

Inverse photoemission study of InP, InAs, and InSb

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Unoccupied bulk and surface electronic states of InP, InAs, and InSb are determined via inverse photoemission from their cleaved (110) surfaces. With use of a tunable photon detector, the band dispersion of the lowest p -like bands along the $\Gamma\Sigma KX$ line is mapped and the critical points Γ_{15} and X_1 of the conduction band are determined ($\Gamma_{15}=5.3, 4.5,$ and 4.2 eV and $X_1=2.8, 1.9,$ and 1.8 eV, for InP, InAs, InSb, respectively). Surface resonances are found in the region 1.9–2.7 eV above the valence-band maximum. Resonance effects near the In $4d$ core-level threshold and the onset of In $4d$ luminescence are studied.

BACKGROUND

The series of indium-based III-V compounds is gaining attention for their potential as new device materials. InAs and InSb are good infrared detectors as a result of their small band gap. InP forms a lattice-matched basis for In-Ga-As high-electron-mobility transistors, which have achieved higher speed¹ than comparable AlAs-GaAs structures. At high driving fields the mobility is limited by intervalley scattering between the lowest conduction-band L and X points. According to band-structure calculations these valleys lie higher above the conduction-band minimum in some of the In-based compounds than in GaAs thus allowing higher fields. Using inverse photoemission (for reviews see Ref. 2) we are able to determine the energy versus momentum dispersions of the lower conduction bands in these materials. Previous knowledge is mainly based on optical measurements.³ These measurements do not resolve the momentum but some information can be extracted by fitting a band calculation to the data.⁴ For the higher conduction bands (above the vacuum level) there exist momentum-resolved photoemission data.^{5,6} Unoccupied In-derived surface states have been seen with partial-yield photoemission techniques and electron-energy-loss spectroscopy.^{7,8}

EXPERIMENTAL

The inverse photoemission spectra are recorded using a spectrograph⁹ which employs simultaneous detection of photons with energies between 8 and 28 eV via multichannel plates. A parallel beam of electrons emitted from an electron gun with BaO cathode and Pierce-type geometry impinges on the sample surface. Photons are detected at 45° from the sample normal with equal efficiency for both polarizations. Spectra are displayed by recording the energy distribution of the radiation that is emitted when electrons with a chosen initial energy E_i undergo radiative transitions into conduction-band states with energies E_f . Photon energies are converted into final-state energies according to $E_f = E_i - h\nu$. The reference energy for E_i and E_f is the Fermi level E_F . Its position on the photon ener-

gy scale is determined from the sharp high-energy cutoff in the spectrum of a thin Au film evaporated onto the semiconductor surface. The energies are measured relative to E_F but the energy reference for band calculations is the valence-band maximum E_{VBM} . In order to convert the energy scale we have to determine $E_F - E_{VBM}$. The position of the Fermi level depends sensitively on sample preparation and doping and has been measured by various techniques.^{10–13} A one-to-one correlation between $E_F - E_{VBM}$ and the work function has been established. We use a Kelvin probe to measure the work function and obtain the Fermi-level position in the gap by comparing with previous work-function measurements.¹⁰ All samples were n -type (InP S doped to 10^{18} cm⁻³, InAs to 10^{16} cm⁻³). The samples (3×3 mm² across) were cleaved mirrorlike in a vacuum in the low 10^{-10} -Torr range. Ohmic indium contacts were alloyed into the back of the sample and tested with $I(V)$ measurements.

BULK ENERGY BANDS

The determination of energy bands with inverse photoemission follows the lines described previously for Co,¹⁴ GaP,¹⁵ GaAs,¹⁶ Si,^{17,18} and Ge.¹⁸ Essentially, we keep the momentum parallel to the surface $k_{\parallel}=0$ and vary the perpendicular momentum k_{\perp} along the $\Gamma\Sigma KX$ line by changing the energy E_i of the incident electrons (see Figs. 1–4). In order to determine k_{\perp} we convert E_f into k_{\perp} via the band dispersion of free-electron initial-state bands combined with angle-resolved photoemission results. Two nearly parabolic bands dominate in photoemission (Ref. 5, open symbols in Fig. 4). They correspond to the free-electron parabola shifted down by an inner potential of 8.5 eV and backfolded into the first Brillouin zone by a $[\bar{2}\bar{2}0]$ reciprocal lattice vector (“primary cone,” solid line and open circles in Fig. 4) and by a $[002]$ reciprocal lattice vector (“secondary cone,” dashed line and open triangles in Fig. 4). Looking at the energy dependence of the inverse photoemission spectra of InP(110) (Fig. 1) one observes a single peak near 5 eV (tick marks) for high initial-state energies ($E_i \approx 23$ eV), which splits when E_i is decreased. In this energy region the primary cone dominates (almost all photoemission points are located on it).

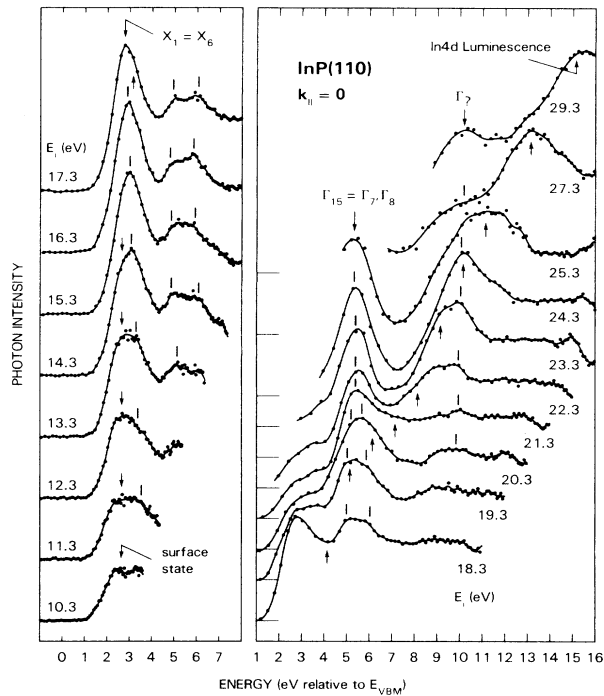


FIG. 1. Inverse photoemission spectra vs initial state energy E_i for InP(110) at electron incidence normal to the surface ($k_{\parallel}=0$). Photon intensities are in photons per incident electron. Tic marks denote bulk interband transitions that are used for determining the energy bands shown in Fig. 4. Up arrows mark the center of the In 4d luminescence peak. Down arrows give the position of a surface resonance (see Fig. 5).

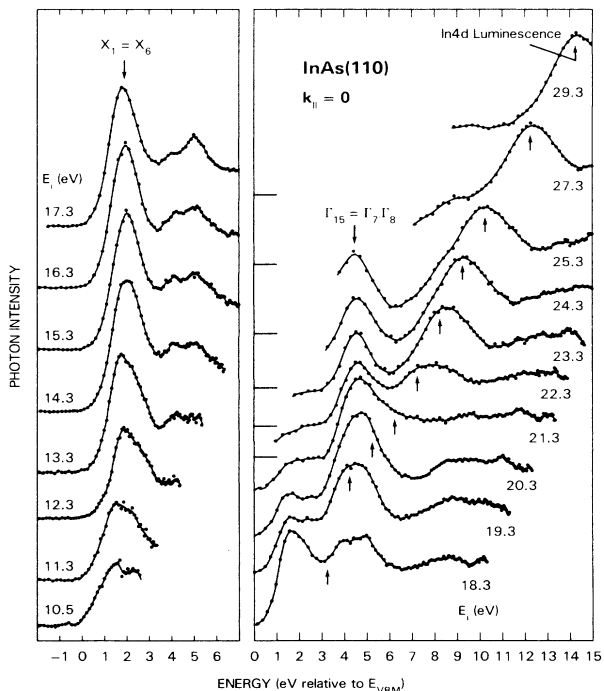


FIG. 2. Similar to Fig. 1 for InAs(110).

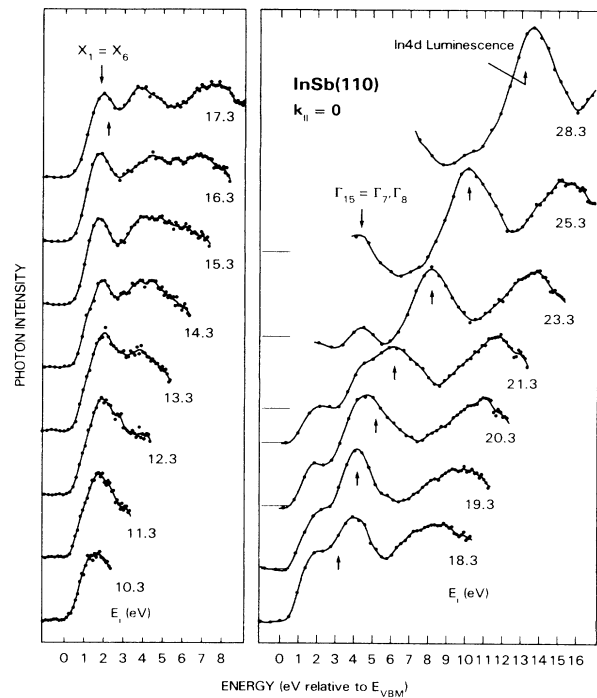


FIG. 3. Similar to Fig. 1 for InSb(110).

Therefore, we use it as the initial-state band and find the band dispersion of the final-state bands that merge into the Γ_{15} point. Below $E_i \approx 19$ eV a new structure appears at about 2.8 eV. In this energy region the primary and the secondary cone are both to be considered. We estimate that the secondary cone dominates in inverse photoemission data for two reasons: It gives a band dispersion that agrees reasonably well with calculations (in contrast to the primary cone). The transition disappears for $E_i \geq 18$ eV, i.e., exactly where the photoemission from the secondary cone (open triangles) vanishes. This cutoff marks the X point. It should be noted however, that resonance phenomena may modulate the inverse photoemission intensity in this energy range (see below). A similar assignment can be made for the InAs(110) and InSb(110) spectra (Figs. 2 and 3) and yields the critical point energies given in Table I. Additional data points near Γ around 10 eV are consistent with the dispersion of the secondary cone (dashed line and open triangles).

Our results can be compared with empirical band calculations^{4,5} and optical data.³ The overall trend, i.e., an energy of the conduction band points decreasing from InP to InAs and InSb, is consistent with the empirical pseudopotential calculation by Chelikowsky and Cohen⁴ and the movement of characteristic optical transitions. This energy shift simply reflects the decreasing overlap between adjacent orbitals which goes along with an increasing lattice constant. However, at a finer level we note significant discrepancies with the calculations. In particular, the conduction-band critical points calculated for InP in Ref. 5 are lower than measured. The same trend (but smaller) is observed when comparing our data with Ref. 4. The optical transitions (cf. Fig. 12 in Ref. 4) in the 5-eV range

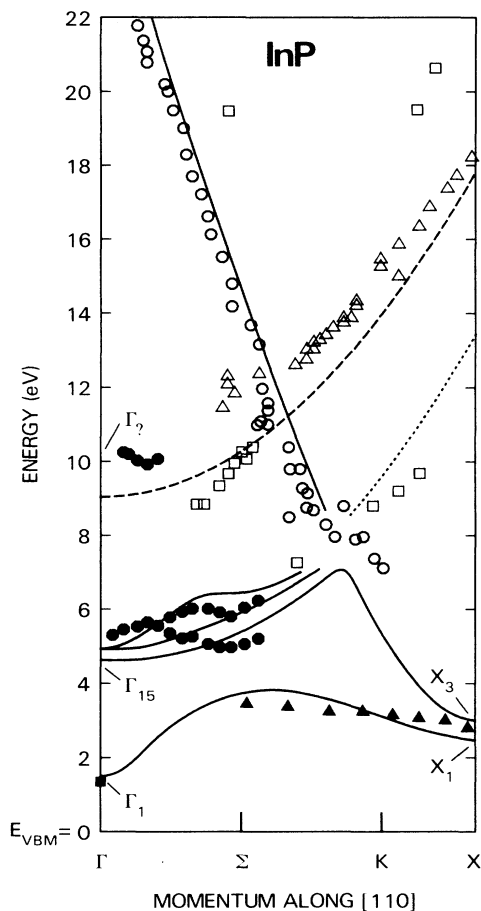


FIG. 4. Energy band dispersions for the conduction bands of InP obtained from the data in Fig. 1 (solid symbols). The open symbols are photoemission result from Ref. 5. The lower conduction bands (solid lines below 7 eV) are reproduced from the pseudopotential calculation of Chelikowsky and Cohen (Ref. 4). The upper conduction bands (lines above 7 eV) correspond to the free-electron parabola shifted down by an inner potential of 8.5 eV and backfolded into the first Brillouin zone. They describe the initial state of the electron in our inverse photoemission experiment. Circles represent transitions involving the primary cone and triangles a secondary cone.

are also higher than calculated, in agreement with our finding. Thus, the inverse photoemission results represent a significant new input for determining the conduction bands of In compounds and give the most accurate critical point energies in the energy range of hot electrons.

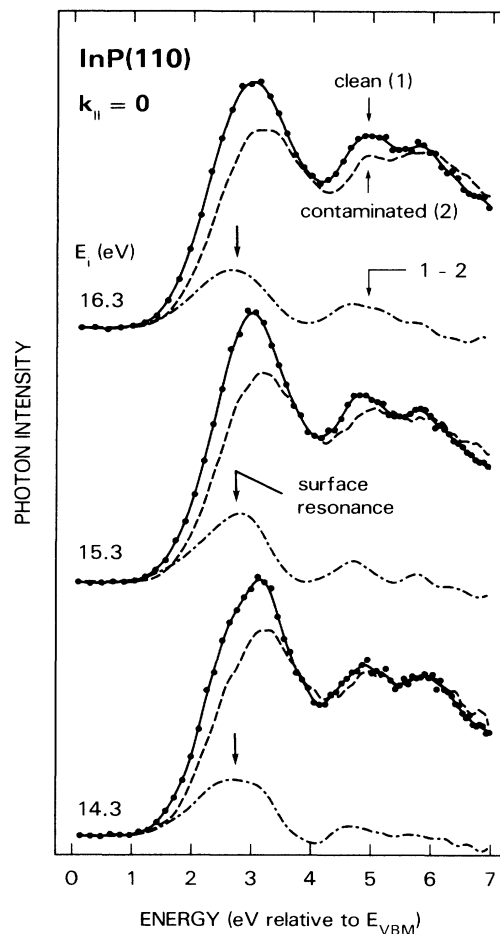


FIG. 5. Observation of a surface resonance on InP(110) with inverse photoemission. Bulk transitions between 4 and 6 eV are less affected by contamination than the surface feature.

SURFACE STATES

The spectra exhibit one feature at about 2 eV above the valence-band maximum that is more sensitive to contamination than the other peaks (Figs. 5–7). This feature does not disperse when the initial energy is changed, i.e., it has no k_{\perp} dispersion. All these properties are characteristic of a surface state.² Only the overlap with a bulk band at the same energy (Fig. 4) shows that one has, strictly speaking, not a surface state but only a surface resonance. Such a surface resonance has been predicted for the (110)

TABLE I. Inverse photoemission results for energies (eV) of conduction-band points relative to the valence-band maximum.

	InP	InAs	InSb	GaP ^a	GaAs ^b
Γ_7	9.5				
$\Gamma_{15} = \Gamma_7, \Gamma_8$	5.3	4.5	4.2		4.8
$X_1 = X_6, X_3 = X_7$	2.8	1.9	1.8		
Surface resonance at $k_{\parallel} = 0$	2.7	1.9	1.9	2.0	2.1

^aReference 15.

^bReference 16.

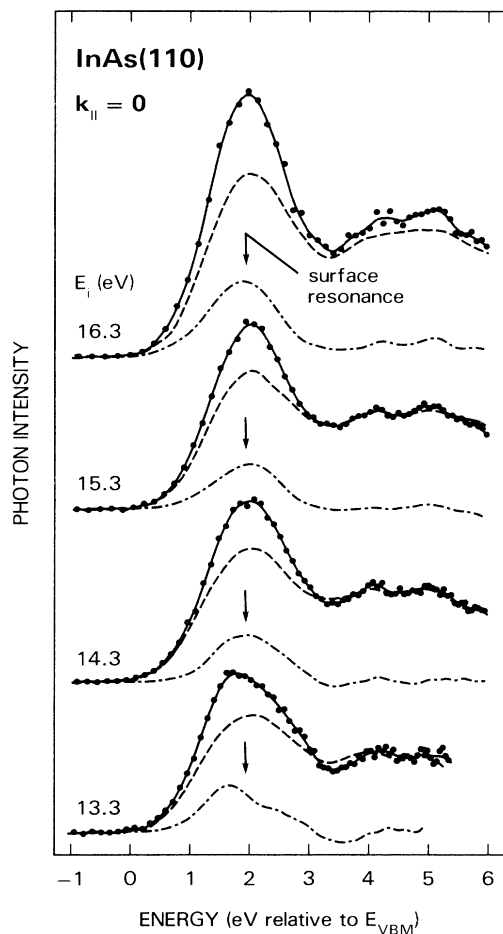


FIG. 6. Similar to Fig. 5 for InAs(110).

surface of III-IV compounds.¹⁹⁻²⁴ It corresponds to the unoccupied p_z orbital of In, which rehybridizes at the surface to sp^2 .

Transitions from the In $4d$ core level into this p_z orbital have been observed optically⁷ and by electron-energy-loss spectroscopy.⁸ These transitions exhibit a significant electron-hole interaction, which is absent in the inverse photoemission experiment. Subtracting the binding energy of the $4d$ level measured in photoemission from the optical transition energy a surface-exciton energy position of 1.0, 0.75, and 0.35 eV above the valence-band maximum has been obtained^{8,10} for InP, InAs, and InSb, respectively. By comparing with our inverse photoemission data (Table I) we deduce an electron-hole interaction of 1.7, 1.15, 1.55 eV for the In $4d$ surface exciton in InP, InAs, and InSb, respectively. These numbers are higher than previous findings for GaAs (0.95 eV, Ref. 16) and GaP (0.96 eV, Ref. 15). However, most of the core-level transitions happen at $k_{\parallel} > 0$, where the surface resonance splits off from the conduction-band minimum according to calculations. Off-normal inverse photoemission data will be required to determine accurate exciton binding energies.

Recently, two-photon photoemission experiments have

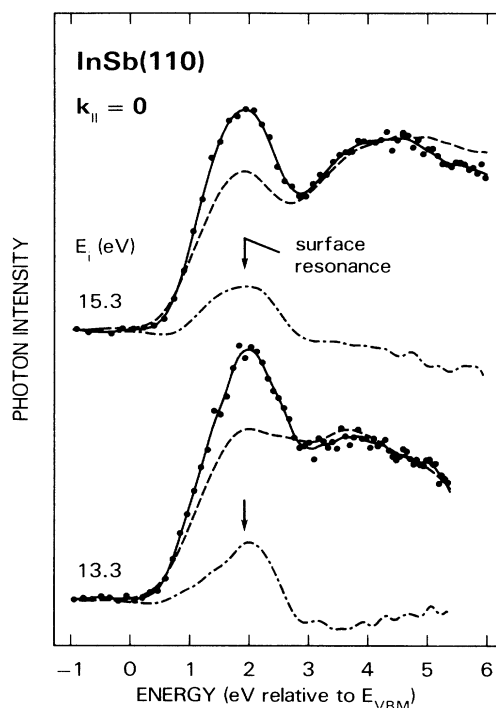


FIG. 7. Similar to Fig. 5 for InSb(110).

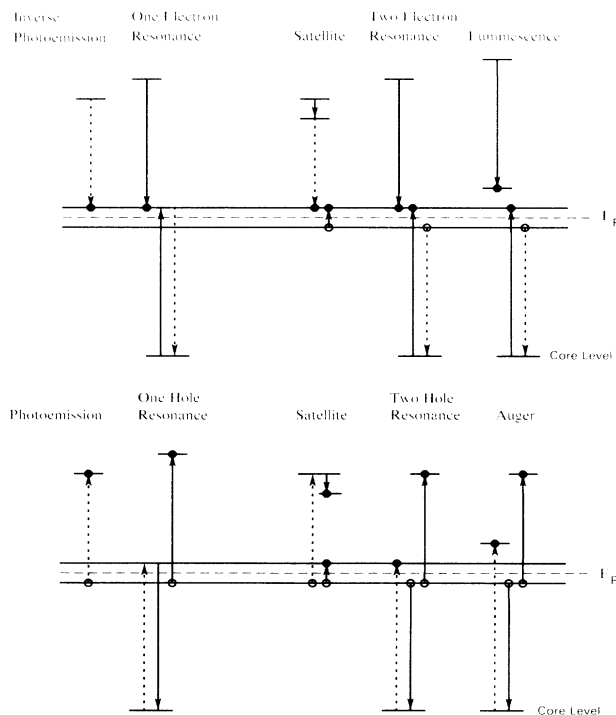


FIG. 8. Possible resonance effects in inverse photoemission and their analogs in photoemission. The diagram has been simplified by assuming discrete states and by neglecting Coulomb and exchange interaction between electronic and holes. Two types of resonances with one or two electrons (holes) in the final state are conceivable. Emitted photons are shown by dashed lines. Electrons (holes) in the final state are represented by solid (open) circles, respectively.

been performed²⁵ for the InP(110) surface. An unoccupied surface state was populated with 2.3-eV photons and subsequently ionized with 10.5-eV photons. From the ionization energy the minimum of the surface state band at $k_{\parallel}=0$ was determined to lie 1.47 eV above the valence-band maximum. A similar energy position (1.5 eV above E_{VBM}) is observed for GaAs(110) with two-photon photoemission.²⁵ Most likely, the two experiments probe two different surface states as calculated in many models.^{19–22} The energy positions and widths differ too much to explain both experiments by the same state.

RESONANT INVERSE PHOTOEMISSION

Resonances of the photoemission intensity at photon energies corresponding to a core-level threshold have been the subject of intense discussions in photoemission.^{26,27} They are a manifestation of many-body interactions and allow us, therefore, to determine the limits of a simple one-electron picture in interpreting photoemission spectra. Analogous resonances are conceivable for inverse photoemission (see Fig. 8). Experimental evidence for such effects exists for high electron energies in the BIS (bremsstrahlung isochromat spectroscopy regime).^{27,28} The shallow In 4d core level gives us an opportunity to study pos-

sible resonance effects at low energies. The energy difference between the In $4d_{5/2}$ core level and the conduction band is about 18 eV.^{7,8,10} Surface transitions have been observed at $h\nu \approx 18$ eV.^{7,8,10} The presence of core excitations can be seen in our spectra (Figs. 1–3) via the luminescent decay of In 4d core holes. A broad luminescence peak is seen at a constant photon energy of about 15 eV. Its apparent shift with E_i in the figures is due to the choice of the energy scale. Where the luminescence peak coincides with an interband transition, one observes an intensity enhancement, e.g., at $E_i = 17$ eV for the transition at the X point. Such an enhancement would be consistent with a two-electron resonance (see Fig. 8), where the energy of the photons emitted at resonance coincides with the energy of luminescence photons. However, we believe that in our case the intensity enhancement is predominantly explained by band-structure effects (i.e., transitions near critical points, see above). Very similar intensity behavior is observed in Cd compounds²⁹ which have a similar band structure but a much lower core-level binding energy than the In compounds.

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