which exhibited many new higher-energy features, and x-ray photoemission spectra; the imaginary part was estimated from escape-depth data and the widths of conduction-band features. The real part changes abruptly at E_F and is otherwise roughly constant, even up to the plasmon energy.

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Many-body corrections to a particular one-electron approximation for the single-particle response of a solid are characterized by the self-energy correction $\Delta(E)$ of the single-particle Green's function $G(E)$. Recently theoretical interest in $\Delta(E)$ for semiconductors has increased because the tendency for density-functional calculations to underestimate the band gap involves $\Delta(E)$ at the band edges.[1-7] In this paper, we obtain results from several experiments and compare the results with a local-density–functional (LDA) calculation to measure in detail the relative values of $\Delta(E)$ for Si and Ge over a wide energy range from the bottom of the valence band through the first 16 eV of the conduction band. Over this energy range, ReΔ exhibits a rapid change at the Fermi energy and is otherwise essentially independent of energy, even near the plasmon energy. The energy dependence of ImΔ, determined for the conduction band, is compared to calculations. The exact significance of this $\Delta(E)$ is discussed further below.

Most efforts to identify self-energy corrections in semiconductors have compared theory with photoemission[8] and optical experiments over a very limited energy range.[1-3,9] Self-energy corrections for energies far from the Fermi energy are very important, however, because the LDA calculation is not expected to approximate accurately the large plasmon contribution to the self-energy and neglects the energy variation of the self-energy. Unfortunately, optical measurements are intrinsically inappropriate for studying the single-particle self-energy because many-body effects other than those contained in $\Delta(E)$ enter the optical spectrum through electron-hole interactions, which can shift spectral features by as much as 0.5 eV.[10] Even without such effects, the hole and electron Δ's are mixed in the spectrum because valence-band and conduction-band critical-point energies appear only as differences. The obvious limitation of photoemission data by themselves is that they provide no information about the conduction band. In addition, the valence band has, in general, few density-of-states (DOS) features to compare with experimental spectra, and the lifetime of the valence-band hole is more difficult to obtain independently than that of the conduction-band electron. Thus, detailed comparisons between theory and experiment are less accurate.

As in recent self-energy studies of metals,[11] the experimental results are obtained from x-ray photoemission spectroscopy (XPS) of the valence band, x-ray bremsstrahlung isochromat spectroscopy (BIS) for the first 25 eV of the conduction band, and elastic electron escape-depth data taken from the literature. The first two give a direct measurement of the spectral weight of $G(E)$, apart from the BIS and photoemission spectroscopy cross sections, and the third yields an independent determination of ImΔ for the conduction band. Detailed BIS spectra for Ge and Si have been reported previously only for the first 5 eV of the conduction band.[10,12] The XPS and BIS spectra were obtained on crystalline samples cleaved *in situ* with the experiment and experimental conditions as described for our earlier studies.[12] The resolution functions of the BIS and XPS measurements were determined from Ag spectra to be Gaussians with widths of 0.6 eV. The XPS and BIS spectra were positioned in energy by superposition of their Fermi levels, which were determined to within ± 0.1 eV from spectra of metal clips in good electrical contact with the sample. The position of the Fermi level relative to the valence-band maximum (VBM) was consistent with the known pinning position due to intrinsic surface states. Our XPS binding energies agree with the most recent XPS and angle-resolved uv-photoemission-spectroscopy results[13] but are ~ 0.4 eV larger than older results which were based on a less accurate position of the valence-band maximum.[14]

Although there are many good LDA calculations of the DOS for Si and Ge, the previous calculations do not extend to sufficiently high energy in the conduction band for our purposes. The present LDA calculations were performed in momentum space[15] with norm-conserving pseudopotentials.[16] The Ge calculation employed scalar-relativistic pseudopotentials. The Ceperley and Alder exchange-correlation potential was

employed.[6] The plane-wave cutoff was 11 Ry, and the Kohn-Sham eigenvalues[17] converged to within 0.1 eV for energies up to 15 eV above the Fermi energy E_F. The DOS was computed from the band structure by use of the tetrahedron method.[18] The results for the valence band and the lower part of the conduction band are in good agreement (<0.1 eV difference) with previous calculations for Si[19] and Ge.[20]

BIS spectra for Si ⟨111⟩ and Ge ⟨111⟩ are shown in Fig. 1. The large rise at 16 eV is partially due to an extrinsic plasmon replica of the conduction-band edge, which limits the comparison with the LDA DOS to lower energies. The smaller features below 16 eV are common to both Si and Ge. The peak energies relative to the VBM are tabulated in Table I. The energies of the lower three peaks are in good agreement with previous x-ray BIS measurements and with the angle-resolved BIS spectra.[11,12] There are also three additional peaks at higher energy which are smaller and substantially broader.

The data of Fig. 1 differ from our theoretical DOS in that the peak and valley positions are shifted and that there is a substantial loss of sharpness of the higher-energy features. These are the self-energy effects of concern. In our previous study it was found that the relative positions of the three low-energy peaks agree well with empirical pseudopotential calculations, but the shift in the energy relative to E_F was not addressed. Also, in the absence of the higher-energy data reported here, no loss of sharpness was apparent.

We attribute this loss of sharpness to the imaginary part of the self-energy, i.e., a lifetime broadening. The energy dependence of the lifetime Γ can be deduced from elastic electron escape-depth data by the relation[21]

$$\Gamma(E) = 2\,\mathrm{Im}\Delta(E) = \hbar v/\lambda(E) = \hbar(2E_{\mathrm{kin}}/m)^{1/2}/\lambda(E), \quad (1)$$

where the velocity v has been approximated by a free-electron relation; E_{kin} is the electron kinetic energy relative to the bottom of the valence band, taken to lie ~ 11.5 eV below the Fermi energy; m is the electron mass; and $\lambda(E)$ is the escape depth.

By use of a compilation of escape-depth data for c-Si,[8] for c-Ge,[22] and Eq. (1), $\Gamma(E)/2$ is shown in Fig. 2.

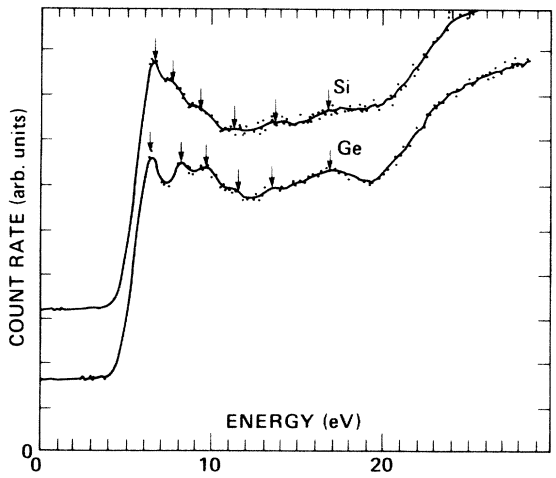

FIG. 1. The points represent raw x-ray BIS spectra for Si and Ge shifted to align at the conduction-band minima of Ge, which lies at 5 eV on this scale. The solid lines are the data with the high-frequency noise removed by smoothing with a Gaussian of width 0.25 eV.

TABLE I. Peak energies relative to VBM (electronvolts) for LDA conduction band and BIS measurements.

Si		Ge	
Theory	Exp.	Theory	Exp.
2.6	3.0	1.9	2.4
3.7	4.3	3.7	4.2
5.3	6.0	4.9	5.5
7.2	7.8	· · ·	7.3
9.5	10.3	9.0	9.3
13.4	13.8	12.2	12.9

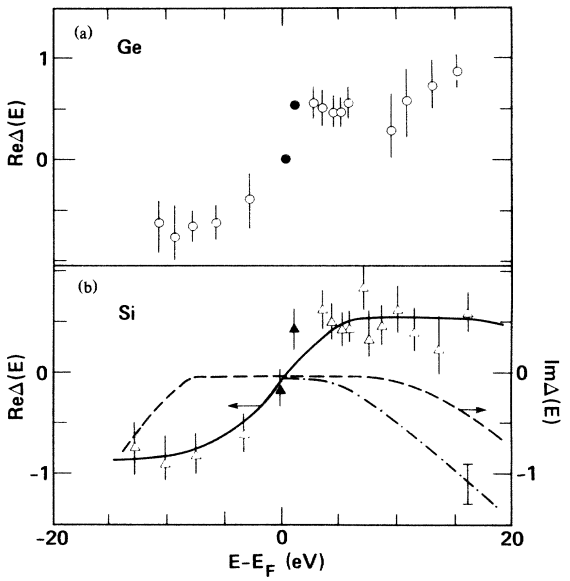

FIG. 2. $\mathrm{Re}\Delta(E)$ (points) for (a) Ge and (b) Si vs first-principles pseudopotential energies measured from the Fermi level which is at 0.55 (0.0) eV above VBM for Si (Ge). The points represent the shift of the absolute energies of the peaks (found in Table I) and valleys of the theory relative to the energies found in experiment. The error bars come from an overall error in positioning the conduction band relative to the valence band (0.15 eV) and from errors in determining the energies of individual DOS features. The solid points indicate the band edge. The solid (dashed) line in (b) is a theoretical calculation from Ref. 3 of the real (imaginary) part of $\Delta(E)$ for Si. The dot-dashed line indicates $\mathrm{Im}\Delta(E)$ vs energy from escape-depth data.

This estimate represents a lower bound because the escape-depth measurements do not detect energy losses less than the core-level widths (~ 0.5 eV) used to measure the escape depth. Below 3.7 eV, $\Gamma(E)$ is dominated by longitudinal-optic phonon emission, is roughly 0.1 eV, and is more or less independent of energy. $\Gamma(E)$ is dominated by electron-hole pair creation[23] above ~ 3.7 eV and is determined by plasmon creation above ~ 13 eV. Since the pair-production and plasmon energies are similar in Si and Ge, the escape depths for various energies and the lifetime broadenings are quite similar.[8]

The LDA DOS was then broadened by a Lorentzian of variable width $\Gamma(E)$ given in Fig. 2, and to compare the calculations with the data, the theoretical value was further broadened by the instrumental resolution. For ease of visual comparison Fig. 3 is drawn with the theory including broadening shifted upwards in energy to match its lowest-energy peak position with that of experiment. The general agreement is excellent in the relative placement, relative height, and shape of all peaks, except that the experimental Ge peak at 7.3 eV is clearly not present in the theory with broadening for Ge. Either this peak arises from factors left out of the calculation giving rise to a shifted peak or the cross section of the small peak in the unbroadened calculation has a markedly enhanced bremsstrahlung cross section compared to the surrounding states. Above 16 eV, the plasmon replica accounts for the discrepancy between theory and experiment. The only other difference is in the relative intensities of states below and above 7 eV. This effect may be due to slow variations of the BIS cross section with energy or to redistributions of spectral weight arising from the energy dependence of the real part of the self-energy. From the close agreement between experiment and the theory with lifetime broadening, we can conclude that one of the primary many-body effects left out of the LDA calculation is the imaginary part of the self-energy (lifetime broadening).

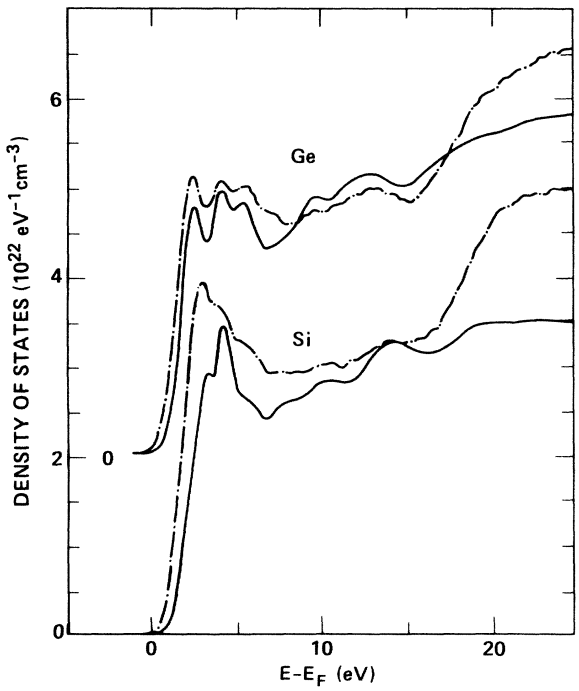

FIG. 3. Smoothed BIS spectra (dot-dashed line) and theoretical DOS (solid line) vs energy above the Fermi energy. The theoretical values have been lifetime broadened by an energy-dependent Lorentzian and the experimental resolution, and have been shifted upwards by 0.8 eV for Si and 0.5 eV for Ge for ease of comparison.

To obtain an estimate of $\mathrm{Re}\Delta(E)$, we now examine the positions of both the peaks and valleys of the theory and experiment in more detail, with the experimental E_F aligned to the theoretical midgap. In Fig. 2, the energy shift of DOS features between theory and experimen is plotted versus the experimental energy of the feature for both Si and Ge. Since the experimental E_F is determined by factors not included in the theory, only the relative values of $\mathrm{Re}\Delta(E)$ in Fig. 2 are meaningful. The overall trend is that the experimental energy separation of valence-band features from conduction-band features for both Si and Ge is roughly 1.2 eV larger than that predicted by LDA theory, while the discrepancy just at the band gap is smaller, ~ 0.6 eV.

Our $\Delta(E)$ shows the difference between the experimental spectral weight of $G(E)$ and that constructed from the LDA density-functional eigenvalues, which, of course, have no formal justification as quasiparticle excitation energies. In general, $G(E)$ is determined by a complex, energy-dependent, nonlocal self-energy operator, and the LDA Kohn-Sham equations essentially approximate the self-energy operator by an exchange-correlation potential which is real, energy independent, and local. As we have seen, the real approximation, which neglects quasiparticle lifetimes, is worse at high energies, where there are many available final states for scattering processes. Neglect of the energy dependence is also expected to be worse at higher energies. The local approximation is expected to break down for systems in which the electron density is inhomogeneous and for excitations at energies where plasmon interactions are important. Various efforts to improve on the LDA for semiconductors focus on one or more of these approximations.[1-7]

One technique to calculate self-energy corrections is to use the Green's-function–screened-Coulomb interaction or *GW* approximation of Hedin and Lundqvist.[24] The roughly rigid shift observed for the bands of Si is predicted by such calculations of Hybertson and Louie[2] and is in reasonable agreement with the calculations of Pickett and Wang (Fig. 2).[3] Closer

examination reveals that the experimental $\mathrm{Re}\Delta(E)$ changes more abruptly near the Fermi level than was calculated in Ref. 3. This difference explains the fact that the band gap (0.95 eV) of Ref. 3 is smaller than the gap found by experiment. Also the experimental $\mathrm{Im}\Delta(E)$ increases more rapidly than predicted by Ref. 3. In comparing to theory it is important to note that the experimental quasiparticle energy for band n and crystal momentum k occurs at the energy E which is a solution of the equation $E-\epsilon_{nk}-\Delta_{nk}(E)=0$, where ϵ_{nk} is the LDA eigenvalue. Although the comparison in Fig. 2 implies that $\Delta_{nk}(E)=\Delta(E)$, our data analysis does not actually distinguish between the E dependence and the (n,k) dependence of $\Delta_{nk}(E)$. Hybertson and Louie have emphasized the importance of the latter in calculating the band gap. Quantifying experimentally the relative importance of the two dependences remains a challenging problem.

Other important points are the following: $\mathrm{Re}\Delta(E)$ near the plasmon energy is nearly the same as for states near the band gap, indicating the relatively slow increase of the plasmon coupling with increasing energy. In the conduction band, $\mathrm{Re}\Delta(E)$ shows a weak energy dependence. In the case of Ge, there is some indication that $\mathrm{Re}\Delta(E)$ increases slightly for energies further from the Fermi energy.

In summary, we have compared the conduction-band features up to 16 eV from the Fermi level with theory. From this comparison, a global measure of the necessary self-energy correction to LDA has been determined. The imaginary part of the self-energy was estimated from elastic escape-depth data and was found to be essential for comparison of experiment with theory. The real part of the self-energy correction changes rapidly at the Fermi level and is relatively constant up to the plasmon energy (16 eV) for both Si and Ge in semiquantitative agreement with recent theories.[2,3]

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