Fermi-level pinning and intrinsic surface states in cleaved GaP

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We have performed photoelectron spectroscopy of the clean GaP(110) surface, obtained by cleaving n-type specimens. The results show that Fermi-level stabilization occurs in a wide range of positions. In some cases nearly flat bands were obtained. The surface Fermi-level position in n-type GaP(110) is then due to extrinsic surface states, probably cleavage defects, as in the case of p-type samples. The density of these extrinsic states depends upon the quality of the cleave. Previously the Fermi-level pinning in n-type GaP(110) surfaces instead was attributed to (empty) intrinsic surface states located at 1.6 ± 0.1 eV above the valence band. GaP(110) was considered an exception among III-V compounds, since in general atomic relaxation removes intrinsic surface states from the fundamental gap. The present results set a lower bound for the energetic position of the empty surface states slightly below the bottom of the conduction band. Therefore GaP(110) exhibits a gap practically free from intrinsic surface states, like the other III-V compounds so far investigated. We have also performed a spectroscopic study of the empty (intrinsic) surface states on the same surface by measuring the absorption edge of the P $2p$ core level. The result shows that the wave functions of the empty dangling-bond states, mainly cationic in origin, have a sizable localization on the anion site as well.

I. INTRODUCTION

As far as the energetic position of intrinsic surface states is concerned, gallium phosphide has long been considered an exception among III-V compounds.[1-7] Theory has shown that while in the case of covalent semiconductors intrinsic surface states are generally found in the fundamental gap, the cleaved surfaces of III-V compounds are usually free from such states, due to surface atomic relaxation.[8,9] Generally speaking, we can say that the empty surface states of these semiconductors are pushed either well inside (InSb, InAs, GaSb) or at the bottom (GaAs, InP) of the conduction band upon surface relaxation. Gallium phosphide was believed to be an exception to this "rule," basically on account of the band bending commonly observed after cleavage in n-type samples (p-type samples exhibited flat bands instead). The band bending was attributed to normally empty intrinsic surface states lying deeply in the forbidden band.

The aim of the present paper is to show that the cleavage face of GaP is by no means an exception, since also in this case intrinsic surface states, in particular the empty ones, are essentially removed from the fundamental gap. The band bending observed in n-type GaP(110) upon cleavage is then due to extrinsic surface states, probably cleavage defects, such as the case of GaAs(110).

The main motivation for the present study was the attempt to solve a puzzling discrepancy regarding the position of empty (intrinsic) surface states in GaP(110). In fact, on one hand many authors identified the bottom of the empty state band with the Fermi-level position at the surface, 1.5–1.7 eV above the top of the valence band, while on the other hand both inverse photoemission results and theoretical calculations located this band approximately 0.5 eV above, near the bottom of the conduction band. The present results are consistent with the latter assessment and demonstrate that any Fermi-level pinning in cleaved GaP(110) is not due to intrinsic surface states but to cleavage-induced extrinsic states.

II. EXPERIMENT

We have performed photoemission spectroscopy of ultrahigh-vacuum cleaved GaP(110) surfaces by using synchrotron radiation. The valence-band spectra were recorded at the Wisconsin Synchrotron Radiation Center with the Mark II Grasshopper monochromator. Instead the partial yield spectra were taken at the Laboratories of the Adone Storage Ring in Frascati, also with a Grasshopper monochromator. In both cases we used n-type samples (S doped, $n=6\times10^{17}$ cm^{-3}), furnished by Bell Labs, Allentown, Pa. The overall energy resolution in the case of the valence-band spectra was 0.25 eV, the cylindrical mirror electron analyzer being operated at a pass energy of 10 eV. Instead the partial yield spectra were recorded with an average energy resolution of about

0.2 eV. Further experimental details have been given elsewhere.[10]

III. RESULTS AND DISCUSSION

A. Fermi-level pinning

We have recently performed an extensive photoemission study of the electronic properties of clean (cleaved) GaP(110) surfaces, aimed at elucidating some aspects of Schottky-barrier formation[10] and oxidation[11] in III-V compounds. In the present paper we restrict ourselves only to clean surface properties, namely, the Fermi-level position of the freshly cleaved GaP(110) surface. The Fermi energy was experimentally determined from a metallic standard and referenced to the edge of the semiconductor valence band. The latter was obtained by linear extrapolation of the leading edge of the spectrum.[10,12] Possible systematic errors induced by this method[12,13] are of the order of the experimental accuracy and in any case do not affect the main conclusion of the present study.

We have observed that the Fermi level at the cleaved surface of n-type samples is not pinned at a single position, as claimed in the literature,[1-4,7,14] but is centered instead around the value most commonly quoted, i.e., 1.7 eV. In some cases we have obtained bands almost flat after cleavage, i.e., a band bending of only 0.1 eV, close to the experimental uncertainty. These findings indicate that the surface position of the Fermi level in GaP(110) is due to cleavage-induced surface states. The density and/or energetic position of these states depend upon the "goodness" of the cleave. A similar behavior has been observed in practically all III-V compounds investigated, including GaAs, as well as in p-type GaP(110).[2]

Typical results obtained in the present work are reported in Fig. 1, where valence-band (VB) spectra corresponding to different cleaves of the same crystal bar are shown. Due to the choice of surface-sensitive conditions ($h\nu=60$ eV) and the high energy resolution, photoemission from surface states shows up in these spectra as a huge peak approximately 1 eV below the top of the VB, E_v, in agreement with previous results.[14-16] The other features of the VB spectrum are bulklike transitions. The curves of Fig. 1 exhibit almost identical shapes, but are shifted one with respect to the other by band bending changes. Minor differences observed in the region of surface states warrants further investigation.

Figure 2 shows the distribution of different values of E_F-E_v we have measured in our study of the cleaved GaP (110) surfaces. The histogram summarizes the results of ten cleaves on GaP bars cut from the same ingot. Half of the data falls in the range 1.5–1.7 eV, in agreement with many others authors.[1-4,7,14] However, in the other cases the Fermi level is much closer to the bottom of the conduction band. These values are associated with a very low band bending and therefore are indicative of "very good" cleaves. In our experience a distinction between good and bad cleaves cannot be done by visual inspection only. Furthermore, the height of the surface state peak in Fig. 1 is not correlated with the band bending so that not even this parameter is an indicator of the goodness of the cleave. Clearly the results of Fig. 2 are not compatible with a distribution of (empty) intrinsic surface states with a density of the order of 10^{15} cm^{-2}, located near the bottom of the conduction band and "tailing" deeply into the forbidden band, as suggested by many authors.[4,6,8,9] They are instead consistent with a band of (empty) intrinsic surface states close to the bot-

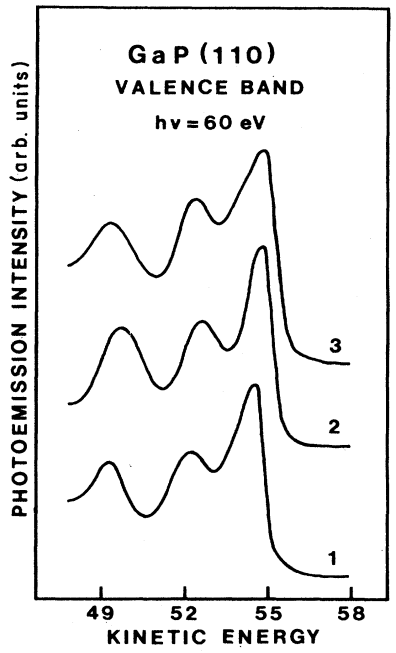

FIG. 1. Angle-integrated photoemission spectra of valence-band electrons (energy distribution curves) of cleaved GaP(110). The curves represent typical results obtained from different cleaves of the same bar. Position of the leading edge changes from curve to curve significantly, while the main features of the curves are reproducible. Minor line-shape differences are observed especially in the highest peak, containing a contribution from surface states. The excitation energy is 60 eV.

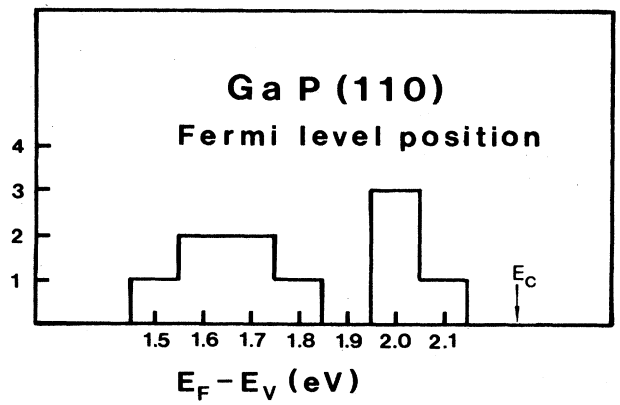

FIG. 2. Histogram representing the distribution of Fermi-level positions with respect to the top of the valence band in n-type GaP(110) for a total of ten cleaves.

tom of the conduction band, with no "tail" at all. Inverse photoemission experiments locate this band at 2.4–3.0 eV,[7] 2.2 eV,[5] and 2.0 eV (Ref. 6) above E_v, while calculations yield values close to the last value.[8] Theory has also shown that in GaP(110) the energetic position of these dangling-bond states does not depend very much upon the relaxation parameters.[8,9] In any case the Fermi-level position at the GaP(110) surface is not related to the intrinsic surface state band, as previously believed, except perhaps for the case of Fermi level very close to the conduction band, i.e., $E_F - E_v = 2.1$ eV.

The main conclusion of the present work is that the Fermi-level position in cleaved GaP(110) is determined by cleavage-related extrinsic states, both in *n*-type and *p*-type samples.

We have also exploited the possibilities offered by the photon source in order to obtain some new insight into the energetic position and the spatial localization of the (empty) intrinsic surface states. The results will be discussed in the remainder of this section, after a brief recall of the previous data on surface core exciton in GaP(110).

B. Surface core exciton

Regarding the surface core exciton in GaP(110), the present work confirms the previous estimate of its binding energy, which is of the order of 1 eV. The "apparent" position of the final states in partial yield photoemission from the Ga 3*d* core level[3,14,17] is a few tenths of eV below the Fermi level. The "real" position of the final states has been deduced either from theory[8] or from the inverse photoemission results.[5,6,7] In this way the exciton binding energy turns out to be 0.8–1.0 eV,[3,5,14,17] in agreement with a theoretical evaluation.[18] On the other hand, should one attribute the Fermi-level pinning to intrinsic surface states located at 1.6±0.1 eV, a much lower value for the exciton binding energy would be inferred.[2,4]

C. Spatial localization of the dangling-bond states

Traditionally, the surface core exciton in GaP(110) has been associated with an optical transition between the Ga 3*d* core level and the empty surface states.[3,14,17] This seems plausible in view of the fact that the wave functions of the empty surface states are thought to be localized predominantly on the cation dangling bond.[8] However, a tight-binding study of the anion and cation decomposition of the surface local density of states in GaAs(110) (Ref. 19) has revealed an appreciable mixing of Ga and As character, in particular for the dangling-bond states. Similar results are expected to be valid for GaP and other semiconductor compounds as well. Indeed optical transitions from the anion core levels to empty surface states have been observed at least in the cases of GaAs(110) and ZnS(110) more than a decade ago.[20] In other cases the failure to detect those transitions was due either to the dipole selection rule[1] or to poor resolution.[21]

We have recorded partial yield spectra of the P 2*p* edge in cleaved GaP(110) and the result is shown in Fig. 3. The hump at the very threshold disappears upon deposition of a small quantity of Ag, as the upper curve shows, while the rest of the spectrum remains substantially unchanged. This structure is then attributed to optical transitions to empty (intrinsic) surface states localized on the anion, having *s*-like character. Probably a second peak, split by spin-orbit coupling, is not resolved because it is buried in the higher-energy part of the spectrum. With respect to the Ga 3*d* edge[3,14,17] the surface-state absorption observed in the P 2*p* edge (i) exhibits an intensity smaller by a factor of at least 5 and (ii) appears closer to the conduction-band edge. The latter finding does not necessarily imply a binding energy for the corresponding excitonic transition smaller than in the case of Ga 3*d*. It may simply mean that anion-derived empty dangling bond states are somewhat higher in energy than the cation-derived states.

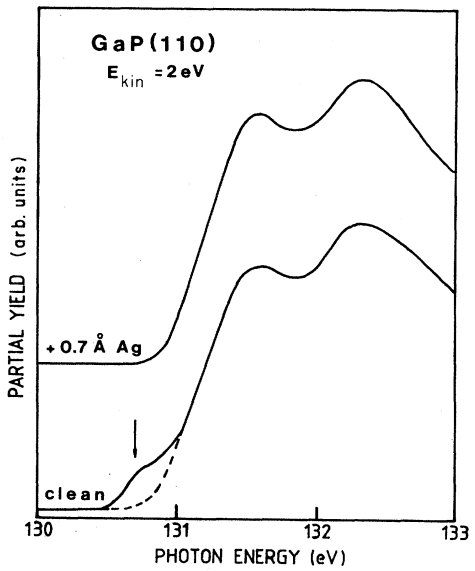

FIG. 3. Partial yield spectra of the P 2*p* absorption threshold in GaP(110), for the cleaved surface (lower curve) and for the same surface with 0.7 Å of Ag (upper curve). The edge of the lower curve shows an extra peak, indicated by the arrow.

IV. CONCLUSIONS

So far the empty surface states originating from dangling bonds of GaP(110) were believed to lie in the forbidden band, at approximately $\frac{2}{3}$ of the band gap.[1–7] This conclusion was based on the assumption that the Fermi-level pinning in cleaved *n*-type samples was due to (empty) intrinsic surface states. In fact, while in *p*-type samples both bent and flat bands were observed upon cleavage, in the case of *n*-type samples only band bending, although not always of the same amount, has been reported. Because of the empty surface states within the forbidden band, GaP(110) has long been considered the only exception among the cleaved faces of III-V compounds, all the others having their energy gaps free from intrinsic surface states. As a matter of fact, these dangling-bond states lying well inside the gap of

GaP(110) were at variance both with theoretical and experimental (inverse photoemission) results. In the attempt of settling the discrepancy, the unusual idea of a tail in the surface-state density has been put forward.

By performing repeated cleaves of *n*-type GaP samples in the same experimental conditions we have observed different positions of the Fermi level over a range of about 0.6 eV, including nearly flat bands. This (i) proves the extrinsic origin of the states responsible for the Fermi-level stabilization energy in *n*-type as well as in *p*-type samples and (ii) sets a lower limit for the bottom of the empty surface state band, this limit being very close to the edge of the conduction band. These conclusions exclude any tail in the surface state distribution and are in agreement with the results of band calculations and inverse photoemission. The large (about 1 eV) excitonic shift of the core to surface state transition is confirmed. Optical transitions from an anion core level (P 2*p*) to empty surface states localized on the anion have been observed in this surface for the first time. This finding demonstrates that the wave functions of the empty dangling-bond states, mainly of cationic origin, are also significantly localized on the anion. Similar results had been obtained previously in GaAs and ZnS (Ref. 20) as well as predicted by calculations.[19]

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