PHYSICAL REVIEW B VOLUME 42, NUMBER 6 15 AUGUST 1990-II

Strong chemical reactivity at the early stages of Yb overgrowth on GaP(110): A synchrotron-radiation study

Lamberto Duò
Surface Science Research Centre, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, United Kingdom

Massimo Sancrotti
Istituto di Fisica, Politecnico di Milano, piazza Leonardo da Vinci 32, I-20133 Milano, Italy

R. Cosso,* S. D'Addato, A. Ruocco, and S. Nannarone
Dipartimento di Fisica, Università degli Studi di Roma, La Sapienza, piazza Aldo Moro 2, I-00185 Roma, Italy

D. Norman
Daresbury Laboratory, Science and Engineering Research Council, WA4 4AD Warrington, United Kingdom

P. Weightman
Surface Science Research Centre, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, United Kingdom

(Received 20 February 1990; revised manuscript received 27 April 1990)

The GaP(110)/Yb interface was studied with use of synchrotron radiation to excite the Ga 3*d* and the P 2*p* semiconductor core levels, the quasiatomic Yb 4*f* states together with the valence-band region, and the P $L_{2,3}VV$ Auger line shape in Yb coverages ranging from 0.2 to 5 monolayers. Strong reactivity was found at the interface region with semiconductor surface disruption and the formation of intermixed Yb-Ga-P products distributed on the substrate surface from the lowest coverage range investigated up to about 1 monolayer. Ga surface segregation with Yb-Ga alloying and Yb phosphide-like product trapping at the interface are dominant in the highest coverage range, resulting in a strong gradient concentration of the substrate chemical species, along a direction normal to the semiconductor surface. The reacted contributions in the Ga 3*d*, the P 2*p*, and the Yb 4*f* levels suggest a highly heterogeneous character of the growing interface with the presence of a multiplicity of atomic sites for each of the reacted atoms. Primarily divalent character of Yb atoms was found over all the coverage range investigated, as derived by Yb 4*f* spectroscopy. From the changes shown by the P $L_{2,3}VV$ line shape it was possible to model the evolution of the local density of states in Yb—P bonds in terms of Yb 5*d*- and P 3*p*-derived states mixing. The results are compared with the growth mechanisms of other III-V-semiconductor–rare-earth-metal interfaces.

INTRODUCTION

In recent years the overgrowth of rare-earth (RE) metals on semiconductors has attracted increasing attention.[1]

The growing interest in these systems may be interpreted first as an extension of the long-standing problem of semiconductor-metal interfaces.[2,3] The second reason may be found in some specific properties of these systems, such as their very low Schottky-barrier heights, which make them particularly appealing for electronic-device technology.

Another good motivation for this kind of research resides in the fundamental aspects of RE 4*f* electronic states in solids as mixed-valence, Kondo-like behavior and bulk-to-surface valence transitions.[4]

However, few cases of RE-semiconductor interfaces have been reported so far and these are confined to a very restricted set of RE's species grown on top of Si,[1] Ge,[5] GaAs,[6-10] InP,[11,12] InSb,[12] and CdTe.[12] More explicitly the formation of GaP-RE interface systems has not yet been reported in the literature to our knowledge.[13]

On the other hand, recent investigations on GaP-metal interfaces[14,15] seem to show a still open controversy as far as the behavior of their Schottky-barrier heights is concerned, calling therefore for a wider study of GaP-metal contacts.

This work reports the first experimental study of the GaP(110)/Yb interface, performed at room temperature. The early stages of the interface formation were studied via core-level photoemission tuned in a high-surface sensitive mode, allowed by the unique tunability of synchrotron radiation. We have followed, in the coverages ranging from 0.2 to 5 monolayers, the evolution of the Ga 3*d* and the P 2*p* semiconductor core levels and the quasiatomic Yb 4*f* states. Photoemission measurements were combined with the P $L_{2,3}VV$ Auger line shape to give a deeper understanding of the valence states redistribution versus coverage. Our main goal is to focus on the chemical characterization of the growing interface, with particular attention to the electronic states modifications experienced versus coverage, by the atomic species. Two regimes of strong chemical reactivity can be singled out as a function of Yb coverages. In the submonolayer range the Ga and P dislodged atoms tend to alloy with deposited Yb in binary and/or ternary forms with uniform average composition, whereas the higher coverages explored show the presence of a concentration gradient resulting in a pronounced tendency to anion trapping at the interface with formation of Yb phosphide-like compounds and cation segregation with consequent Yb-Ga alloying. Yb atoms appear in a basically divalent configuration. P 3*p*- and Yb 5*d*-derived orbitals hybridization is the basis of Yb—P bonding, as derived from the P $L_{2,3}VV$ Auger data analysis.

EXPERIMENTAL

Lightly doped *n*-type GaP bars ($E_g=2.26$ eV; $n=3\times10^{16}$ cm^{-3}) were cleaved *in situ*, with the standard knife-anvil technique, to produce mirrorlike (110) faces. The base pressure during the measurements was lower than 6×10^{-11} mbar. High-purity Yb metal was evaporated with a pressure lower than 7×10^{-10} mbar. Evaporation rates of about 0.5 Å/min were monitored with a quartz microbalance. The coverages are presented in monolayers (ML), where 1 ML is defined as one adatom per substrate surface atom (1 ML$=9.52\times10^{14}$ atoms/cm^2$=3.92$ Å).

All the measurements were performed at the Synchrotron Radiation Source in Daresbury (United Kingdom) on the beam line 6.1.[16]

The photon energy used was $h\nu=80$ eV for Ga 3*d* and 160 eV for P 2*p*, producing photoemitted electrons with kinetic energies (KE's) of about 55 and 25 eV, respectively.

The overall instrumental resolution, in terms of full width at half maximum (FWHM), was 0.42 eV at $h\nu=80$ eV (Ga 3*d* and Yb 4*f*), 0.73 eV at $h\nu=160$ eV (P 2p), and 0.5 eV for the Auger measurements.

Each coverage studied is a result of a Yb evaporation on a freshly cleaved surface. Soon after each evaporation and immediately before a new cleavage, the trivalent-to-divalent signal intensity ratio of the Yb 4*f* levels was derived, at $h\nu=80$ eV and $h\nu=181.5$ eV (Yb $4d\rightarrow4f$ resonance[17]). In both cases, for every coverage the trivalent signal was confined to a tiny fraction of the divalent emission.

RESULTS

In Figs. 1 and 2 the Ga 3*d* and the P 2*p* core-level spectra are respectively shown, at different Yb coverages, after a linear background subtraction and intensity normalization to their maximum height. We have performed a line-shape analysis of the Ga 3*d* and the P 2*p* core-level emission using spin-orbit split doublets corresponding to surface, bulk, and reacted contributions. The optimized parameters found for the as-cleaved GaP(110) surface are given in Table I. They are in excellent agreement with previous results reported in the literature.[15,18,19] In addition to the experimental data (dotted) in Figs. 1 and 2, the total fit (solid line), together with the surface (*S*) and bulk (*B*) emissions, when detectable, are given. The remaining part of the fit is presented as "reacted" *R*. Since both the surface and the reacted

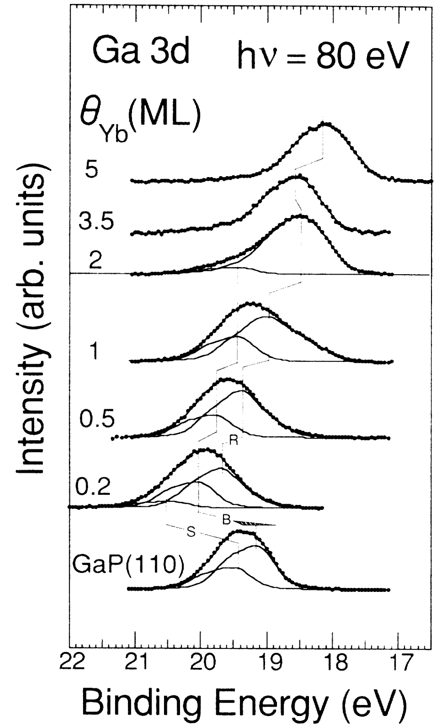

FIG. 1. Ga 3*d* ($h\nu=80$ eV) intensity normalized and linear background subtracted spectra (dots) as a function of Yb thickness. The solid line is the total least-squares fit; bulk, *B*; surface, *S*; and reacted contributions are also indicated. For the position range of the as-cleaved GaP(110) spectrum see text.

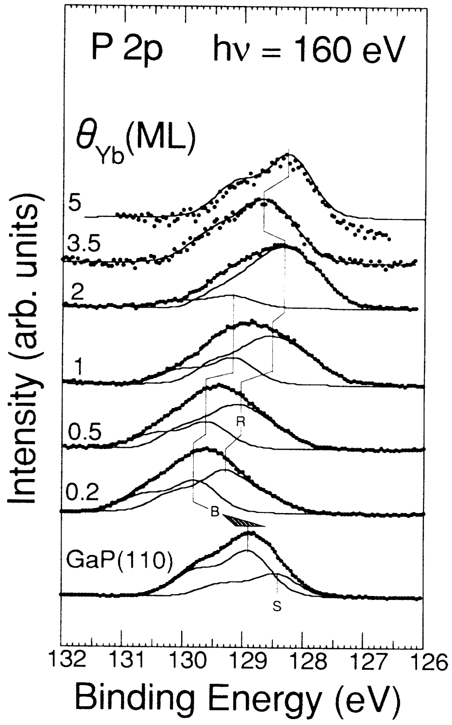

FIG. 2. P 2*p* ($h\nu=160$ eV) spectra (all as indicated in caption of Fig. 1).

TABLE I. The values of the Lorentzian linewidth (full width at half maximum), the Gaussian linewidth, the spin-orbit (s.o.) splitting, the surface-to-bulk (SB) core-level binding-energy shift, the spin-orbit branching ratio, and the surface-to-bulk intensity ratio determined by a least-squares optimization for the Ga 3*d* and the P 2*p* core levels on as-cleaved GaP(110), as shown in Figs. 1 and 2, respectively.

	ΔE_L/eV	ΔE_G/eV	$\Delta E_{\mathrm{s.o}}$/eV	ΔE_{SB}/eV	$R_{\mathrm{s.o}}$	R_{SB}
Ga 3*d*	0.17	0.42	0.45	+0.38	1.53	0.49
P 2*p*	0.185	0.73	0.88	−0.46	1.85	0.48

components of the P 2*p* core level fall within the same energy range, they are shown together. Most probable, however, the signal from the surface is strongly damped just from the very early stage of the interface formation as it is clear from the Ga 3*d* analysis. Therefore we can consider this mixed contribution as primarily reacted, even from the lowest coverage analyzed.

For the as-cleaved samples, the Fermi-level (FL) position inside the gap was not reproducible, in different cleaves,[19,20] and varied from about 0.9 to 1.4 eV above the valence-band maximum. Those spectra, shown in Figs. 1 and 2, obtained from a clean surface, have therefore to be considered just as a possible case, being in Figs. 1 and 2 indicated the extreme situations found during the experiment (for a total of 8 cleaves). Nevertheless, as soon as some Yb atoms are evaporated onto the GaP surface, the KE's of the spectra become independent of the initial band bending and are therefore well reproducible in different cleaves, already from the lowest coverage explored here, similarly to the case of Tm overlayers onto *n*- and *p*-type GaAs.[10]

In Fig. 3(a) the attenuation curves of bulk and surface components for both Ga 3*d* and P 2*p* core levels are given, as obtained from Figs. 1 and 2. Their intensity $I(\Theta)$ has been normalized, for each coverage, to the corresponding bulk and surface signal $I(0)$ of the as-cleaved GaP measured before the Yb depositions. With the same procedure, in Fig. 3(b), the intensities of the total and the reacted contribution $I(\Theta)$ are normalized to the total core-level area $I(0)$ of the as-cleaved GaP.

Spectra of the so-called valence-band (VB) region, taken at photon energy of 80 eV are shown in Fig. 4. Divalent character of the deposited Yb atoms, variously involved in different chemical interactions, is dominantly found. In fact, the spectra display strong Yb 4*f* emission lying near the FL and corresponding to divalent contributions with $4f^{13}$ final-state configurations, whereas the intensity in the trivalent region of the Yb 4*f* states from about 4 to 14 eV below the FL, as due to $4f^{12}$ final-state multiplets, is negligible. Metallic Yb is shown as a reference. Its 4*f* emission is totally divalent and the feature at 4–6 eV below the FL is due to plasmon losses.

Higher-resolution Yb $4f^{2+}$ measurements were also performed: the experimental spectra (dotted), after an intensity normalization and an integral background subtraction, are shown in Fig. 5 ($h\nu$=80 eV) together with the total fitting obtained (overlapped solid line). In the

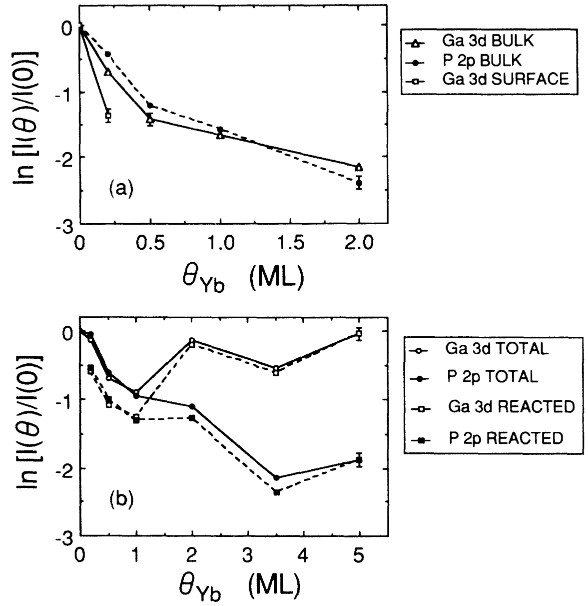

FIG. 3. Ga 3*d* ($h\nu$=80 eV) and P 2*p* ($h\nu$=160 eV) core-level attenuation curves as obtained from the fittings shown in Figs. 1 and 2, respectively; (a) bulk and surface contributions $I(\Theta)$ normalized to the corresponding as-cleaved GaP(110) emission $I(0)$; (b) total and reacted contributions $I(\Theta)$ normalized to the as-cleaved GaP(110) total emission $I(0)$.

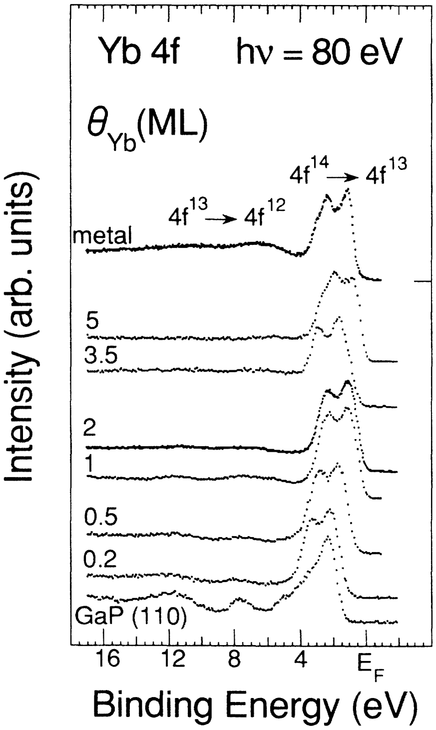

FIG. 4. Valence-band intensity normalized spectra ($h\nu$=80 eV) for the GaP(110)/Yb interface as a function of Yb coverage. The divalent ($4f^{14}\rightarrow 4f^{13}$) and the trivalent ($4f^{13}\rightarrow 4f^{12}$) emission regions are shown.

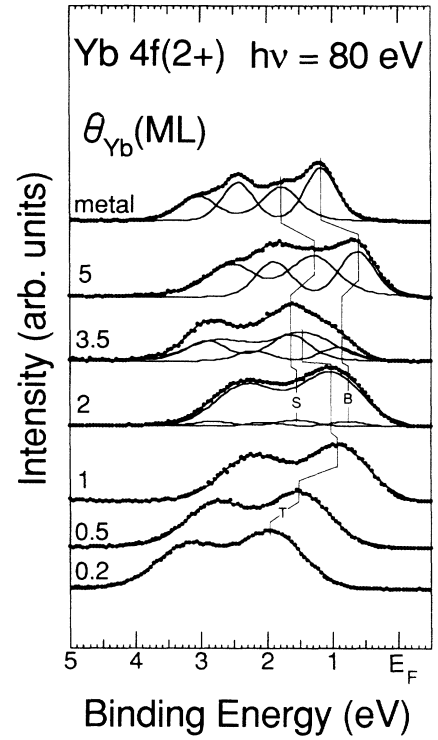

FIG. 5. Yb $4f^{2+}$ intensity normalized and integral background subtracted spectra (dots) with $h\nu=80$ eV. The overlapped solid line is the total line-shape (LS) fit. The intermixed Yb-Ga-P (T), the surface Yb-Ga (S), and the bulk Yb-Ga (B) compounds are also indicated. The metallic Yb is shown as a reference.

submonolayer coverage range the spectra have similar shape and are well fitted with a single broad doublet with spin-orbit splitting of 1.27±0.02 eV (indicated as T in Fig. 5). From 2 ML up to the highest coverage, two other doublets have to be considered in the fitting, narrower than the previous one and with the same spin-orbit splitting. The metallic Yb 4f fitting gave good agreement with the parameter values already reported in the literature.[21]

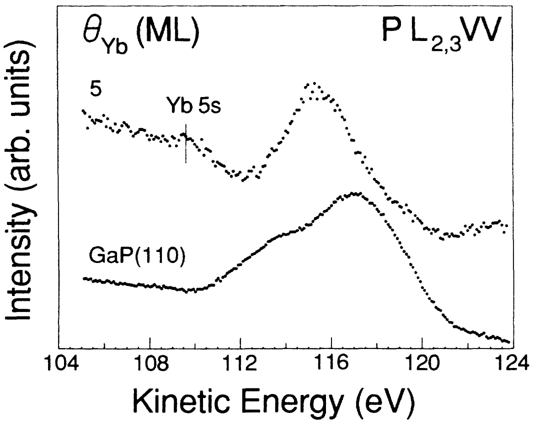

FIG. 6. Intensity normalized photon excited P $L_{2,3}VV$ Auger line shapes (displayed in the integral mode) for the as-cleaved GaP and for the interface with $\Theta=5$ ML Yb, taken at $h\nu=165$ eV. At 5 ML the Yb 5s peak is present.

Finally, Fig. 6 shows the two intensity normalized spectra of the photon excited P $L_{2,3}VV$ Auger line shape for the as-cleaved GaP surface and for the interface with 5 ML of Yb, taken with $h\nu=165$ eV. A quantitative and more detailed analysis of the GaP/Yb P $L_{2,3}VV$ Auger line at different Yb coverages, on the basis of recently published electron-excited experiments addressing the Si $L_{2,3}VV$ Auger line in Si-RE intermixed systems,[22-25] will be reported elsewhere.[26]

DISCUSSION

The great changes exhibited by the Ga 3d and P 2p core-level spectra, as displayed in Figs. 1 and 2 give rise to a series of observations.

(i) At 0.2 ML there is a strong intensity attenuation of the surface with respect to the bulk component of the Ga 3d signal. This clearly points toward a surface disruption occurring over an extended substrate area, thus confining metal clustering, if any, to minor levels. In this coverage range the growth mode can therefore be regarded as basically two-dimensional. Moreover, 0.2 ML of Yb onto GaP causes the appearance of a reacted emission on the low-binding-energy (BE) side for both of the core lines, suggesting a removal of Ga and P atoms from their pristine locations. These reacted components cannot be simply interpreted in terms of a single spin-orbit split doublet, suggesting a multiplicity of atomic sites for the dislodged atoms and a complex heterogeneous character for the morphology of the grown interface already occurring from the lowest coverage.

(ii) An increase of Yb deposition confirms the tendency toward a strong disruption, with a progressive reinforcement of the reacted Ga 3d and P 2p components relative to the emission coming from the unperturbed substrate atoms. Furthermore, the line-shape evolutions induced in the two core lines show an initial broadening (at 0.5–1 ML) and subsequently tend toward a progressive narrowing, especially for P 2p.

(iii) At 5 ML the P 2p line is fitted with a single doublet thus indicating a rather uniform chemical environment around the P sites.

(iv) All these points indicate the presence of strong concentration gradients, along a direction normal to the surface, for the chemical species involved in the interface formation, as in the case of other III-V-compounds–Yb interfaces.[6,10,11]

(v) The decreasing trend of the Ga 3d and P 2p bulk attenuation curves [Fig. 3(a)] can be approximated by two 1/e decays with different attenuation lengths: 1.5 Å up to 0.5 ML, and 5–6 Å in the range 0.5 up to 2 ML. In the first region this value is clearly much smaller than the photoelectron ED (≈5.6 Å, see results) suggesting that at the very early stages of the interface growth a strong modification of the chemical environment takes place for semiconductor atoms at the surface with consequent conversion into reacted forms. At higher Yb thicknesses, the similarity between the 1/e length and the ED indicates instead that saturation of the surface disruption has been reached.

(vi) In the submonolayer range, the Ga 3*d* and P 2*p* reacted and total components [Fig. 3(b)] attenuate with a similar rate versus coverage indicating a uniform average spatial distribution for the reacted atoms. This could correspond to the formation of a ternary, even though nonstoichiometric, Yb-Ga-P compound, or to more complicated morphologies with a variety of chemically nonequivalent small islands.

(vii) In contrast, from 1 ML on, the attenuation curves clearly indicate a sort of discontinuity: the Ga 3*d* decreasing trend is inverted, while the P 2*p* maintains monotonic. These results suggest the existence of two chemically and spatially distinct pseudophases: a Yb phosphide-like compound trapped at the interface and Yb-Ga alloyed forms on top of it, due to the segregation of Ga atoms diluted in the Yb overlayer.

(viii) The continuous BE shifts of the reacted Ga 3*d* at increasing coverages are related to differing local coordinations for Ga atoms. The final position of this peak ($\mathrm{BE} \approx 18.1$ eV at 5 ML) seems to rule out the possibility of purely elemental character for the segregated Ga. The 3d BE of metallic Ga is, in fact, about 18.4–18.7 eV as quoted in Ref. 27, thus suggesting a Yb coordination for the Ga atoms.

(ix) The line-shape evolution of the reacted P 2*p* and the trend of the attenuation curves, coherently with indications emerging from the Yb 4*f* and P $L_{2,3}VV$ analysis (see below), suggest the presence of a nonstoichiometric Yb-P intermixed system characterized by a pronounced gradient in its average composition in a direction normal to the sample surface.

The analysis of the Yb 4*f* levels in their divalent region (Fig. 5) shows a shift, of about 1 eV, toward the FL, in the coverage range 0.2–1 ML, without significant line-shape changes. A fraction of this shift (≈ 0.6 eV) can be associated with band-bending effects (see Figs. 1 and 2) due to the semiconductor-overlayer interactions, considering the nonmetallic character of the system in this coverage range. The remaining part of the 4*f* movements has a chemical origin and indicates an increased Yb local coordination. Consistently with the evolution of the reacted Ga 3*d* and P 2*p* core-level signals and the P $L_{2,3}VV$ line shape, the large doublet which fits the Yb 4*f* line shape between 0.2 and 1 ML could imply chemical alloying between Yb and both Ga and P atoms in a variety of Yb-Ga and Yb-P combinations. In this respect we found strong similarities with previously reported results on other III-V-semiconductor–Yb interfaces,[6,10,11] at variance with the overgrowth of Yb on elemental semiconductors[1,5,25] where the Yb 4*f* line shape in the submonolayer range points toward a very weak interaction of deposited atoms with the substrate. At higher Yb thicknesses (from 2 ML up) three Yb doublets are singled out in the Yb 4*f* analysis . Taking into account the pronounced tendency of reacted P atoms to be trapped nearby the GaP substrate and the general trend displayed by Ga atoms to efficiently segregate to the topmost interface layers, these 4*f* components are assigned as follows:

(a) Progressively buried Yb-Ga-P products with strong decreasing intensity relative to the total 4*f* area versus coverage (indicated as *T* in Fig. 5). Coherently with the Ga 3*d* and P 2*p* core line behavior in the same coverage range this doublet suggests the formation of an intermixed variously bonded Yb—Ga—P system.

(b) Segregated contributions of Yb-Ga alloyed systems. Considering the Yb thicknesses involved at these stages of the interface growth it is reasonable to expect both surfacelike (*S* in Fig. 5) and bulklike (*B* in Fig. 5) emissions. In particular at 3.5 and 5 ML, the relative intensities of these Yb components indicate the tendency toward a more bulklike situation with metallic asymptotic behavior for Yb atoms. The slight but monotonic decreasing versus coverage of the surface-to-bulk energy shift of the two components from 0.79 eV at 2 ML to 0.61 eV for the pure metal (passing through 0.73 eV at 3.5 ML and 0.66 eV at 5 ML) suggests an increasing dilution of Ga atoms into the deposited Yb in the highest coverages.

The generally recognized bandlike nature of the P $L_{2,3}VV$ Auger feature, allows us to follow the evolution of the P 3(*sp*) derived valence electron states projected onto the P sites.[28] The information derived from the P Auger line shape is important even because the strong Yb 4*f* emission in the VB region rules out the possibility of directly measuring the valence states by photoemission. The P $L_{2,3}VV$ Auger spectra show an increased loss of asymmetry and a progressive and parallel narrowing of the total line shape moving from the clean substrate up to the highest Yb thicknesses (Fig. 6). On the basis of the strong similarities emerging when comparing these trends with those observed in the case of the Si(111)/Yb interface,[22,25] we are led to interpret the spectra in terms of an increasing sampling, within the low-depth sensitivity of the Auger electrons ($\mathrm{KE} \approx 115$ eV), of P atoms chemically bonded with a sizeable amount of deposited Yb atoms.[26,13] Further exploitation of the GaP-Yb versus Si-Yb analogies allows us to model out the chemical bond resulting in the Yb-rich phosphides as a mixing effect between the Yb 5*d*- and the P 3*p*-derived states. These conclusions are in agreement with recent electron state calculations performed for stoichiometric YbP.[29]

The results obtained from the Yb 4*f* spectra are in close analogy with other III-V-semiconductor–Yb interface studies,[6,10,11] and particularly show a qualitative similar shift, at low coverages, of the photoemission structures toward the FL. The same trend in the energy position of the 4*f* levels can be seen in the Si/Yb (Refs. 1 and 25) and Si/Eu (Ref. 30) interfaces in which the RE species mostly show divalent character. On the other hand they are in opposite directions to other reported GaAs/RE interfaces[8–10] with more pronounced trivalent character of the RE involved. On the basis of a thermochemical approach,[31] Prietsch *et al.*[10] pointed out the valency dependence of the involved RE atoms shown by these two different trends in GaAs interfaces. In particular for divalent Yb atoms on GaAs they estimated a shift 0.9 eV to lower BE, with respect to the value of the elemental metal, very similar to the shifts we measured of about 1 eV. All of these similarities seem to suggest a sort of common description, even from a thermodynamical point of view, of the reactivity processes occurring at the GaAs/Yb and GaP/Yb interfaces.

The divalent $4f$ shift of Yb atoms toward the FL reaches its shallowest position at 5 ML, with the $4f_{7/2}$ derived peak at about 0.6 eV below FL. This suggests the presence of a precursor condition toward valence-fluctuation phenomena. A tiny amount of trivalent emission is detected at about 1 ML (Fig. 4). Most probably this has to be ascribed to a fraction of Yb atoms in stable trivalent configuration. On the other hand, the almost complete bulk trivalency of nearly stoichiometric YbP (Ref. 32) suggests the formation of Yb—P bonds. Subsequent Yb deposition would then tend to bury this trivalent pseudophase, resulting in a decreased Yb^{3+}/Yb^{2+} emission ratio.

Recent photoemission studies on reactive GaP–transition-metal interfaces[19] seem to indicate that once the semiconductor surface disruption initiates, due to the metallic-overlayer dislodging effects, the behavior of Ga and P atoms released from the sample surface are the same independent of the particular semiconductor substrate. The general conclusions of Ref. 19 find a confirmation in our experimental results, after a comparison with GaAs/Yb and InP/Yb interface studies.[6,10,11] In particular, in both GaAs/Yb and GaP/Yb interfaces, the mechanisms responsible for the spatial separation, in a direction normal to the semiconductor surface, between anionic and cationic Yb pseudophases, are basically the favorable energetics of Ga segregation and the formation of Yb—P or Yb—As bonds acting as a diffusion barrier against further anionic outdiffusion. The InP/Yb case displays a more accentuated metallic character for segregated In atoms[11] consistent with a weaker In solubility and a weaker tendency to form bonds compared with Ga. Similar results can be found comparing other transition-metal reactive interfaces involving GaP, GaAs, and InP [e.g., the case of Ti (Refs. 19, 33, and 34)], with the only substantial difference that, in the InP/Yb case, In segregation seems to be much weaker.[11] As a consequence, in the case of InP/Yb there are no evidences of the abovementioned spatial separation between Yb-In and Yb-P compounds. From this point of view a unified interpretation of RE interfaces onto III-V semiconductors appears to be more difficult than in the case of transition metals,[19] and a more systematic study of these systems is desirable.

CONCLUSIONS

Strong chemical reactivity is found at the early stages of formation of the GaP(110)/Yb interface. Disruption and outdiffusion of P and Ga atoms are already active in the submonolayer range, with the appearance of reacted Yb-Ga-P pseudophases. At higher coverages, surface segregation of Ga results to be steadily efficient, while P atoms chemically reacted to form Yb phosphide-like products are preferentially trapped in a thin layer, subsequently buried by Ga ions diluted in the Yb overlayer. The differing behaviors of Ga and P result in a spatial separation between Yb-Ga and Yb-P compounds in a direction normal to the GaP surface. The Yb atoms have basically divalent character with $4f^{14}$ configuration, with small trivalent contributions at about 1–2 ML, mainly attributed to Yb trivalency in the Yb phosophide-like compounds. Analysis of the P $L_{2,3}VV$ line shape suggests a mixing of the Yb $5d$- and P $3p$-derived states to be at the basis of the chemical bond in the Yb phosphide-like products. A comparison with other III-V-semiconductor–Yb interfaces shows strong similarities in the observed trends apart from the reacted character of cation segregation for Ga in the GaP/Yb and GaAs/Yb cases compared to the more metalliclike situation of the segregated In atoms in InP/Yb interface.

ACKNOWLEDGMENTS

The authors are pleased to acknowledge Paul Unsworth for his important contribution before and during the experiments. Special thanks are due to F. M. Quinn and D. S. L. Law for assistance at the SRS beamline. We are grateful to J. Hegarty of MCP company for preparing for GaP bars. M. Newell is also acknowledged. This work was partially supported by a twinning contract between the Physics Departments of Politecnico di Milano and the University of Rome and University of Liverpool, supported by the Science Programme of the European Community.

---

[*] Present address: Surface Science Research Centre, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, United Kingdom.

[1] See the following reviews: G. Rossi, Surf. Sci. Rep. 7, 1 (1987); L. Braicovich, in *The Chemical Physics of Solids Surfaces and Heterogeneous Catalysis*, edited by D. A. King and P. A. Woodruff (Elsevier, Amsterdam, 1988), Vol. 5.

[2] For an up to date book on these topics, see *Metallization and Metal—Semiconductor Interfaces*, Vol. 195 of *NATO Advanced Study Institute, Series B: Physics*, edited by I. P. Batra (Plenum, New York, 1989).

[3] For detailed discussions, see the following reviews: L. J. Brillson, in *Handbook on Synchrotron Radiation*, edited by G. V. Marr (North-Holland, Amsterdam, 1987), Vol. 2; R. Ludeke, *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis* (Ref. 1), p. 39; G. Margaritondo and A. Franciosi, Ann. Rev. Mater. Sci. **14**, 67 (1984); W. Moench, *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis* (Ref. 1), p. 11; W. E. Spicer, R. Cao, K. Miyano, C. McCants, T. T. Chiang, C. J. Spindt, N. Newman, T. Kendelewicz, and I. Lindau, *ibid.* (Ref. 1), p. 139; J. H. Weaver, in *Analysis and Characterization of Thin Films*, edited by K. N. Tu and R. Roseberg (Academic, New York, 1988); R. H. Williams, in *Physics and Chemistry of III-V Compound Semiconductor Interfaces*, edited by C. W. Wilmsen (Plenum, New York, 1985).

[4] See, for example, *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr., L. Eyring, and S. Huefner (North-Holland, Amsterdam, 1987), Vol. 10.

[5] J. Nogami, C. Carbone, D. J. Friedman, and I. Lindau, Phys. Rev. B **33**, 864 (1986).

[6] J. Nogami, M. D. Williams, T. Kendelewicz, I. Lindau, and W.

E. Spicer, J. Vac. Sci. Technol. A **4**, 808 (1986); M. D. Williams, J. Nogami, T. Kendelewicz, R. S. List, K. A. Bertness, I. Lindau, and W. E. Spicer, Solid State Commun. **58**, 15 (1986), and acknowledgments therein.

[7] J. H. Weaver, M. Grioni, J. J. Joyce, and M. del Giudice, Phys. Rev. B **31**, 5290 (1985); A. Fujimori, M. Grioni, J. J. Joyce, and J. H. Weaver, *ibid.* **31**, 8291 (1985).

[8] M. Grioni, J. J. Joyce, and J. H. Weaver, Phys. Rev. B **32**, 962 (1985).

[9] M. Prietsch, M. Domke, C. Laubschat, and G. Kaindl, Phys. Rev. Lett. **60**, 436 (1988).

[10] M. Prietsch, M. Domke, C. Laubschat, and G. Kaindl, Phys. Rev. B **38**, 10 655 (1988).

[11] P. De Padova, X. F. Jin, B. Carriere, R. Pinchaux, and G. Rossi, Surf. Sci. **211/212**, 675 (1989).

[12] B. M. Trafas, C. M. Aldao, C. Capasso, Y. Shapira, F. Boscherini, I. M. Vitomirov, and J. H. Weaver, Phys. Rev. B **40**, 9811 (1989).

[13] For a preliminary discussion of the GaP(110)/Yb interface, see Lamberto Duò, Massimo Sancrotti, M. Newell, P. Weightman, D. Norman, R. Cosso, S. D'Addato, A. Ruocco, and S. Nannarone, in Proceedings of the 7th International Conference on Solid Surfaces, Koeln, 1989 (Vacuum, in press).

[14] L. J. Brillson, R. E. Viturro, M. L. Slade, P. Chiaradia, D. Kilday, M. Kelly, and G. Margaritondo, Appl. Phys. Lett. **50**, 1379 (1987); P. Chiaradia, L. J. Brillson, M. Slade, R. E. Viturro, D. Kilday, N. Tache, M. Kelly, and G. Margaritondo, J. Vac. Sci. Technol. B **5**, 1075 (1987).

[15] K. E. Miyano, R. Cao, T. Kendelweicz, A. K. Wahi, I. Lindau, and W. E. Spicer, Phys. Rev. B **41**, 1076 (1990).

[16] M. R. Howells, D. Norman, G. P. Williams, and J. B. West, J. Phys. E **11**, 199 (1978), and references therein.

[17] L. I. Johansson, J. W. Allen, I. Lindau, M. H. Hecht, and S. B. M. Hagstrom, Phys. Rev. B **21**, 1408 (1980).

[18] A. B. McLean and R. Ludeke, Phys. Rev. B **39**, 6223 (1989).

[19] B. M. Trafas, F. Xu, M. Vos, C. M. Aldao, and J. H. Weaver, Phys. Rev. B **40**, 4022 (1989).

[20] P. Chiaradia, M. Fanfoni, P. Nataletti, P. De Padova, L. J. Brillson, M. L. Slade, R. E. Viturro, D. Kilday, and G. Margaritondo, Phys. Rev. B **39**, 5128 (1989).

[21] S. F. Alvarado, M. Campagna, and W. Gudat, J. Electron Spectrosc. **18**, 43 (1980); L. I. Johansson, A. Flodstrom, S. E. Hornstrom, B. Johansson, J. Barth, and F. Gerken, Solid State Commun. **41**, 427 (1982); W. D. Schneider, C. Laubschat, and B. Reihl, Phys. Rev. B **27**, 6538 (1983); M. H. Hecht, A. J. Viescas, I. Lindau, J. W. Allen, and L. I. Johansson, J. Electron Spectrosc. **34**, 343 (1984).

[22] M. Sancrotti, I. Abbati, A. Rizzi, L. Calliari, F. Marchetti, and O. Bisi, Surf. Sci. **189/190**, 300 (1987); M. Sancrotti, A. Rizzi, and F. Marchetti, Phys. Rev. B **37**, 3120 (1988).

[23] M. Sancrotti, E. Vescovo, L. Calliari, and F. Marchetti, in *Auger Spectroscopy and Electronic Structure,* Vol. 18 of *Springer Series in Surface Science,* edited by G. Cubiotti, G. Mondio, and K. Wandelt (Springer-Verlag, Berlin, 1989), p. 116; M. Sancrotti, A. Iandelli, G. L. Olcese, and A. Palenzona (unpublished).

[24] For a theoretical and experimental study on Ca silicides as prototypes of Yb-Si systems, see M. Sancrotti, I. Abbati, L. Calliari, F. Marchetti, O. Bisi, A. Iandelli, G. L. Olcese, and A. Palenzona, Phys. Rev. B **37**, 4805 (1988); L. Calliari, F. Marchetti, M. Sancrotti, O. Bisi, A. Iandelli, G. L. Olcese, and A. Palenzona, *ibid.* **41**, 7569 (1990).

[25] G. Rossi, J. Nogami, I. Lindau, L. Braicovich, I. Abbati, U. del Pennino, and S. Nannarone, J. Vac. Sci. Technol. A **1**, 781 (1983).

[26] M. Sancrotti and L. Duò *et al.* (unpublished).

[27] See, *Photoemission in Solids,* edited by M. Cardona and L. Ley (Springer-Verlag, Berlin, 1978), Vols. 1 and 2, Appendix, and Refs. 16 and 20 quoted therein.

[28] M. Sancrotti, F. Ciccacci, M. Fanfoni, P. Nataletti, and P. Chiaradia, Surf. Sci. **211/212**, 651 (1989); M. Sancrotti, F. Ciccacci, M. Fanfoni, and P. Chiaradia, in Proceedings of the 7th International Conference on Solid Surfaces, Koel, 1989 (Vaccum, in press).

[29] R. Monnier, L. Degiorgi, and D. D. Koelling, Phys. Rev. Lett. **56**, 2744 (1986).

[30] J. Nogami, C. Carbone, J. J. Yeh, I. Lindau, and S. Nannarone, in *Proceedings of the 17th International Conference on the Physics of Semiconductors,* edited by J. D. Chadi and W. A. Harrison (Springer-Verlag, New York, 1985), p. 201; G. Rossi, J. Nogami, I. Lindau, and J. J. Yeh, Surf. Sci. **152/153**, 1247 (1985).

[31] A. Fujimori, M. Grioni, and J. H. Weaver, Phys. Rev. B **33**, 726 (1986).

[32] L. Degiorgi, T. Greber, F. Hulliger, R. Monnier, L. Schlapbach, and B. T. Thole, Europhys. Lett. **4**, 755 (1987); T. Greber, L. Degiorig, R. Monnier, L. Schlapbach, F. Hulliger, and E. Kaldis, J. Phys. (Paris) Colloq. **48**, C9-943 (1987).

[33] R. Ludeke and G. Landgren, Phys. Rev. B **33**, 5526 (1986); M. W. Ruckman, M. del Giudice, J. J. Joyce, and J. H. Weaver, *ibid.* **33**, 2191 (1986).

[34] C. M. Aldao, I. M. Vitomirov, F. Xu, and J. H. Weaver, Phys. Rev. B **37**, 6019 (1988).