

Surface-state band gap of InP(110) by polarized surface differential reflectivity

S. Selci, A. Cricenti, A. C. Felici, C. Goletti, and G. Chiarotti

Istituto di Struttura della Materia del CNR, via Enrico Fermi 38, I-00044 Frascati, Italy

(Received 20 November 1990; revised manuscript received 23 April 1991)

We present surface-differential-reflectivity results on the polarization dependence of optical transitions on InP(110) surfaces in the energy range between 2.0 and 4.0 eV. The surface dielectric function has been computed for light electric-field vectors along the $[1\bar{1}0]$ and $[001]$ directions. The data show two anisotropic peaks at 2.6 eV (excited with the light electric-field vector along the $[1\bar{1}0]$ direction) and 3.5 eV (excited with the light electric-field vector along the $[001]$ direction), and an almost isotropic behavior for the peak at 3.1 eV and the shoulder at 2.9 eV. From a comparison with photoemission data and calculated surface-state wave functions, an optical surface-state band gap of 2.6 eV can be assigned to the X point in the surface Brillouin zone.

The InP(110) surface has recently been the subject of a great deal of both experimental and theoretical work. Angle-resolved ultraviolet photoemission (ARUPS),^{1,2} k -resolved inverse photoemission (KRIPES),²⁻⁴ picosecond time-resolved photoemission,⁵ surface differential reflectivity (SDR),⁶ and electron-energy-loss spectroscopy,⁷ together with a strong theoretical effort,⁸⁻¹⁰ have contributed to obtaining the energy position and the dispersion of filled and empty states of the clean surface. However, there is disagreement among different experiments for the evaluation of the surface-state band gap.

Photoemission experiments have detected a filled (ARUPS) (Ref. 1) and an empty (KRIPES) (Ref. 3) surface-state band at the X point in the surface Brillouin zone (SBZ), respectively, 0.9–1.0 eV below (filled state) and 2.0 eV above (empty state) the valence-band maximum, thus resulting in a surface-state band gap of 2.9–3.0 eV at X . By following the experimental band dispersion, the band gap at Γ is estimated to be 2.95 eV.^{1,3} Surface optical transitions on cleaved InP(110) have been detected by SDR at 3.1, 3.6, and 3.8 eV with unpolarized light.⁶ At variance, polarization modulated reflectivity (PMR) spectroscopy at liquid-helium temperature have shown three anisotropies peaked at 2.75, 3.04, and 3.60 eV.¹¹ The fact that SDR and PMR show different optical anisotropies is not too surprising. In fact different experimental setups are used: samples are cleaved in liquid helium and oxidized in liquid-helium vapor in PMR, while in SDR samples are cleaved at room temperature in ultrahigh vacuum (UHV) and oxidized in UHV condition; the anisotropy is measured in SDR referred to the sample itself, while it is obtained with respect to a dummy sample in PMR. Surface-state band gaps have also been determined at all symmetry points of the surface Brillouin zone by simultaneously measuring the energy of the filled surface state by ARUPS and of the unoccupied surface state by KRIPES:² the resulting gaps have been 2.4 eV at Γ , 2.9 eV at X , 3.1 eV at X' , and 3.2 eV at M in the SBZ.

In this paper we present SDR results performed at room temperature with polarized light on InP(110) sur-

faces. The surface-state band gap results to be 2.6 eV. From a comparison with photoemission data and from the polarization dependence and the calculated parity⁸ of the wave functions involved, we assign this transition to occur at the X point in the SBZ.

SDR spectroscopy involves measuring the reflectivity of a sample when the surface is clean and after an exposure (E) to an external gas.^{12,13} The experimental results are given in terms of $[(\Delta R/R)(E)]$, i.e., the relative variation of reflectivity between these two conditions:

$$\left[\frac{\Delta R}{R}(E) \right] = \frac{R_{\text{clean}} - R_{\text{ox}}(E)}{R_{\text{ox}}(E)}, \quad (1)$$

where $R_{\text{ox}}(E)$ refers to the case of oxygen as the contaminating gas. The analysis of $\Delta R/R$ is done in the frame of a microscopic three-layer model in which the media involved [vacuum, surface (or oxide), and substrate] are assumed to have a definite anisotropic dielectric function.¹⁴ The general relation obtained between $\Delta R/R$ and the surface and oxide dielectric function is

$$\frac{\Delta R}{R} = d [A(\epsilon'_s - \epsilon''_{\text{ox}}) - B(\epsilon'_s - \epsilon'_{\text{ox}})], \quad (2)$$

where d is the surface thickness, ϵ'_s and ϵ''_s are the real and imaginary part of the surface dielectric function, ϵ'_{ox} and ϵ''_{ox} are the real and imaginary part of the dielectric function of the forming oxide. A and B contain the dependence upon bulk properties and have been computed in Ref. 6. Through the Kramers-Kronig relations (yielding an additional equation between ϵ'_s and ϵ''_s) it is possible to determine ϵ'_s and ϵ''_s , having given reasonable assignment to ϵ'_{ox} and ϵ''_{ox} .¹⁴

The experimental apparatus has been described in detail elsewhere.¹² A rotatable polarizer was inserted in that apparatus thus giving light polarized along the $[1\bar{1}0]$ or $[001]$ directions. InP n -type samples ($n = 1 \times 10^{17} \text{ cm}^{-3}$) were cleaved in UHV environment (base pressure $< 1 \times 10^{-10}$ Torr) with the double wedge technique obtaining reproducible flat mirrorlike surfaces. During oxidation the ion pump was valved off, to avoid release of

activated gas caused by the prolonged use at relatively high pressure (10^{-5} Torr or higher). The ionization gauge was kept on during the oxidation in an enclosed position far from the sample. The $\Delta R/R$ experimental accuracy was better than 2×10^{-4} .

Figure 1 shows the energy dependence of $\Delta R/R$ with the light electric-field vector along the $[1\bar{1}0]$ and $[001]$ directions. The derived results for ϵ_s'' and ϵ_s' in the two cases of light polarization are reported in Figs. 2 and 3, respectively. The surface dielectric function shows two transitions at 3.1 and 3.5 eV already reported in previous experiments with unpolarized light.⁶ The transition at 3.8 eV also reported in Ref. 6 is not visible in the present data because of the signal cutoff due to the used polarizer. The peak at 2.6 eV instead has not been clearly detected in the previous work⁶ because of the worse energy resolution (in these polarized SDR experiments the number of points has been doubled as compared to the unpolarized ones with an energy resolution of 50 meV).

The transition at 2.6 eV is excited, within the experimental error, only with the light electric-field vector along the $[1\bar{1}0]$ direction: contributions around this energy with the light electric-field vector along the $[001]$ direction are of the same order of the experimental noise in $\Delta R/R$ thus appearing just as a background without any structure in the derived ϵ' and ϵ'' . A shoulder around 2.9 eV is present, mainly, with the light polarized along the $[1\bar{1}0]$ direction. The peak at 3.1 eV is slightly reduced upon changing the light polarization. The peak at 3.55 eV shows a marked dependence upon the light polarization, being stronger with the light electric-field vector along the $[001]$ direction.

These results are in qualitative agreement with self-consistent calculation from Manghi *et al.*⁸ of the energy position and parity with respect to the mirror-plane symmetry¹⁵ at the high-symmetry points of the SBZ. In fact calculated bands assign possible optical transitions between dangling-bond bands (A_5 to C_3 in Ref. 8) at 2.5 eV (at X in the SBZ) with the light electric-field vector along the $[1\bar{1}0]$ direction at 3.05 eV (at Γ and X' in the SBZ) with the light electric-field vector along the $[001]$ direction. Mixed transitions between dangling-bond and

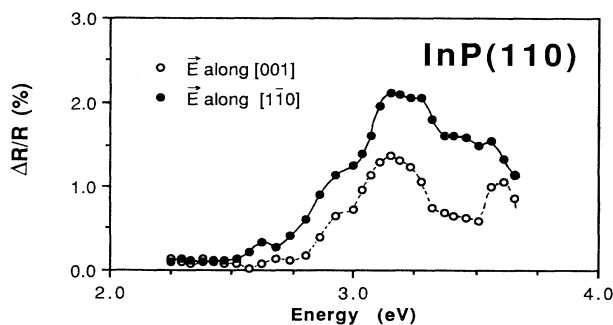


FIG. 1. Experimental $\Delta R/R$ spectra vs photon energy for cleaved InP(110) surface. The light electric-field vector is polarized along the $[1\bar{1}0]$ (solid circles) and $[001]$ (open circles) directions.

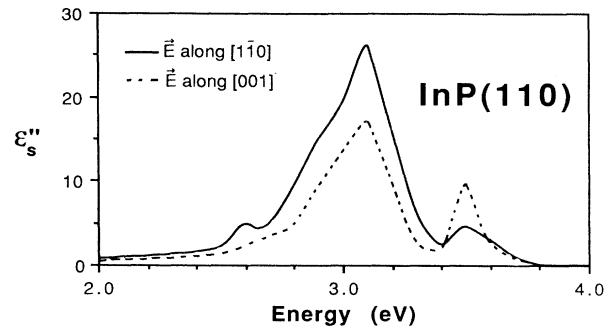


FIG. 2. Computed ϵ_s'' for the two polarizations.

back-bond states (A_5 to C_4 or A_4 to C_3 in Ref. 8) are at 2.4 and 3.3 eV (at Γ in the SBZ) with the light electric-field vector along the $[001]$ direction, at 2.9 eV (at M in the SBZ) with the light electric-field vector along the $[1\bar{1}0]$ direction, at 3.3 and 3.8 eV (at X in the SBZ) with the light electric-field vector along the $[1\bar{1}0]$ direction, at 3.5 eV (at X' in the SBZ) with the light electric-field vector along the $[001]$ direction. Other back-bond bands from Ref. 8 not localized on the surface layer have not been taken into account for the evaluation of possible optical transitions within our energy range. In summary from this theoretical computation we can have two possibilities: (1) the optical transition at 2.6 eV is between dangling-bond bands so that it is localized at X in the SBZ; (2) the same transition is, instead, a transition between one dangling-bond and one back-bond band so that it will be localized at M or along the $X-M$ line in the SBZ. If now we take into account also the experimental results of angle-resolved photoelectron spectroscopy^{1,2} and KRIPES (Refs. 2-4) then the possible bands which could give optical transitions around 3.0 eV are only dangling-bond ones.

The surface-state band gap evaluated from Cartensen *et al.*² is not in agreement with our data since in that work the gap is 2.4 eV at the Γ point. Even though pseudopotential calculations cannot give the correct energies for the bands' position, they are very helpful in determining the parity of the bands with respect to the mirror-

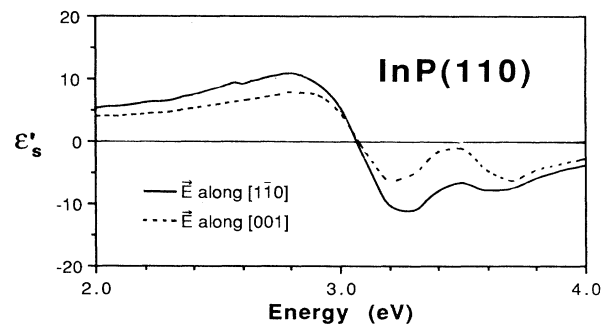


FIG. 3. Computed ϵ_s' for the two polarizations.

plane symmetry. Since the parity of filled and empty dangling-bond (and also back-bond) wave functions at Γ (Ref. 8) is the same (both are even) optical transition can be excited only with the light electric-field vector contained in the mirror plane, i.e., parallel to the $[001]$ direction. In our data the transition at 2.6 eV is excited only with the light electric-field vector parallel to the $[1\bar{1}0]$ direction, i.e., perpendicular to the mirror plane, thus resulting in a transition at X . This wrong assignment of the band gap at Γ in Ref. 2 can be due to the poorer energy resolution (630 meV) of the KRIPES spectrometer thus making it more difficult to separate out the bulk and surface contributions.

The surface-state band gap in SDR (2.6 eV) is 0.3–0.4 eV less than the value (2.9–3.0 eV) obtained at X in the

SBZ by putting together ARUPS (Ref. 1) and KRIPES (Ref. 3) results, thus giving a discrepancy very similar to Si(111)-(2 \times 1),¹⁶ GaAs(110), and GaP(110).¹⁷ Very recently this discrepancy has been explained for Si(111)-(2 \times 1) in terms of both experimental accuracy (0.15 eV) in KRIPES (Ref. 16) and an excitonic effect present in the SDR data (0.15 eV).^{16,18} It might be possible that we have the same kind of effect also on these III-V compounds.

In conclusion, the experimental results on the optical properties of the InP(110) surface in the 2.0–4.0-eV photon range show that the direct surface-state band gap occurs at 2.6 eV. From the calculated surface-state wave functions it can be established that this gap is at the X point in the surface Brillouin zone.

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