# Nearly flat bands at the GaP(110) surface

P. Chiaradia, M. Fanfoni, and C. Goletti
*University of Rome Tor Vergata, Via Ricerca Scientifica, 00133-I Rome, Italy*
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We have revisited the issue of (empty) intrinsic surface states at the GaP(110) surface and related Fermi-level position, since previous results based on photoemission experiments were uncertain due to the effect of surface photovoltage. The photovoltage problem has been overcome by combining kelvin-probe measurements and photoemission spectroscopy. We confirm that on well-cleaved samples almost flat bands are observed, while the usual pinning position of the Fermi level at 1.5–1.7 eV above the top of the valence band is due to extrinsic surface states associated with cleavage defects. Therefore, intrinsic surface states of GaP(110) are very close to the bottom of the conduction band.

## INTRODUCTION

It is well known that silicon surfaces possess electronic states inside the forbidden gap, of *intrinsic* nature, resulting in an electric field, or band bending, near the surface.[1] On the other hand, the cleavage faces of III-V compounds are characterized by flat bands, at least as long as the density of *extrinsic* surface states associated to cleavage defects is low.[2] This means that there are no *intrinsic* surface states inside the fundamental gap of the cleavage faces of III-V compounds. The physical explanation is that, in the case of binary compounds, dangling-bond states—already split in the ideally terminated crystal—are completely removed from the forbidden gap by surface relaxation.

However, in *n*-type GaP, the Fermi level was always found at 1.5–1.7 eV above the top of the valence band $E_v$,[2–6] corresponding to a band bending larger than 0.5 eV. This Fermi level pinning was interpreted as evidence of (empty) intrinsic surface states of acceptor type, well inside the forbidden band. For this reason, GaP was long believed to be the only exception to the general rule stated above.[2–5,7–9]

Near the end of the 1980s this conclusion was questioned by Benkacem *et al.* with work-function measurements, giving evidence of (almost) flat bands in GaP(110).[10] The authors claimed that "the assumption of no intrinsic surface states in the band gap of GaP is very credible." This statement was in substantial accord with both theoretical calculations[11] and inverse photoemission results,[7–9] which agreed in locating empty surface states of GaP(110) near the bottom of the conduction band.

Shortly thereafter another article appeared, based on photoemission measurements, claiming that (i) the commonly observed Fermi-level pinning at 1.5–1.7 eV above $E_v$ in GaP(110) was due to *extrinsic* rather than *intrinsic* surface states, and (ii) in very good cleaves only a small band bending was observed and therefore near-flat bands could be obtained.[12] At this point, one could think that there is no reason for considering GaP an exception in the III-V compound family: GaP behaves very much like GaAs and the other family members in which pinning of the Fermi level is observed only in bad cleaves, due to cleavage defects,[2] the only difference being that, for some reason, good cleaves are fairly common with GaAs and instead rather exceptional with GaP.

Unfortunately, in spite of the apparent soundness of the experimental evidence, this conclusion was in turn soon questioned, because of possible nonequilibrium conditions due to surface photovoltage (SPV), in the photoemission experiment of Ref. 12. Until the advent of very intense synchrotron-radiation sources, SPV effects in photoemission were basically neglected, because most were very small,[13] with only a few exceptions.[14,15] However, in 1990 they were recognized to be important in the case of intense beams and large-gap materials, depending also upon other parameters, including temperature and doping.[16,17] Nonequilibrium conditions in photoemission may alter the band-bending determination severely.[13–18] As a consequence, many photoemission results obtained in experimental conditions where SPV effects could have played a role[19–21] had to be revisited.[22–24] Indeed, also, in the case of Ref. 12, a suspect of SPV is *a priori* legitimate, for the same reason as in Ref. 21, especially because of the large gap of GaP (2.26 eV). If confirmed, this would imply that near-flat bands were due to nonequilibrium conditions and it would invalidate the above conclusions regarding the Fermi-level position and the absence of intrinsic surface states in the forbidden gap of GaP(110).

One should also mention that in a subsequent photoemission investigation, performed after the issue of SPV in photoelectron spectroscopy with high-intensity sources had been raised, a single case of (almost) flat bands in cleaved GaP surfaces was reported.[25] However, this work is not conclusive since the SPV effect, although rated negligible, was not directly measured.[25] At this point, it is evident that the whole matter can be clarified only by another photoemission experiment, in which SPV effects are fully controlled.

A method to account for SPV effects in photoemission spectroscopy with high-flux synchrotron-radiation sources has been developed recently.[24] This method allows one to correct the spectra for SPV shifts and determine the exact band bending from photoemission data.

In the present paper, we report results obtained by ap-

 

plying the above method to clean cleaved GaP(110) surfaces. We conclude that indeed *very good cleaves* exhibit Fermi-level positions close to the bottom of the conduction band, significantly higher than 1.5–1.7 eV above $E_v$, as usually reported in the literature. These results definitively confirm the rightness of previous experimental investigations[7–10,12,25] and theoretical predictions[11] locating empty intrinsic surface states of GaP(110) near the bottom of the conduction band.

## EXPERIMENT

The photoemission measurements were performed at the Synchrotron Radiation Center of the University of Wisconsin-Madison at Stoughton, Wisconsin. Electron distribution curves (EDC's) were obtained with a photon energy of 60 eV and a cylindrical mirror analyzer. The monochromator setting was never changed and the pass energy of the electron analyzer was the same for all spectra. The angle of incidence was 45° and the total resolution was better than 0.3 eV.

GaP samples, *n* type (Te doped) with carrier concentration $5\times10^{17}$, were supplied by Showa Denko. Ohmic contacts were made by evaporating Ge, Au, and Ni in sequence and annealing to 450 °C. The samples were cleaved in a vacuum of $1\times10^{-10}$ mbar, by using the knife-against-anvil method. Notches were cut only on one side of the bars, which measured $5\times5\times20$ mm$^3$. Large areas of exceptionally good quality, by visual observation, were obtained in the following way. (i) The knife was very sharp (asymmetric angle of 15°) and, consequently, the notches were deep. (ii) Both sample mounting and manipulator length allowed the sample to comply to the lateral forces exerted by the cleaver. (iii) The pressure on the knife was gently increased. We emphasize also that a careful positioning of the sample, with respect to the cleaver, turned out to be crucial. The use of an approaching optical device (telescope) was mandatory in this respect. Contact-potential-difference measurements were performed with an out-of-standard kelvin probe, supplied by Besocke Delta-PHI GmbH (Jülich, Germany), featuring a reduced tip of about 0.6 mm$^2$, made of gold.

The method used for subtracting SPV shifts in photoemission spectra has been described elsewhere.[24] All measurements were performed at room temperature.

## RESULTS AND DISCUSSION

Figure 1 shows a typical valence band of clean cleaved GaP(110), with many structures clearly visible, including a strong peak just below the edge, due to surface states. It is relatively simple, from a graphical point of view, to linearly extrapolate the leading side of the spectrum, in order to obtain the edge of the band $E_v$, as shown in the inset. However, in spite of this apparent simplicity, the issue of valence-band-edge determination from EDC spectra is very delicate.

Apart from SPV and instrumental broadening effects (which will be discussed later on), it is clear that the presence of a strong emission from surface states superimposed to the bulk emission may alter the leading-edge

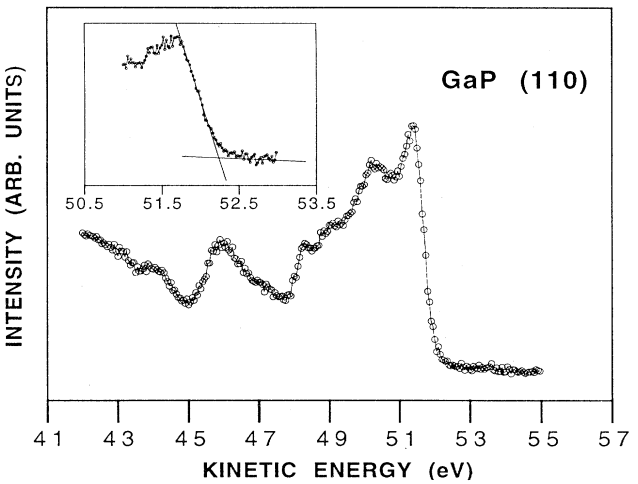


FIG. 1. Angle-integrated photoemission spectrum (energy distribution curve) of the valence band of cleaved GaP(110). The photon energy is 60 eV, the angle of incidence is 45°. The inset shows an accurate spectrum of the leading edge (data points every 20 meV) with a sketch of the linear extrapolation method used to determine the top of the band.

measurement. Ideally, one should subtract the surface-state contribution from the EDC of Fig. 1 and perform a linear extrapolation of the resulting bulklike spectrum. In practice, we have used the following approximate method. The two spectra of Fig. 2(a) represent valence-band EDC's of GaP(110) taken in a separate experiment, with the same photon energy (nominally) and slightly worse resolution. With respect to the spectra of Fig. 1, the angle of incidence of the beam and the azimuthal orientation of the sample are different. By changing the latter parameters, one can either enhance or depress the surface-state emission near the edge. In this way, spectra that are more surfacelike and more bulklike are obtained, as clearly visible in Fig. 2(a). The inset shows that the edges of the two experimental curves, as determined by linear extrapolation, coincide. Moreover, by subtracting one curve from the other, one obtains the line shape of the surface-state contribution. As a next step, we have simulated a bulklike spectrum starting from the EDC spectrum of Fig. 1, by subtracting the surface-state contribution, using a trial-and-error procedure. The result is shown in Fig. 2(b). One can see that the lower curve is very similar to the bulklike spectrum of the GaP valence band.[26–29] Also, in this case, the linearly extrapolated edges of the two curves coincide, as shown in the inset of Fig. 2(b). The explanation is that the surface states are deep into the valence band (the peak is about 0.8 eV below the top): although the slope of the linear extrapolation changes significantly, one can see that in this case the edge is practically unaffected by the presence of a high surface-state peak. However, in other cases, by using the same procedure, we found a small shift (of the order of 0.1 eV) in the linearly extrapolated edges of bulklike and surfacelike spectra, i.e., $E_v$ shifts closer to $E_f$ upon correction. Whether or not this shift is found de-

pends upon the spectral resolution, which is fairly sensitive to surface inhomogeneities of the sample. Therefore, the above analysis should be performed case by case.

After determining the edge of the valence band, one can estimate the Ga 3*d* binding energy (the only core level accessible without changing the photon energy). We measured 18.30±0.1 eV, by taking the center of the half maximum width, in reasonable agreement with the value of 18.45 eV reported by Miyano *et al.*[26] Incidentally, the Ga 3*d* EDC (not shown here) exhibited the well-known line shape[24–26,30] and upon deconvolution yielded a chemical shift of 0.3 eV for the surface component.

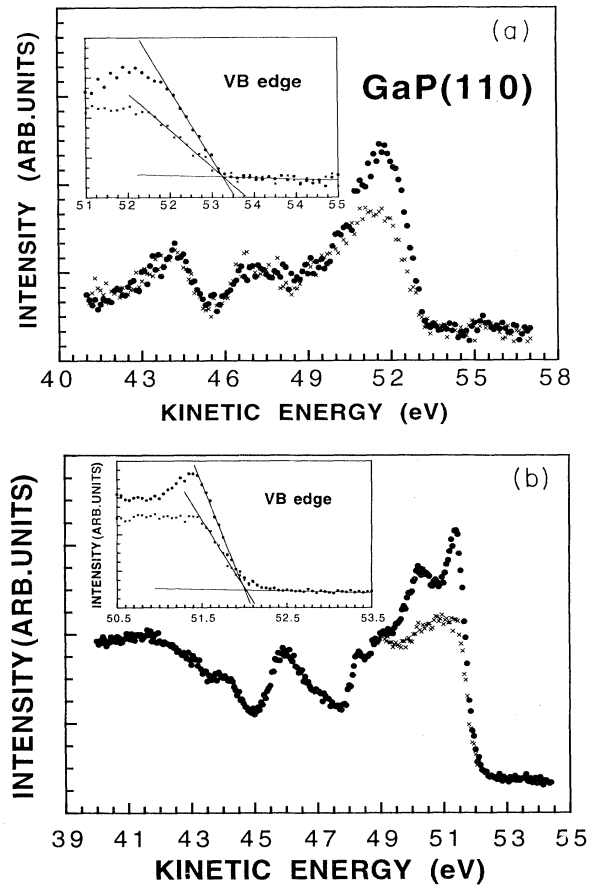


FIG. 2. Panel (a) shows two angle-integrated photoemission spectra (energy distribution curve) of the valence band of cleaved GaP(110), taken in a different experiment. The photon energy is 60 eV (nominal value) and the total-energy resolution is 0.4 eV. The angle of incidence and the azimuthal rotation of the sample have been adjusted in such a way as to enhance and depress, respectively, the surface-state emission about 1 eV below the top of the valence band. In particular, the upper curve has been obtained with a larger component of the electric vector normal to the surface, with respect to the lower curve, while the component parallel to the surface was along the direction of the chains, i.e., [$\bar{1}$10]. The two spectra have been normalized and superimposed. The inset shows a detail of the spectrum with the linearly extrapolated band edges. Panel (b) shows the energy distribution curve of Fig. 1 (upper curve) and the same curve in which the surface-state contribution (evaluated from the curves of panel a) has been subtracted away (lower curve) in order to simulate a bulklike spectrum of the valence band (see the text). The inset shows a detail of the spectrum with the linearly extrapolated band edges.

The Fermi-level position $E_f$ is determined from an EDC spectrum taken from a gold sample. In this way, one obtains a *raw* value of $E_f - E_v$, to be corrected for SPV and also for a systematic error, due to instrumental broadening. We discuss the SPV correction first.

The SPV shift is measured by comparing the work-function determinations by contact-potential difference (kelvin probe, in the dark) and photoemission (secondary-electron cutoff, under illumination) both for a metallic sample—for calibration—and for cleaved GaP.[24] In the case of the clean surface illuminated by the photoemission beam, we obtain a low SPV: 0.15 eV. This value is to be compared with much larger SPV shifts observed when a Schottky barrier develops by depositing a few monolayers of a metal on the surface, typically 0.4–0.8 eV, depending on the metal. Since the SPV tends to flatten the bands, its value *underestimates* the band bending, being equal to it only in the case of saturation. That the band bending of the clean surface was much lower than in the case of metal-GaP(110) interfaces was qualitatively confirmed by shining visible light from a table lamp onto the sample, during the kelvin-probe measurements. While in the case of metal-GaP interfaces a large effect was observed, no change was detected in the case of the cleaved surface. We would like to emphasize that the above method for SPV determination[24] is particularly useful when the Fermi level is not visible in the photoemission spectra, as in the present case.

The second correction is due to the instrumental broadening affecting the determination of the top of the valence band, as discussed by Kraut and co-workers.[31] We evaluate this correction of the order of 0.1 eV, in agreement with a previous estimate.[24] Therefore, the separation $E_f$-$E_v$ is 0.1 eV larger than given by the extrapolated edge of the valence band, apart from the SPV correction. In conclusion, we measure $E_f$-$E_v$, $=2.00\pm0.05$ eV. Two other cleaves, performed with the above precautions, yielded the same value within the error bar.

We conclude that in carefully cleaved GaP, the Fermi level lies *at least* 2 eV above the top of the valence band (we cannot exclude that even better cleaves give a higher position). Since in the bulk the distance between the Fermi level and the bottom of the conduction band is about 0.05 eV for our samples, an *upper limit* for the band bending due to *intrinsic* surface states is 0.2 eV. This result confirms the conclusions of the previous photoemission investigation,[12] implying that SPV effects were negligible, at least in the spectra on which those conclusions were based. In spite of the fact that recent calculations are available,[17] surface photovoltage is still hardly predictable, since it depends on many parameters.

Indeed theoretical calculations show that GaP(110) is unique in the III-V compound family in the sense that it is the only case in which surface states are not completely removed from the fundamental gap by relaxation.[11]

Moreover, the calculations show that the energetic position of surface states is weakly dependent upon structural parameters.[32] The previous experimental determinations of empty (intrinsic) surface states by inverse photoemission,[7–9] although less accurate due to poor energy resolution, as well as other findings[10,25] were all correct.

In conclusion, we have performed a photoemission experiment on well-cleaved GaP(110), combined with contact-potential measurements in order to determine the SPV shift in the photoemission data. The measured Fermi-level position, indicating that almost flat bands can be achieved, proves that intrinsic surface states are located near the bottom of the conduction band. The commonly measured Fermi-level pinning at 1.5–1.7 eV above $E_v$ (Refs. 2–6) is instead due to extrinsic surface states associated with cleavage defects. We can now answer the question of whether GaP is an exception among the III-V compounds. It is true that the energy gap of the (110) face is not free from (empty) intrinsic surface states. However, these states are very close to the bottom of the conduction band. GaP behaves differently with respect to the other member of the family, but the difference is small. Therefore, to consider it as an exception is a matter of taste.


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