Ultraviolet-photoemission-spectroscopy study of the interaction of atomic hydrogen with cleaved InP: A valence-band contribution

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Angular-resolved ultraviolet-photoemission spectroscopy has been used to follow the evolution of the valence-band spectrum of InP(110), cleaved in ultrahigh vacuum, at particular stages of its interaction with atomic hydrogen. Photons in 17–65-eV energy range were used, and electrons at normal emission were energy analyzed. During the first interaction stage, H bonds covalently to the substrate. It induces a removal of the P-associated surface states near the top of both parts of the valence band, and the growth of two additional structures around 4.5 and 6 eV below the valence-band edge. These evolutions arise from the bonding of H to P and very likely to In. The analysis indicates that the first interaction stage may be more complex than a mere adsorption. The decomposition stage at heavy hydrogenation is confirmed by a clear metallic Fermi edge from In and an evolution of the spectra compatible with the presence of an overlayer of P-hydrogenated species.

I. INTRODUCTION

Recently, we have reported on a study of the interaction of atomic hydrogen with cleaved InP,[1-3] which was carried out by low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), electron-energy-loss spectroscopy (EELS) from plasmon excitations, and photoemission-yield spectroscopy (PYS). From these results, we have proposed that the interaction takes place in two successive stages. The first interaction stage is an adsorption during which one H atom per surface unit cell binds covalently with the substrate. Then a dissociation occurs whereby In metal is formed together with a hydrogenated compound of P. The latter remains adsorbed and is at the origin of a peculiar phenomenon by which the photoemission signal disappears completely around specific photon energies.

In order to further characterize the InP(110)+H system, an ultraviolet-photoemission-spectroscopy (UPS) study has been undertaken at LURE, the Orsay synchrotron radiation laboratory. Angular-resolved electron distribution curves (EDC's) from the valence band (VB), as well as the In $4d$ and P $2p$ core levels, have been measured after cleavage and after interaction with specific hydrogen doses. The latter were chosen so as to bring the system to particular stages of the interaction scheme, namely around completion of the adsorption stage and at a well-established dissociation. The measurements have been performed at various photon energies to take advantage of the escape-depth variation with the kinetic energy of the electrons, and so vary the sensitivity to the surface. In the present paper, we report the results concerning the valence-band contribution, while those concerning the

substrate elements core levels are planned to be published separately.[4]

II. EXPERIMENTS

For the valence-band study, two series of experiments have been performed at LURE in a stainless-steel ultrahigh-vacuum chamber connected first to the ACO storage ring (where ACO denotes Anneau Circulaire d'Orsay), then to super ACO. Photons were monochromatized by a toroidal grating, in the 28–65-eV energy range for the ACO runs (1200 lines/mm grating; 700 and 100 μm for the entrance and exit slits, respectively), and in the 17–24-eV range on super ACO (300 lines/mm grating; 100 and 80 μm for the entrance and exit slits, respectively). The beam was incident in the $(1\bar{1}0)$ plane at 45° from the sample surface. Photoelectrons were detected at normal emission with a spherical analyzer having an angular resolution better than 1° and an energy resolution of 250 meV.

Atomic hydrogen was produced by thermal dissociation of H_2 at a hot tungsten filament ($T \approx 1750$ °C) held in front of the sample surface, about 65 mm away from it in the direction of the normal. For a given gas pressure, this setup gives a flux of H atoms striking the surface about 20% larger than that from the arrangement used previously.[1] We shall refer to the total dose of H_2, expressed in langmuirs (1 L $= 10^{-6}$ Torr s), with the hot filament turned on, as determined from the partial exposures. In the super ACO runs, the sample was exposed to hydrogen doses from 5×10^2 to 3×10^3 L, which bring the system to the completion of the adsorption stage. Whereas in the ACO experiments, the hydrogen doses considered were $\sim 2 \times 10^3$, $\sim 6 \times 10^3$, and $\sim 6 \times 10^5$ L.

The first two should bring the InP(110)+H system some-
what before and somewhat after completion of the ad-
sorption stage. In the proposed scheme, this initial in-
teraction process saturates at a H coverage of 0.5 mono-
layer, i.e., one H atom per surface unit cell, after a dose
of about 3×10^3 L.[1] With the highest dose, an important
dissociation of the substrate should take place with, in
particular, the formation of metallic indium.

n-type InP single crystals from MCP Electronics Ltd.
($n = 1.3 \times 10^{17}$ cm^{-3}) were cut into bars with notches for
cleavage along the (110) plane, and cleaved at a base pres-
sure in the low 10^{-10}-Torr range. Immediately after
cleavage, the valence-band and core-level spectra were
recorded for various photon energies. The measurements
were repeated after each hydrogen exposure once the
pressure was back in the low 10^{-9}-Torr range. AES fa-
cilities enabled us to check the cleanliness of the sample,
an essential feature to bring the system in the desired
state.[5] No Auger peaks other than those of the substrate
were observed at the end of the runs.

III. RESULTS

A. Energy references

As expected, metallic indium is formed after interac-
tion with the highest dose of hydrogen, which, as we shall
see shortly, gives a sharp Fermi edge on the VB spectra.
We have used this peculiarity of the InP(110)+H system
to position the Fermi level E_F on the kinetic-energy
scales of our ACO measurements. The extension to the
EDC from the clean surface or after the lower H expo-
sures is relevant since the adjustable electrostatic poten-
tials of the electron energy analyzer were kept constant
throughout the experiment.

One of the effects of atomic hydrogen is to shift all the
spectra towards higher kinetic energies for our n-type
samples. This is illustrated in Fig. 1 for the VB and In $4d$
spectra. The 0.45-eV shift, observed for a good cleavage
and due to a H-induced band bending, is in very good
agreement with the PYS results.[1] The other changes that
occur upon H interaction make it difficult to determine
the position of E_{VS}, the valence-band edge at the surface,
from the photoemission spectra. Therefore, E_{VS} was
placed with respect to E_F using the work-function and
ionization-potential values determined from the PYS
measurements as a function of the hydrogen dose. This
approach is possible up to 10^4 L H$_2$,[1] and for a good
cleavage. When the cleavage was poor, or the highest hy-
drogen dose not large enough, as in the super ACO mea-
surements, the position of E_{VS} on the kinetic-energy scale
was determined by linear extrapolation of the main VB
spectrum edge on the high-kinetic-energy side.

One should note that, for our samples, the effective De-
bye length L_D is ~ 120 Å. This quantity, which evalu-
ates the extent of the space-charge region when a band
bending occurs, is much larger than the escape depths of
the photoelectrons. The latter are indeed expected to
vary between mainly 5 and 15 Å when the electron kinet-
ic energy ranges from 60 to 10 eV,[6] as in our measure-
ments. Thus a smearing of the spectra due to band-
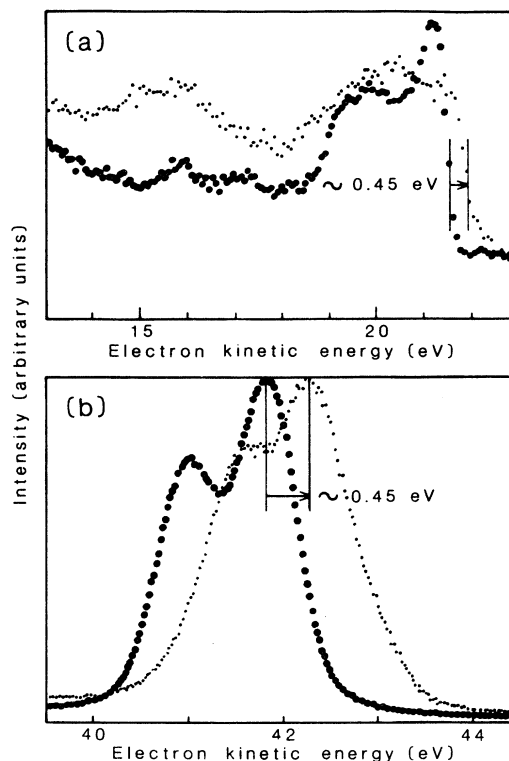bending effects should be greatly reduced.

FIG. 1. Valence-band spectra for $h\nu=28$ eV (a) and In $4d$
core-level spectra for $h\nu=65$ eV (b) measured on the clean
cleaved InP(110) surface (large dots) and after its exposure to
atomic hydrogen at a dose of 2×10^3 L H$_2$ (small dots).

B. Valence-band spectra

Examples of InP(110) VB spectra are given in Figs. 2
and 3 as recorded after cleavage (curves 1) and after in-
teraction with hydrogen (curves 2–4 in order of increas-
ing exposure) for the photon energies 21 eV (Fig. 2), 38
eV [Fig. 3(a)], and 50 eV [Fig. 3(b)]. In these plots, the
energy reference is E_{VS} and the positions of E_F are indi-
cated. Because of the Fermi-level pinning induced by H
at the early stages of the interaction,[1] we have assumed in
the case of the highest dose (curves 4 of Fig. 3) that E_F
remains pinned in the gap at the position it had before.
This means that, on the energy scales of Fig. 3, E_F has
the same position for curves 4 as for curves 3.

The after-cleavage spectra (curves 1 of Figs. 2 and 3)
are in good agreement with those of Sorba *et al.*[7] Some
discrepancies in the relative intensities of the structures
may arise from different experimental conditions such as
the polarization of the light, the azimuth, and angle of in-
cidence. The main remarkable features are the following.
The sharp and intense peak observed at 0.37 eV below
E_{VS} for $h\nu=28$ eV [Fig. 1(a)] has been assigned[7] to the
phosphorus-derived dangling-bond surface state of re-
laxed InP(110). A fairly narrow peak is observed at 5.7
eV below E_{VS} for all photon energies. It becomes more
prominent as $h\nu$ increases from 28 to 65 eV, while the
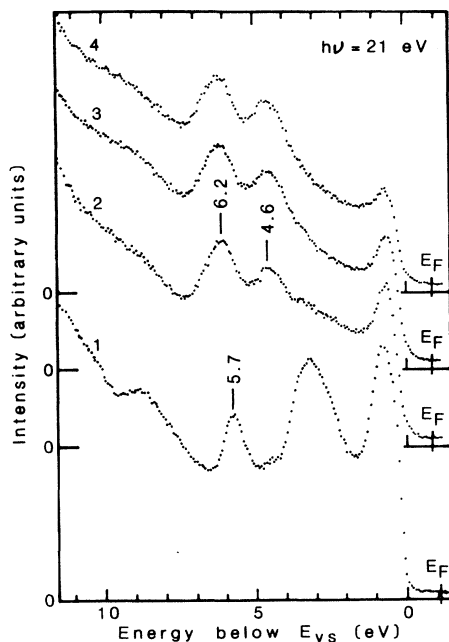closest structure on the lower-binding-energy side ap-

FIG. 2. Normal-emission valence-band photoelectron spectra for $h\nu = 21$ eV from cleaved InP(110): curve 1, after cleavage; curves 2–4, after 5×10^2, 1×10^3, and 3×10^3 L of thermally excited hydrogen, respectively. The energy is referred to E_{VS}, the valence-band edge at the surface. Each spectrum is normalized to the highest signal. There is no normalization to the photon flux.
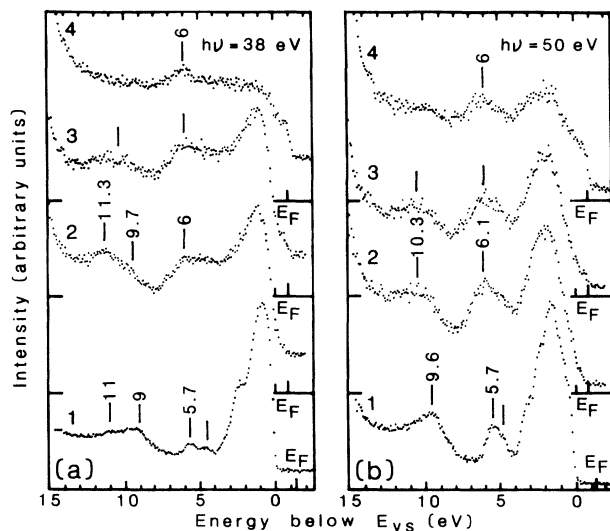

FIG. 3. Normal-emission valence-band photoelectron spectra for photon energies of (a) 38 and (b) 50 eV from cleaved InP(110): curve 1, after cleavage; curves 2–4, after interaction with 2×10^3, 6×10^3, and 6×10^5 L of thermally excited hydrogen, respectively. The energy is referred to E_{VS}, the valence-band edge at the surface. E_F is the Fermi level. Each spectrum is normalized to the highest signal. There is no normalization to the photon flux.

proaches it. It corresponds to the dispersionless structure assigned by Sorba et al.[7] to a surface state or a possible density-of-states emission, and observed at 5.9 eV by these authors. Between these two features, several peaks appear that have been related[7] to transitions from that part of the bulk valence-band structure of InP situated above the heteropolar gap.[8] A broad dispersing peak is observed at larger binding energies, which is attributed[7] to transitions from the s-like Σ_6 band below the heteropolar gap.

After 5×10^2 L H_2 (curve 2 of Fig. 2), the VB spectra of InP have undergone important changes. The most obvious evolutions are (i) the large decrease of emission near the top of the valence band, and (ii) the growth of two additional structures at ~ 4.6 and ~ 6.2 eV below E_{VS}. The spectra from the top of the valence band to about 4-eV binding energy are far less structured than after cleavage. The large binding-energy contribution from the band below the heteropolar gap is also affected by the H interaction.

To enhance the changes that have occurred, the differences between the VB spectra after 5×10^2 L and those after cleavage have been determined, each curve being previously normalized to its signal around 12–13 eV below E_{VS}, i.e., below the whole valence band. The same qualitative results are obtained for all $h\nu$. They are illustrated in Fig. 4(a) for $h\nu = 21$ eV, where we clearly see (1) an increase of signal in the gap above E_{VS}; (2) the decrease of emission in the range from E_{VS} to about 3.5 eV below it; (3) the growth of two peaks around ~ 4 and ~ 6.5-eV binding energy; (4) a decrease of signal around 9–9.5-eV binding energy; and (5) an increase of emission around 10–11 eV below E_{VS}.

When the hydrogen dose increases beyond 5×10^2 L and up to 3×10^3 L, the changes occurring in the VB spectra are not very important (Fig. 2, curves 3 and 4). We notice essentially a further decrease of the emission in the range from E_{VS} to about 3.5-eV binding energy.

The evolutions upon H interaction, observed at low photon energy, as in Fig. 2, are not all so obvious in the other spectra after 2×10^3 L H_2 (Fig. 3, curves 2). This may come from the change in resolution between the two sets of experiments, and also from the change in sensitivity of the various structures when changing $h\nu$. These spectra are superimposed on a relatively larger background than after cleavage. The emission decrease at the top of the valence band is quite clear. In particular, the P-derived surface state, which was close to E_{VS}, seems to have completely disappeared. For $h\nu = 28$ eV [Fig. 1(a)], for which this state was most prominent, a small structure is still visible near E_{VS} but at about 0.6 eV below it. The emission that appears in the gap up to E_F is also well seen, and the distribution edge is far from being metallic, in agreement with the PYS results.[1] However, the two additional structures are not resolved: the narrow feature at 5.7 eV below E_{VS} is no longer observable; instead, a broad peak appears, the maximum of which is slightly displaced towards larger binding energies (~ 6.0 eV below E_{VS}). Concerning the contribution from the band below the heteropolar gap, its maximum shifts towards
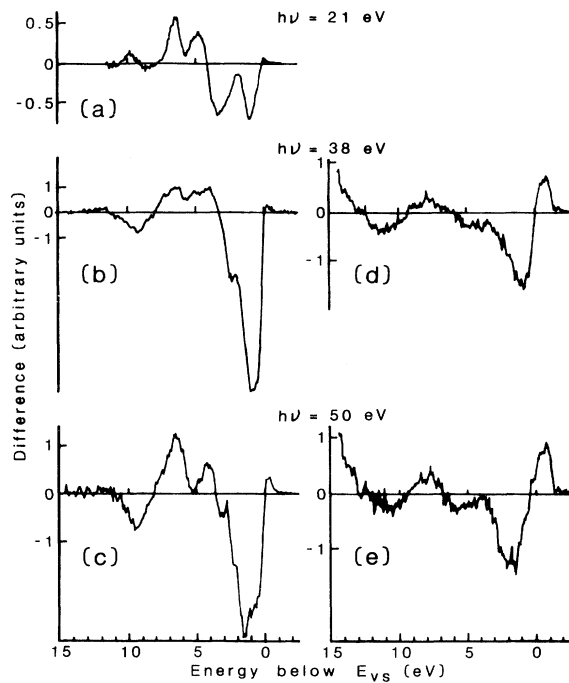
FIG. 4. Difference curves, for $h\nu=21$, 38, and 50 eV, determined from the valence-band spectra after each spectrum had been normalized to its value around 12–13 eV below E_{VS}. (a) gives the difference between curve 2, after 5×10^2 L, and curve 1, after cleavage, of Fig. 2. (b) and (c) are the differences between curve 2, after 2×10^3 L, and curve 1, after cleavage, of Fig. 3, for $h\nu=38$ and 50 eV, respectively. (d) and (e) are the differences between curve 4, after 6×10^5 L, and curve 2, after 2×10^3 L, of Fig. 3, for $h\nu=38$ and 50 eV, respectively. The energy is referred to E_{VS}.

larger binding energy by about 0.6 eV, for $h\nu=50$ and 65 eV; for $h\nu=38$ eV, besides a similar shift in energy, there is a change in the relative intensity of the two initial structures at 9 and 11 eV so that the maximum now appears at 11.3 eV below E_{VS}. If we consider the difference curves between the VB spectra after 2×10^3 L and those after cleavage, a remarkable agreement exists with similar curves obtained after a smaller hydrogen dose, as can be seen in Fig. 4 (curves on the left-hand side).

The changes that occur in the valence-band spectra after 6×10^3 LH$_2$ (curves 3 of Fig. 3) are not as drastic as after the first exposure to H (compare with curves 2). One should notice the further emission increase in the gap up to E_F. Although this growth of states is fairly large, their contribution is not fully metallic yet, in agreement with the evolution of the In 4d spectra.[4] Concerning the remainder of the spectra, there is a slight further decrease of the emission in the range from E_{VS} to about 4-eV binding energy, and also of the structure around 10 eV. In other words, there is a relative increase of the peak at about 6 eV below E_{VS}.

After 6×10^5 L H$_2$ (curves 4 of Fig. 3), the spectra exhibit a sharp, truly metallic edge in agreement with the

PYS results[2] at this large exposure. A relative increase of the background is observed together with a relative increase of the peak around 6 eV below E_{VS}, which is now the dominant feature for $h\nu=28$ and 38 eV. Other changes occurring beyond the adsorption stage are seen on the difference curves between the VB spectrum after 6×10^5 L and that after 2×10^3 L (Fig. 4, curves on the right-hand side). These reveal (1) the further increase of signal beyond E_{VS} due to the formation of a metal; (2) the further decrease of emission in the range from roughly E_{VS} to ~3.5 eV below it; (3) no change, or a slight decrease, from ~3.5-eV to ~6-eV binding energy; (4) the growth of a structure around 8 eV below E_{VS}, i.e., in the heteropolar gap; and (5) the decrease of signal around 10.5–11 eV below E_{VS}.

IV. DISCUSSION

The appearance of a metallic edge on the last curves, which can arise from nothing else but indium metal, confirms the dissociation of the substrate at large exposures. This is also supported by the evolution of the In 4d spectra[4] and agrees with the interaction scheme proposed.[1,2]

The important evolutions of the InP valence-band spectra observed after H interaction reveal that great rearrangements have occurred in the electronic structure at the surface through the removal of surface states characteristic of the initially clean cleaved InP, and the appearance of additional surface states arising from chemical bonds after H chemisorption (we shall not distinguish here between true surface states and surface resonances). It has been reported[9] that changes in the valence-band spectra in the presence of an adlayer may also be due to modifications in bulk state emission through changes in the matching probability at the surface between final states inside the crystal and the free electrons outside it. Although such effects are very likely, we shall assume they are not dominant in the present data, and we shall discuss our results essentially in terms of surface states. These concern the $\overline{\Gamma}$ point of the (110) surface Brillouin zone since the detected electrons have no component of the wave vector parallel to the surface at normal emission.

Theoretical calculations of the surface electronic structure, and in particular the determination of surface-state dispersion curves, have been performed on InP(110),[10−12] as well as on the clean relaxed (110) surface of other III-V compounds.[12−17] The great similarity in the properties of these semiconductors is verified here again, and a general qualitative agreement exists among the theoretical results. To our knowledge, the effect of H on the surface electronic structure of InP(110) has not been studied theoretically. However, some investigations have been performed on the GaAs(110)+H system.[18−20] They will serve as a guide for our discussion. Because of the discrepancies that appear as to which surface or H-induced states exist at $\overline{\Gamma}$ (Fig. 5), we shall not pay too much attention to the symmetry points at which the states have been found in the calculations.

(a)
clean relaxed InP(110)

(b)
H-covered
unrelaxed
GaAs(110)

Refs. (10) (11) (11) (12) (19) (20)

C_3
C_4
C_4
C_3
C_4
C_3
C_3

A_6
A_5
A_4
A_6
A_5
A_5
A_4
A_3
C_2

Energy (eV)

5

C_1

H_2
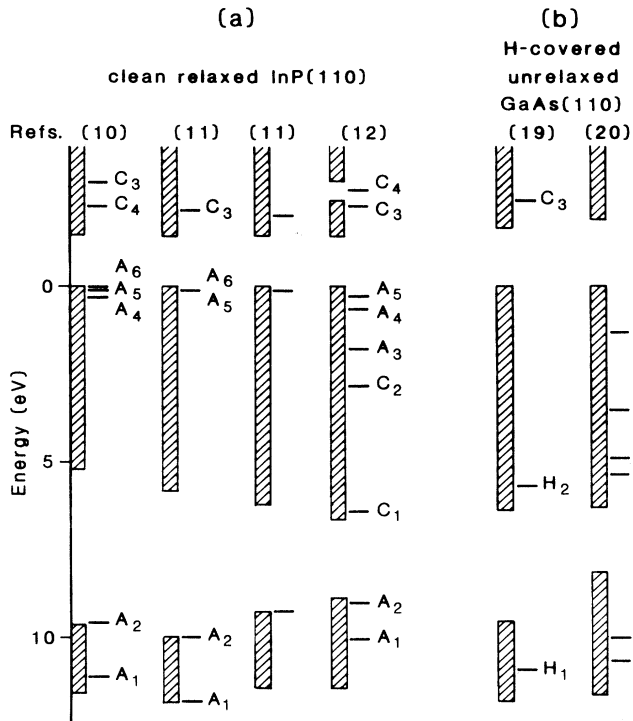
10

A_2
A_2
A_2
A_1
A_1
A_1
A_1
H_1

FIG. 5. Results of theoretical calculations concerning the surface states present at the $\bar{\Gamma}$ point of the two-dimensional Brillouin zone of (a) clean relaxed InP(110), and (b) H-covered unrelaxed GaAs(110). Energies are referred to the valence-band maximum. The shaded bars correspond to the projected bulk states at $\bar{\Gamma}$. The labeling of the states, where available, are those given in the references.

A. After 2×10^3 L of hydrogen

Several parts of the initial spectra are most affected by the H interaction after 2×10^3 L H_2: (i) near E_{VS}, (ii) around 6 eV below E_{VS}, and (iii) around 10 eV below E_{VS}.

(i) Near E_{VS}, we observe the removal of the predominantly p-like surface states localized on the anions of the first layer.[10-17] The highest occupied state, which seems to be completely removed, is the anion-derived dangling-bond state (A_5).[21] The anion-associated backbond state (A_4) is slightly deeper in the valence band, by at most 1 eV. In fact, a reduction of the emission occurs over the whole region within about 3 eV from E_{VS}. Around 2–3 eV below E_{VS}, essentially p-like anion-derived states (A_3), localized on the second layer[13,17] or on the second and the first layers,[12,15,16] can be found on the clean surface together with mostly s-like cation-derived states (C_2) localized on the surface layer.[12,16] This removal of states, which is observed also with GaAs(110) upon H interaction in the low-dose regime,[22,23] is compatible with an ideal unrelaxed configuration of the substrate atoms in the presence of chemisorbed H.[19]

(ii) The region around 6 eV below E_{VS} corresponds to the bottom of the "upper" valence band situated above the heteropolar gap. Tight-binding calculations on the clean surface[12,16] in this region yield a predominantly s-like state (C_1) localized on the cation of the subsurface layer, which may contribute to the dispersionless structure at 5.7 eV below E_{VS}. Upon H exposure, the shift to about 6 eV below E_{VS} is consistent with the results of the tight-binding approach of Beyer et al.,[18] who considered the adsorption of one H atom on a relaxed GaAs(110) surface. They showed that, in this region of the valence band, there is a maximum in the local density of states (LDOS) at the H atom as well as at the substrate atom to which it chemisorbs, whether it is the cation or the anion. For either chemisorption site, the maximum of the substrate atom LDOS is slightly displaced towards larger binding energies when compared to the LDOS feature from which it is derived in the physisorption limit.

However, a model in which H binds to substrate atoms along the dangling-bond directions of an ideal surface configuration (geometry A of Refs. 19 and 20) is probably more appropriate considering the observed evolution near E_{VS} and previous LEED results,[3] and extending to InP recent results of total-energy calculations[20] on H/GaAs(110). Then, according to the pseudopotential approach of Manghi et al.[19] on GaAs(110) covered by one monolayer of H atoms, the additional structure at 6 eV would correspond to a state localized on hydrogen having a significant contribution from an In s-like state localized on the second InP layer when H is adsorbed on P. This H_2 state exists at $\bar{\Gamma}$ and comes from state C_1 of the clean surface. One should note that this H_2 state was found only as a weak resonance at $\bar{X}$ in Ref. 20. Considering this discrepancy and the variety of results at $\bar{\Gamma}$ for the clean surface, we cannot exclude the contribution to the 6-eV structure of states formed by the In s orbital of the first layer and hydrogen adsorbed on In atoms (state H_3 of Ref. 19). The other peak, which grows around 4–4.5-eV binding energy, may arise from states formed by the P p dangling-bond orbital and hydrogen adsorbed on P atoms (state H_4 of Ref. 19), as well as from states coming from the In p dangling-bond orbital and hydrogen adsorbed on In (state H_5 of Ref. 19). By comparing the surface-state energy positions of the clean relaxed GaAs(110) surface[14] to those of the H-covered unrelaxed surface,[19] it appears that H lowers the states to which it binds. This tendency is extended to InP and outlined in Fig. 6.

(iii) The region around 10 eV below E_{VS} corresponds to the top of the "lower" valence band appearing below the heteropolar gap. On the clean surface, all calculations there give an anion-derived s-like state localized on the surface plane (A_2). The main effect of H is to shift the observed structure in the EDC to slightly larger binding energy (Fig. 3). It agrees with the results of Manghi et al.,[19] which yield a hydrogen-induced state (H_1) arising from a combination of the hydrogen orbital with the anion s-like state of the surface layer. This H_1 state is deeper in the valence band than the clean surface A_2 state from which it is issued (Fig. 6). Thus, the observed changes in the VB spectra (removal of states around 9 eV, appearance of states around 10.5 eV, Fig. 4, curves b and
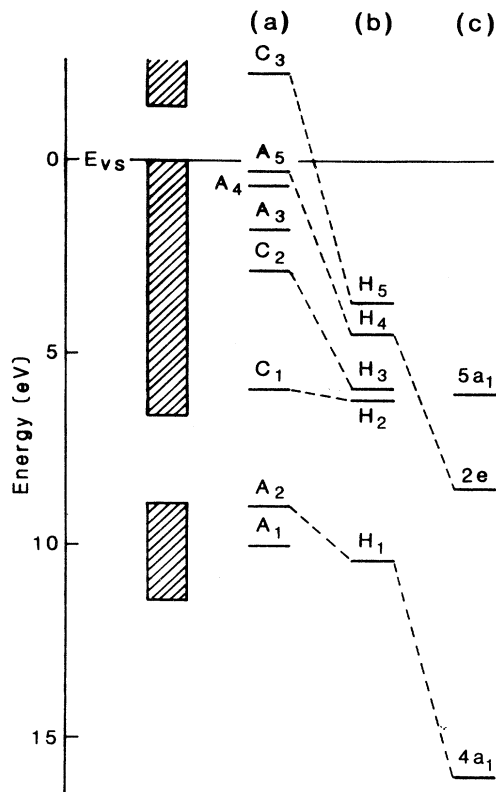
FIG. 6. Possible evolution of the electronic states at InP(110) in going from (a) the clean relaxed surface (according to Ref. 12 at $\bar{\Gamma}$) to (b) the H-adsorbed situation [by analogy with the H/GaAs system (Ref. 19)], and (c) to adsorbed P-hydrogenated radicals such as PH_2 (the reported energy levels are those of PH_3). The shaded bars correspond to the projected bulk states at $\bar{\Gamma}$. Energies are referred to the valence-band maximum.

c) are consistent with the bonding of H to P.

In summary, after 2×10^3 L H_2, the changes observed in the valence-band spectra of InP(110) seem to arise from the bonding of H to both substrate atoms with clearer evidence for bonding to P. This is in apparent contradiction with the interaction scheme proposed.[1] According to it, the initial adsorption state saturates with one H atom per surface unit cell, H binding covalently to the substrate. It is thus tempting to assume that H binds to one kind of atom only identified as In from high-resolution electron-energy-loss spectroscopy[24] and photoemission measurements[25] at low hydrogen doses. The present results do not necessarily contradict this simple scheme. After exposure to 2×10^3 L H_2, the InP surface may not be characteristic of the adsorption stage alone. Indeed, there is evidence from the In $4d$ spectra[4] for the presence of small In clusters after this dose, indicating that the dissociation has already begun, at least at some points of the surface, such as cleavage defects. The disorder associated with this situation may explain the relative increase of the background signal and a possible smearing of the structures after exposure to H. On the other hand, the first interaction stage may in fact be much more com-

plex than suggested here since the evolutions observed after 2×10^3 L of hydrogen have been seen also after 5×10^2 L. Even though there is an initial bonding of H to In, a bonding to P might occur before the dissociation stage. Also, some penetration of H into the substrate cannot be completely excluded.[4]

The question arises as to the nature of the H-induced band of states observed in PYS.[1] It is centered at about 0.06 eV below E_{VS} and saturates with a H coverage of 0.5 monolayer. We suggest that its tail in the gap is responsible for the emission observed up to E_F in the present experiments at this stage of the interaction (curves 2 of Fig. 3). From their position in the valence band close to E_{VS}, these states cannot be related to any of the surface states localized on H, as reported by Manghi *et al.*[19] for GaAs(110), when the substrate is in the ideal unrelaxed configuration. One possibility is that they might come from the H-induced modification of an anion-derived surface resonance having mainly p-like character in the plane of the surface, and which is localized in the first layer (A_6 of Ref. 14) or in the second layer (A_6 of Refs. 10 and 11; A'_2 of Refs. 12 and 16). Such states appear on both the clean and the chemisorbed surfaces[19,12] with, very likely, a different energy position in the latter case as compared to the former. PYS where photons strike the sample surface at normal incidence may be more sensitive to such states than angle-resolved UPS.

B. After 6×10^5 L of hydrogen

At very high exposures, the peak at about 6 eV below E_{VS} is the dominant feature of the valence-band spectra (Fig. 3, curves 4), the contribution around 10.5 eV has decreased, while a contribution has appeared around 8 eV in the heteropolar gap (Fig. 4, curves d and e). Similar evolutions have been observed with GaAs(110)+H,[23,26] for which system, upon high H doses, a strong attenuation around 11 eV, the enhancement of a peak at 5.5 eV, and the growth of an additional feature at 8.5 eV in the heteropolar gap have been reported. These observations have been interpreted as evidence for the removal of As from the surface, for the presence of an increased amount of H adsorbed on Ga sites, and for the existence of a localized H-induced state characteristic of an As-depleted surface, respectively. Such explanations can be transposed to the InP(110)+H system.

A peak in the heteropolar gap of GaAs, at 7.7 eV below E_{VS}, together with a feature at 5 eV, have been observed also when an As-stabilized GaAs(100) surface has been exposed to hydrogen multipolar plasmas.[27] These results have been compared to local densities of states[28] calculated in a tight-binding approximation on ideal Ga- or As-terminated (100) surfaces, the dangling bonds of which have been saturated by hydrogen thus forming dihydride surfaces. The peak at 7.7 eV would correspond to a state localized on Ga in the Ga-H chemisorption, whereas the 5-eV structure would arise from As—H bondinglike states. In the latter case, the As s-like states are shifted to 13 eV below E_{VS}. If these results are more representative of the presence of dihydrides than of the (100) face, they lead to a slightly different interpretation

than above.

We propose an alternative interpretation, which is not exclusive of the previous ones, and which agrees with the two-step process of H interaction with InP(110),[1,2] in particular with the dissociation stage that has now been reached. Metallic indium has formed together with P-hydrogenated species having a degree of hydrogenation larger than 1 (P_xH_y with $y/x > 1$). These species, which may predominantly be PH_2 radicals, are expected to display a much more molecularlike behavior than the surface P—H bonds involved at the adsorption stage. They would be responsible for the unusually strong quenching of the PYS signal referred to as the "black-hole" phenomenon in PYS.[2,29] They must also contribute to the photoemission signal and their molecularlike electronic levels should compare to those of phosphine PH_3, which are known.[30–33] We suggest that the dominant feature at 6 eV below E_{VS} is characteristic of such P-hydrogenated radicals. This leads to an ionization energy of 11.07 eV since the Fermi level is 0.9 eV above E_{VS} and the work function is 4.17 eV. This ionization energy is close to that of PH_3, which is 10.6 eV.[30–32] For comparison, the electronic levels of PH_3 have been reported in Fig. 6. Their energy positions may explain all the observed evolutions of the valence-band spectra at this stage of the interaction. The coincidence between the contribution of the P-hydrogenated radicals and the adsorbed H contribution at 6 eV would explain why this structure is strongly dominant in the spectra obtained after high hydrogen exposure.

V. CONCLUSION

The evolutions of the valence-band spectra of cleaved InP(110) upon interaction with atomic hydrogen are compatible with the two-step process proposed previously.[1,2] The present results confirm that H forms covalent bonds with the substrate during the adsorption stage. This induces (i) a removal of the P-associated p-like surface states of the clean surface located near the valence-band edge, (ii) the growth of two structures around 4.5 and 6 eV below the valence-band maximum, and (iii) a removal of the P-associated s-like surface states of the clean surface located below the heteropolar gap. These changes, characteristic of the adsorption stage, have been interpreted as arising from the bonding of H to P and to In. However, this bonding of H to both P and In, the observation that at low doses H binds to In only,[24,25] and the fact that the adsorption stage appears to saturate around half a monolayer of H atoms (one atom per surface unit cell)[1] indicate that the first interaction stage is more complex than a mere adsorption on the substrate. This complexity arises also from the In $4d$ spectra.[4] We think more investigations, both experimental and theoretical, are necessary to better understand the initial interactions of H with cleaved InP.

The dissociation of the substrate upon heavy hydrogenation with the formation of metallic indium is also supported by the present study. Furthermore, the evolutions of the spectra with a predominant structure around 6 eV, an increased emission around 8 eV in the heteropolar gap, and a decrease of the peak around 10 eV below the valence-band edge appear compatible with the presence of an adsorbed overlayer of P-hydrogenated species. We tentatively identify the "6-eV" feature with the highest occupied electronic state of the adsorbed species in its ground state. However, direct evidence for the presence of such P-hydrogenated species remains to be given.

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