

Precise Determination of the Valence-Band Edge in X-Ray Photoemission Spectra: Application to Measurement of Semiconductor Interface Potentials

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A highly precise method for locating the valence-band edge in x-ray photoemission spectra is reported. The application to measuring semiconductor interface potentials is discussed. X-ray photoemission-spectroscopy experiments on Ge and GaAs(110) crystals have given Ge $3d$, Ga $3d$, and As $3d$ core level to valence-band edge binding-energy differences of 29.55, 18.81, and 40.73 eV to a precision of ± 0.02 eV. For illustration, the valence-band discontinuity at an abrupt Ge/GaAs(110) heterojunction is determined to be 0.53 ± 0.03 eV.

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We report a method for markedly increasing the precision in locating the valence-band edge in spectra observed by XPS (x-ray photoemission spectroscopy). It is shown, by use of this method, how the binding-energy difference between a semiconductor core level and the valence-band edge can be precisely determined and how the result enters into the measurement of heterojunction band discontinuities, Schottky-barrier heights, and interface band bending. Accurate XPS determination of the above quantities requires that experimental values of core level to valence-band-edge energies be known with a precision better than the ± 0.1 eV uncertainty typically quoted in the literature. A procedure for obtaining a better precision has not been previously discussed. A determination of the valence-band discontinuity for the Ge/GaAs(110) heterojunction precise to ± 0.03 eV will be given. A precision of this order is needed to critically test models that predict heterojunction band discontinuities.

The disruption of a perfect crystal lattice produced by the presence of either a metal, semiconductor, or vacuum interface is generally accompanied by a deviation of the charge distribution near the interface from that deeper in the bulk semiconductor. Consequently, Poisson's equation predicts a spatially varying electrostatic potential V_{BB}^X which bends all of the bands or energy levels by the same amount as a function of distance away from the interface. For semiconductor X in Fig. 1(a), the energy of a core level E_{CL}^X , the valence-band maximum E_v^X , and the conduction-band minimum E_c^X , are shown in the bulk (b) and at an interface (i) with either a metal, semiconductor Y , insulator, or vacuum. Binding energy E_B is measured with respect to the Fermi level E_F ($E_B = 0$). The band gap E_G^X ,

position of the Fermi level in the bulk relative to the valence-band edge δ^X , band-bending potential V_{BB}^X , and depletion-layer width W are also shown in Fig. 1(a).

Given an XPS measurement of the position of the core level $E_{CL}^X(i)$ at the interface and the binding-energy difference ($E_{CL}^X - E_v^X$) between core level E_{CL}^X and the valence-band maximum E_v^X , it follows from Fig. 1(a) that the position of the conduction-band minimum at the interface is given by

$$E_c^X(i) = (E_{CL}^X - E_v^X) + E_G^X - E_{CL}^X(i), \quad (1)$$

the position of the valence-band maximum at the interface is given by

$$E_v^X(i) = E_{CL}^X(i) - (E_{CL}^X - E_v^X), \quad (2)$$

and the band-bending potential V_{BB}^X at a surface or interface is given by

$$qV_{BB}^X = (E_{CL}^X - E_v^X) + \delta^X - E_{CL}^X(i). \quad (3)$$

The experimental determinations of E_{CL}^X and E_v^X for Ge and GaAs were carried out with a UHV modified Hewlett-Packard model-5950A XPS spectrometer which has a monochromatized Al $K\alpha$ ($h\nu = 1486.6$ eV) x-ray source; this system has been described previously.¹ Each XPS spectrum was collected by repeatedly (> 100 scans) sweeping a 50-eV energy interval. The energy interval contained both the core level(s) of interest and the valence-band region. The spectrometer energy scale was calibrated to 0.02%. The (110) specimens of Ge and GaAs were prepared by etching in dilute HF and 4:1:1 ($H_2SO_4:H_2O_2:H_2O$) acid solutions, respectively. This was followed by *in situ* sputter and anneal cycles until the 1×1 low-energy electron diffraction pattern characteristic of GaAs(110) (Ref. 2) and a complex pattern which resembles the reported³ $c(8$

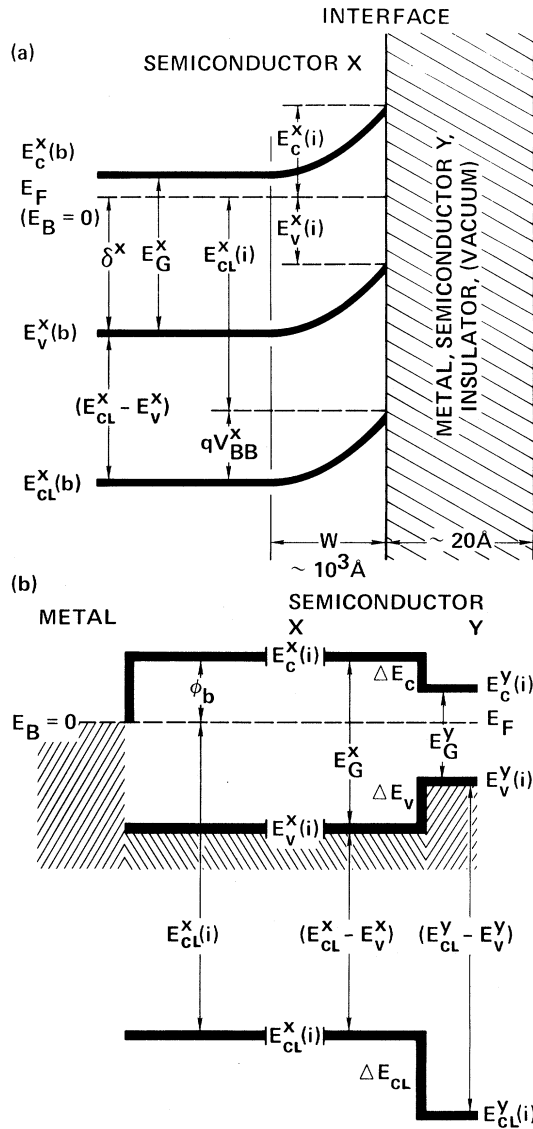


FIG. 1. (a) Generalized energy-band diagram at an abrupt interface between a semiconductor and vacuum, metal, insulator, or a different semiconductor; (b) schematic flat-band diagram at a metal-semiconductor (left) or heterojunction (right) interface.

$\times 10$) pattern characteristic of room-temperature Ge(110) were obtained. A background function which is proportional to the integrated photoelectron peak area was subtracted from the data to correct for the effect of inelastic photoelectron scattering. The core-level energy position was defined to be the center of the peak width at half of the peak height. This procedure made it unnecessary to resolve the spin-orbit splitting of the relatively narrow Ga, Ge, and As $3d$ levels to obtain high-precision peak positions. The es-

cape depth of the photoelectrons in the experiment here is $\sim 20 \text{ \AA}$. This escape depth (several atomic layers) minimizes any complications caused by potential variation spread over 1 or 2 atomic layers at an abrupt interface and also is insensitive to band bending at the interface which occurs over a typical width of $\sim 1000 \text{ \AA}$.⁴

The energy levels defined in Fig. 1(a) as measured within the $\sim 20 \text{ \AA}$ XPS sampling depth are shown in Fig. 1(b) for a heterojunction interface and for a metal-semiconductor interface. The Schottky-barrier height $\phi_b = E_c^x(i)$ at the metal-semiconductor interface is given by Eq. (1) and the valence-band discontinuity ΔE_v at the heterojunction interface is given by

$$\Delta E_v = (E_{CL}^y - E_v^y) - (E_{CL}^x - E_v^x) - \Delta E_{CL}, \quad (4)$$

where $\Delta E_{CL} \equiv E_{CL}^y(i) - E_{CL}^x(i)$. The effect of interface states is to shift the potential within the sampled region on both sides of an interface by the same constant value. Thus, any potential shift due to interface states or other sources of band bending cancel.

The determination of $(E_{CL} - E_v)$ depends on locating the position of the valence-band maximum E_v in the XPS data with greater accuracy than has been generally attempted previously. The required accuracy is achieved by fitting the XPS valence-band data in a limited region around the estimated position of E_v with an instrumentally broadened valence-band density of states (VB DOS) $N_v(E)$ chosen so that

$$N_v(E) = \int_0^\infty n_v(E') g(E - E') dE'. \quad (5)$$

The recent Chelikowsky-Cohen⁵ nonlocal pseudopotential VB DOS has been used for $n_v(E')$ in Eq. (5) to analyze the Ge and GaAs data shown in Fig. 2. The instrumental resolution function $g(E)$ is separately determined by observing Au $4f$ core-level line shapes in metallic gold. These lines have an inherent linewidth ($\sim 0.29 \text{ eV}$),⁶ narrower than $g(E)$, and narrower than most photoelectron lines of other solids. Typical experimentally observed Au $4f$ line shapes $W_{4f}^{\text{Au}}(E)$ have full widths at half maximum (FWHM) of 0.86 eV and are related to $g(E)$ by

$$W_{4f}^{\text{Au}}(E) = \int_{-\infty}^\infty g(E - E') L(E') dE', \quad (6)$$

where $L(E')$ is a Lorentzian line shape (FWHM = 0.29 eV) and represents the inherent lifetime broadening of the Au $4f$ levels. Both $W_{4f}^{\text{Au}}(E)$ and $g(E)$ in (6) are analytically representable as the fold of Gaussian and Lorentzian line shapes

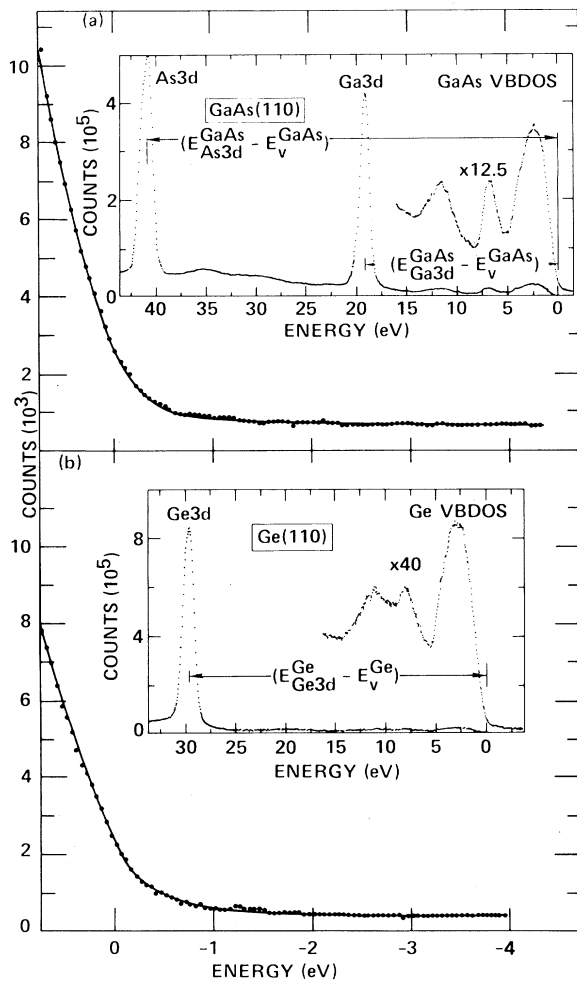


FIG. 2. Least-square fit of instrumentally broadened theoretical VBDOS (solid curve) to XPS data (points) in the region of the valence-band edge for (a) GaAs and (b) Ge. Insets show the XPS spectra which contain the VBDOS and the outermost core levels. The energy scale is zero at the valence-band edge.

(Voigt functions).⁷ Instrumental resolution functions $g(E)$ determined from Eq. (6) and used to analyze the data in Fig. 2 have typical FWHM = 0.81 eV and are the result of folding a Gaussian with a Lorentzian which has a half width equal to 20% of the Gaussian half width.⁸

Our procedure for precisely determining the valence-band edge employs the method of least squares. The position of the valence-band maximum E_v is determined by fitting the leading edge of the experimental XPS spectrum $I(E)$ to $N_v(E)$ with

$$I(E) = SN_v(E - E_v) + B, \tag{7}$$

TABLE I. Core level to valence-band maximum binding-energy difference (eV) for Ge and GaAs.

$E_{Ge\ 3d}^{Ge} - E_v^{Ge}$	$= 29.55 \pm 0.02$ eV
$E_{Ga\ 3d}^{GaAs} - E_v^{GaAs}$	$= 18.81 \pm 0.02$ eV
$E_{As\ 3d}^{GaAs} - E_v^{GaAs}$	$= 40.73 \pm 0.02$ eV

where S is a scale factor and B is a constant random-noise background. The fits obtained for Ge and GaAs are shown by solid curves in Fig. 2. As only the leading edge of the XPS valence-band spectrum is fitted, where the orbital symmetry is essentially p in character, matrix-element effects enter only through the constant scale factor S in Eq. (7).

By using the technique discussed above, $(E_{Ge\ 3d}^{Ge} - E_v^{Ge})$, $(E_{Ga\ 3d}^{GaAs} - E_v^{GaAs})$, and $(E_{As\ 3d}^{GaAs} - E_v^{GaAs})$ have been obtained from measurements of (110) oriented single crystals of Ge and GaAs. The results obtained from analysis of the data shown in Fig. 2 are presented in Table I.

The valence-band discontinuity ΔE_v for an abrupt Ge/GaAs(110) heterojunction can now be obtained by using the previously reported value of $\Delta E_{CL} = (E_{Ge\ 3d}^{Ge} - E_{Ga\ 3d}^{GaAs}) = 10.21 \pm 0.01$ eV and the results from Table I in Eq. (4). This leads to

$$\Delta E_v = 0.53 \pm 0.03 \text{ eV}$$

for the valence-band discontinuity at an abrupt Ge/GaAs(110) heterojunction interface. Our experimental evidence¹ indicates that this value of ΔE_v is intrinsic to an abrupt Ge/GaAs(110) interface. The precision of the method presented here can provide a sensitive test for the effect of interface nonideality on the magnitude of ΔE_v .

In summary, the method reported here for precisely determining core-level to valence-band-edge binding-energy differences makes possible the use of XPS for high-accuracy measurements of heterojunction band discontinuities, Schottky-barrier heights, and interface band-bending potentials.

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⁴For a heavily doped semiconductor with a depletion width $<10^3 \text{ \AA}$, a small correction to E_{CL}^X and E_v^X may be required due to the potential variation within the photoelectron sampling depth. For the moderate doping levels of our samples ($<10^{17} \text{ cm}^{-3}$), this correction was $<0.01 \text{ eV}$.

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⁸Phonon broadening of the Au $4f$ lines used to determine $g(E)$ was calculated following P. H. Citrin *et al.* [Phys. Rev. B **16**, 4256 (1977)] and was found to affect the $g(E)$ width by $<0.01 \text{ eV}$; a similar result was found by P. H. Citrin *et al.* [Phys. Rev. Lett. **41**, 1425 (1978)]. This contribution to $g(E)$ affects the position of the derived value of E_v by $<0.01 \text{ eV}$.

Pressure Dependence of Superconducting Transition Temperature of High-Pressure Metallic Te

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Existing data at high pressures of Berman, Binzarov, and Kurkin show that the various metallic forms of Te have considerable variation of their superconduction temperatures, T_c , depending upon the phase and the pressure; the observed T_c 's ranged from 2.5 to 4.3°K over the pressure span of 40 to 150 kbar. The present experiments, with use of a diamond-tipped apparatus with a cryogenic arrangement, have extended the pressure range to over 300 kbar. The results indicate that a new metallic phase develops in the 150–180-kbar region, which has a higher T_c of about 6.5°K.

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Many covalently bonded crystalline materials such as Si, Ge, Te, Se, etc., which are insulators or semiconductors in their usual low-pressure forms, transform to metallic phases under sufficient pressure,¹⁻⁴ some of these "high-pressure metals" exhibit superconductivity at low temperatures.⁵⁻⁹ In 1973, Berman, Binzarov, and Kurkin⁹ (BBK) published their results for an extensive series of high-pressure cryogenic experiments with Te in which they explored the T_c of the metallic forms of Te over the pressure range of about 38–260 kbar (which corresponds to about 38–150 kbar on the modern pressure scale.^{10, 11}) Their findings are shown here in Fig. 1, in which T_c is plotted against P (modern scale). They concluded that in this range there are three different metallic phases: the first (38–60 kbar) having an unusually large positive dT_c/dP ; the second (60–75 kbar) with a nearly zero dT_c/dP ; and the third (75 kbar and up) with a strong negative dT_c/dP .

With our new apparatus¹² one of the early runs (to test the apparatus and procedure) was made with a specimen of Te because it was known to be superconducting. The run was made at about 220 kbar. This specimen exhibited an excellent superconduction transition as shown in Fig. 2, but at

a much higher temperature than observed by BBK. This discrepancy indicated that Te may have a different metallic phase at the higher pressure.

This report gives the results of a recent series of experiments done with our apparatus¹³ in which a specimen was compressed at room temperature in eight successive steps from 50 to 305 kbar and was tested at each step for superconductivity by cooling it to about 2.7°K. At the lower pressures our results agree moderately well with those of BBK, and at higher pressures a new metallic phase with the higher T_c does indeed develop, as was suggested by our earlier experiment.

The series of tests spanned a period of 44 days, as each warmup took a few days of time. After warming through the T_c zone, measurements were taken of the resistance of the "normal-state" metal on up to room temperature to provide information for determining the Grüneisen "characteristic temperature" of electrical conductivity, Θ .¹⁴

The room-temperature resistance behavior during the eight stepwise loadings is shown in Fig. 3(a). The room-temperature electrode resistance of about 0.18Ω needs to be subtracted from the values shown in order to get the specimen resistance. Note that during the first cryogenic temperature cycle, at 7.2 tons loading, the room-