[2]B. J. Thaler, J. B. Ketterson, and J. E. Hilliard, Phys. Rev. Lett. 41, 336 (1978).
[3]R. M. White and C. Herring, Phys. Rev. B 22, 1465 (1980).
[4]L. N. Liebermann, J. Clinton, D. M. Edwards, and J. Mathon, Phys. Rev. Lett. 25, 232 (1970); L. N. Liebermann, D. R. Fredkin, and H. B. Shore, Phys. Rev. Lett. 22, 539 (1969); U. Gradmann, J. Magn. Magn. Mat. 6, 173 (1977); G. Bergmann, Phys. Rev. Lett. 41, 264 (1978).
[5]O. K. Andersen, Phys. Rev. B 12, 3060 (1975); T. Jarlborg and G. Arbman, J. Phys. F 7, 1635 (1977).
[6]L. Hedin, B. I. Lundqvist, and S. Lundqvist, Solid State Commun. 9, 537 (1971).
[7]O. Gunnarson and B. I. Lundqvist, Phys. Rev. B 13, 4274 (1976).
[8]D. D. Koelling and B. N. Harmon, J. Phys. C 10, 3107 (1977).
[9]J. E. Hilliard, in *Modulated Structures—1979*, edited by J. M. Cowley *et al.*, AIP Conference Proceedings No. 53 (American Institute of Physics, New York, 1979), p. 507; R. W. Vook and C. T. Horng, Philos. Mag. 33, 843 (1976).
[10]A. J. Freeman and R. E. Watson, Phys. Rev. Lett. 5, 498 (1960).
[11]A. J. Freeman and R. E. Watson, in *Magnetism, Vol. IIA*, edited by G. Rado and H. Suhl (Academic, New York, 1965).
[12]J. Q. Zheng, C. Falco, J. B. Ketterson, and I. K. Schuller, to be published.
[13]G. P. Felcher, J. W. Cable, J. Q. Zheng, J. B. Ketterson, and H. E. Hilliard, to be published.

Surface Core-Level Binding-Energy Shifts for GaAs(110) and GaSb(110)

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Surface $3d$ and $4d$ core-level binding-energy shifts have been resolved in photoemission from GaAs(110) and GaSb(110), which yield new information on semiconductor surface reconstruction. The shifts (~0.3 eV) are toward higher (lower) binding energies for the surface cations (anions), in agreement with a simple model involving the known surface relaxation of GaAs(110) with a geometry-dependent initial-state charge transfer. Surface core-excitation binding energies, core-level widths, escape depths, etc., are reevaluated.

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We have observed shifts in the $3d$ and $4d$ core-level photoemission binding energies of surface-layer atoms relative to bulk atoms for the (110) cleavage surfaces of GaAs and GaSb. Recently, such shifts have been reported for several $5d$ metals.[1-3] These surface binding-energy shifts, which measure the change in the electrostatic potential at the core, yield new information on charge redistribution in the surface layer which accompanies the large reconstruction and/or relaxation that invariably occurs for semiconductors.[4] GaAs(110) is the prototype surface since its atomic structure is the best understood of any semiconductor; there is general agreement that surface As atoms move outwards and surface Ga atoms move inwards, with a ~25° bond-angle rotation[5,6] and a charge transfer from Ga to As surface atoms.[7] For GaAs(110), we find that the surface Ga $3d$ level is shifted to larger binding energy by $\Delta E_B = +0.28$ eV, while the As $3d$ level is shifted to smaller binding energy by $\Delta E_B = -0.37$ eV relative to their bulk counterparts. Comparable binding-energy shifts are observed for GaSb (110): $\Delta E_B(\text{Ga } 3d) = +0.30$ eV and $\Delta E_B(\text{Sb } 4d) = -0.36$ eV.

To our knowledge, the only calculations of such geometry-dependent binding-energy shifts for semiconductors are *ab initio* valence-band calculations using small clusters which have been used to study the reconstruction and/or relaxation and oxidation of GaAs(110).[4] Barton, Goddard, and McGill[4] have reported core-level shifts of $\Delta E_B(\text{Ga } 3d) = -0.19$ eV and $\Delta E_B(\text{As } 3d) = +0.24$ eV for relaxed surface atoms (25° bond-angle rotation) relative to unrelaxed surface atoms. However, these shifts (of opposite sign) cannot be directly compared to our experimental shifts, which are measured relative to bulk atoms. Semiconductor surface core-level shifts relative to bulk atoms have not been calculated using *ab initio* self-consistent methods for lack of experimental data. However, tight-binding calculations have estimated that the surface relaxation is accompanied by a charge transfer from Ga to As surface

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atoms,[7] and that the charge transfer for the ideal (110) surface is reduced by about a factor of 2 by a 25° bond-angle rotation. Under the assumption that initial-state charge-transfer effects are predominant, this result together with the relaxation-dependent shift calculated by Barton, Goddard, and McGill[4] is consistent both with the observed directions and magnitudes of surface Ga and As core-level shifts relative to the bulk.

The observation that Ga 3*d* surface core-level binding energies are ~0.3 eV larger than bulk values implies that Ga 3*d* surface core-exciton binding energies are larger than previously estimated.[8] Namely, Ga 3*d* surface-exciton binding energies are ≳0.8 eV, for GaAs and GaP, or about an order of magnitude larger than the corresponding bulk Ga 3*d* exciton binding energies.[9] Recent surface core-exciton calculations by Altarelli, Bachelet, and Del Sole[10] for a simple model show good agreement with these results.

The photoemission data were taken with a display spectrometer[11] and a toroidal grating monochromator at the Synchrotron Radiation Center at Stoughton. The combined system resolution (monochromator and spectrometer) in the photon energy range 20–80 eV was about 0.15 eV, as determined from the Fermi-level edge of a metal substrate. The samples used were lightly Zn-doped *p*-type single crystals of GaAs, GaSb, and GaP with freshly cleaved (110) surfaces. The working pressure in the vacuum chamber was better than 10^{-10} Torr.

Figure 1 shows several angle-integrated photoemission spectra for Ga(3*d*), As(3*d*), and Sb(4*d*) core levels in GaAs and GaSb; results for GaP are very similar (not shown). Since the escape depth for photoelectrons depends strongly on kinetic energy, surface-to-bulk core-level emission intensity ratios can be varied by using different photon energies. Two spectra for each core level are displayed in Fig. 1: one with a photon energy ~10 eV above threshold, which shows mainly the bulk emission (large escape depth); the other at a photon energy ~40 eV above threshold, which shows significant surface core-level emission (small escape depth). At the lower photon energies, emission from the spin-orbit–split core-level pair ($d_{5/2}$,$d_{3/2}$) from the bulk is clearly observed; at the higher photon energies, an additional set of surface core levels separated by the same spin-orbit splitting which is shifted relative to the bulk levels is observed. The surface and bulk $d_{5/2}$ core-level positions for As and Sb as well as the surface and bulk $d_{3/2}$ core-level

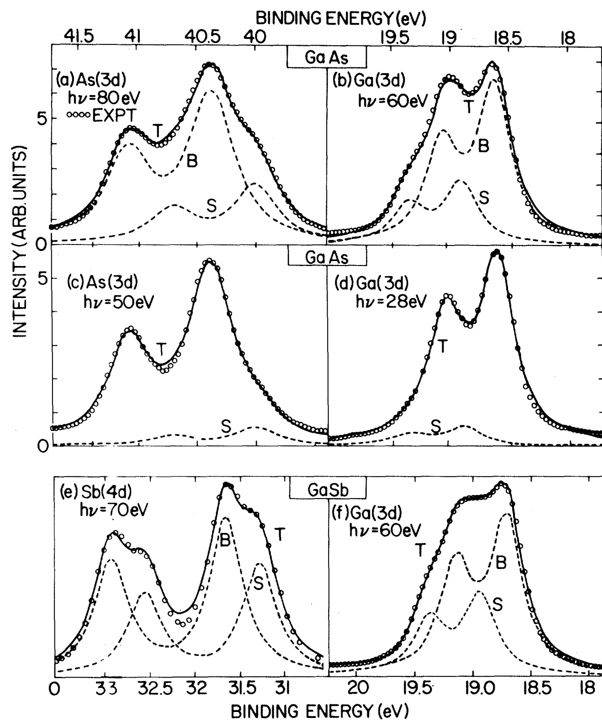

FIG. 1. Photoemission spectra for 3*d* and 4*d* core levels in GaAs(110) and GaSb(110). Spectra for low photon energies (~10 eV above threshold) show mainly bulk emission (B) while spectra for higher photon energies (~40 eV above threshold, small escape depth) show additional surface core-level emission (S). BG denotes the inelastic secondary-electron background.

positions for Ga are indicated in Fig. 1 (to be discussed).

After subtracting smooth secondary-electron backgrounds from the spectra in Fig. 1, the core-level spectra (primary emission) shown in Fig. 2 (circles) are obtained. Each curve is numerically fitted with four Lorentzians, two for the bulk and two for the surface, with the same $d_{5/2}$-$d_{3/2}$ spin-orbit splittings, the same $d_{5/2}$-$d_{3/2}$ intensity branching ratios, and the same spectral widths for the bulk and surface contributions. The fitting results are shown as solid and dashed curves in Fig. 2 for the total, bulk, and surface contributions. The agreement between experiment and this simple theoretical fit is excellent, thus justifying the assumption that there is primarily only one significant surface core-level shift involved in each case. Since the core-level lifetime broadenings are much larger than the experimental resolution, it is justified to use Lorentzian line shapes for fitting.[12] The results of the above analysis, including the binding energies, surface

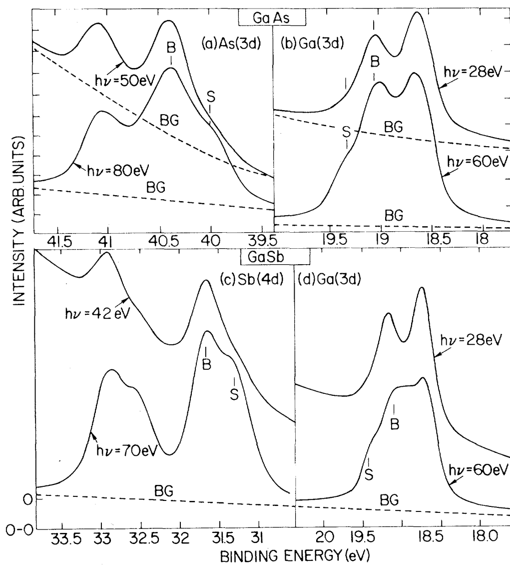

FIG. 2. Photoelectron $3d$ and $4d$ core-level spectra with secondary-electron backgrounds (BG) subtracted (circles) and fitting results shown as solid and dashed curves for the total (T), bulk (B), and surface (S) contributions (see text).

core-level shifts, spin-orbit splittings, spectral widths, escape depths, etc., are listed in Table I, where we have taken the Ga $3d_{5/2}$ binding energies to be 18.60, 18.70, and 18.40 eV, referred to the valence-band maximum for GaAs, GaSb, and GaP, respectively.[8] The escape depths l were calculated from the measured surface- to bulk-intensity ratios R using the relation[3] $l/d = [2\sqrt{2}\ln(1+R)]^{-1}$, where d is the cubic lattice spacing (5.65 and 6.10 Å for GaAs and GaSb, respectively). The measured ratios for final-state energies of about 40 eV above threshold were $R = 0.40$ for Ga and As in GaAs and $R = 0.52$ for Ga and 0.72 for Sb in GaSb (see Fig. 2). We tentatively attribute the larger surface contributions for GaSb and their asymmetry to a larger inelastic scattering cross section for Sb relative to As and Ga. The escape depth for GaAs at ~40 eV final energy is about 6 Å, in good agreement with our earlier photoemission measurements.[13]

The observed surface core-level shifts reflect initial-state changes in the electrostatic potential in the atomic core region due to charge transfer (configurational and chemical shifts) as well as changes in final-state relaxation shifts.[14] We consider the final-state relaxation shifts first. For the long-range part, a core hole localized at the surface experiences only half-space dielectric screening as compared with the full-space dielectric screening in the bulk; therefore differential surface core-level shifts are expected to be negative. On the other hand, the existence of empty surface states with large excitonic binding energies with the surface core holes[8,15] implies more effective dielectric screening for a surface core hole than for a bulk core hole; therefore this should lead to positive surface core-level shifts. It is difficult to calculate these final-state shifts quantitatively; yet they might be expected in general to be of the same sign for the cations and the anions. Experimentally, the ob-

TABLE I. Summary of measured and deduced bulk and surface quantities. These include bulk and surface binding energies referred to the valence-band maximum for the $d_{5/2}$ component of each core level, and their difference (surface core-level shift). Spectral widths and spin-orbit splittings for surface and bulk core levels are deduced from the numerical fit shown in Fig. 2. The escape depths depend on the photoelectron final energies (E) which are shown in the square brackets. All energy values are in units of eV.

	GaSb		GaAs		GaP
	Ga(3d)	Sb(4d)	Ga(3d)	As(3d)	Ga(3d)
Bulk binding energies $E_B(d_{5/2})$	18.70	31.67	18.60	40.37	18.40
Surface binding energies $E_S(d_{5/2})$	19.00	31.31	18.88	40.00	18.68
Surface core-level shifts $\Delta E_B = E_S - E_B$	0.30	−0.36	0.28	−0.37	0.28
3d and 4d spectral widths (FWHM)	0.32	0.44	0.33	0.43	0.33
$d_{5/2}$-$d_{3/2}$ spin-orbit splittings	0.43	1.25	0.44	0.70	0.43
Escape depths (Å) [E (eV)]			19 [9]	19 [10]	···
	4.5 ± 0.6 [40]		5.9 [41]	5.9 [40]	···
Ga($3d_{5/2}$)→surface exciton transition energies	19.37	···	19.68	···	19.69
Ga(3d)→surface exciton spectral widths	~0.20	···	~0.3	···	~0.25
Lower bounds of surface exciton binding energies	0.7[a]	···	0.8	···	0.8

[a]Relative to indirect edge at X, L.

served surface core-level shifts are *positive* for the cations and *negative* for the anions with comparable magnitudes; therefore, the differential final-state relaxation shifts are *probably* less important than initial-state shifts in the present case. Such bidirectional shifts are in fact consistent with a simple interpretation invoking initial-state charge transfer as previously mentioned.

The Ga $3d_{5/2}$-$3d_{3/2}$ spin-orbit splittings in Table I are consistent with those obtained via partial-yield spectra for the Ga $3d$ to empty–surface-state excitonic transitions.[8] These excitonic transitions have measured full widths of 0.2–0.3 eV (slightly instrument broadened) which are significantly smaller than the corresponding widths deduced from the core-level photoemission data (Table I). This is possibly due to excitonic screening effects which could increase the lifetime of the excitation (i.e., viewed crudely as an "excited neutral localized excitation") relative to that of the usual $3d$ core-hole excitation. The measured surface core-exciton transition energies and Ga $3d$ surface core-level binding energies have been used to deduce lower bounds for the surface exciton binding energies (Table I), since bounds on lowest energies of the single-particle empty surface states are known from surface Fermi-level-pinning experiments.[8] The large surface exciton binding energies ($\gtrsim 0.8$ eV for GaAs and GaP) compared with the bulk values (~ 0.1 eV)[9] are consistent with the results of a simple model calculation[10] by Altarelli, Bachelet, and Del Sole.

In summary, we have observed surface core-level shifts for GaAs, GaSb, and GaP. Such shifts should provide a critical test for various theoretical models for the surface relaxation of GaAs, GaSb, etc. Similar measurements for reconstructed Si(111)-7×7, Si(111)-2×1, and Si(100)-2×1 surfaces should provide new information concerning many long-standing questions about these surface geometries.[8] For example, Chadi *et al.*[16] have recently proposed an interesting model for the Si(111)-7×7 surface which is buckled (2×1)-like in nature with ringlike arrangements of positively and negatively charged surface atoms with a charge transfer up to 0.3 electron. According to this model, both positively and negatively shifted surface core levels should be observed with intensity ratios given by the corresponding numbers of surface atoms, etc.

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[1] P. H. Citrin, G. K. Wertheim, and Y. Baer, Phys. Rev. Lett. 41, 1425 (1978).

[2] T. M. Duc, C. Guillot, Y. Lassailly, J. Lecante, Y. Jugnet, and J. C. Vedrine, Phys. Rev. Lett. 43, 789 (1979).

[3] J. F. van der Veen, F. J. Himpsel, and D. E. Eastman, Phys. Rev. Lett. 44, 189 (1980).

[4] J. J. Barton, W. A. Goddard, III, and T. C. McGill, J. Vac. Sci. Technol. 16, 1178 (1979).

[5] S. Y. Tong, A. R. Lubinsky, B. J. Mrstik, and M. A. van Hove, Phys. Rev. B 17, 3303 (1978); A. Kahn, E. So, P. Mark, and C. B. Duke, J. Vac. Sci. Technol. 15, 580 (1978).

[6] J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B 20, 4150 (1979); D. J. Chadi, Phys. Rev. B 18, 1800 (1978).

[7] K. C. Pandey, unpublished.

[8] W. Gudat and D. E. Eastman, in *Photoemission and the Electronic Properties of Surfaces*, edited by B. Feuerbacher, B. Fitton, and R. F. Willis (Wiley, New York, 1978), Chap. 11, pp. 315–352.

[9] D. E. Aspnes, M. Cardona, V. Saile, M. Skibowski, and G. Sprüssel, Solid State Commun. 31, 99 (1979).

[10] M. Altarelli, G. Bachelet, and R. Del Sole, J. Vac. Sci. Technol. 16, 1370 (1979).

[11] D. E. Eastman, J. J. Donelon, N. C. Hien, and F. J. Himpsel, to be published.

[12] The Lorentzian line shape corresponds to Doniach-Sunjic line shape with zero asymmetry parameter; this is appropriate for semiconductors. There are likely also second- and subsurface-layer shifts; because of the quality of our one-surface Lorentzian fit, these are unresolved and presumably much smaller than the outer-layer shift.

[13] T.-C. Chiang, J. A. Knapp, D. E. Eastman, and M. Aono, Solid State Commun. 31, 917 (1979).

[14] See, for example, A. R. Williams and N. D. Lang, Phys. Rev. Lett. 40, 954 (1978).

[15] J. C. McMenamin and R. S. Bauer, J. Vac. Sci. Technol. 15, 1262 (1978).

[16] D. J. Chadi, R. S. Bauer, R. H. Williams, G. V. Hansson, R. Z. Bachrach, J. M. Mikkelsen, Jr., F. Houzay, G. M. Guichard, R. Pinchaux, and Y. Pétroff, Phys. Rev. Lett. 44, 799 (1980).