Differences between GaAs/GaInP and GaAs/AlInP interfaces grown by movpe revealed by depth profiling and angle-resolved X-ray photoelectron spectroscopies

M.C. López-Escalante , M. Gabás , I. García , E. Barrigón , I. Rey-Stolle , C. Algora , S. Palanco , J.R. Ramos-Barrado

ABSTRACT

GaAs/GaInP and GaAs/AlInP interfaces have been studied using photoelectron spectroscopy tools. The combination of depth profile through Ar⁺ sputtering and angle resolved X-ray photoelectron spectroscopy provides reliable information on the evolution of the interface chemistry. Measurement artifacts related to each particular technique can be ruled out on the basis of the results obtained with the other technique. GaAs/GaInP interface spreads out over a shorter length than GaAs/AlInP interface. The former could include the presence of the quaternary GaInAsP in addition to the nominal GaAs and GaInP layers. On the contrary, the GaAs/AlInP interface exhibits a higher degree of compound mixture. Namely, traces of P atoms in a chemical environment different to the usual AlInP coordination were found at the top of the GaAs/AlInP interface, as well as mixed phases like AlInP, GaInAsP or AlGaInAsP, located at the interface.

1. Introduction

III–V compound semiconductors are widely studied due to their applications as a fundamental part of a number of microelectronic, optoelectronic and photovoltaic devices. To achieve high quality and reliable devices, not only high quality materials must be obtained, but also abrupt interfaces between different layers must be produced through an exhaustive control of the chemical composition, thickness and inter-diffusions. The optimisation of these interfaces is a fundamental step for obtaining the maximum yield from a particular device [1,2]. The presence of mixed compounds, giving rise to spurious phases or a gradual transition at the interface, is undesirable because it can reduce the performance of optoelectronic devices [3].

In this work, two common III–V semiconductor interfaces have been analyzed, namely, GaAs/GaInP and GaAs/AlInP. Both heterostructures were grown by MOVPE (Metal Organic Vapour Phase Epitaxy) under the conditions described below. For this reason, both interfaces may share the same issues, such as the formation of

mixed phases or even quaternary and quinary compounds which reduce the abruptness of the interface. The reasons are related to the possibility of cation segregation and interdiffusion between the two adjacent layers and with As/P anion exchange during the formation of the layers. Several GaAs/GaInP and GaInP/GaAs interface chemistry studies can be found in literature [4–8]. Most of them report the formation of GaInAs, GaAsP, or quaternary phases like GaInAsP, whose exact compositions and thicknesses would be strongly dependent on growth conditions. However, very scarce information has been found for the GaAs/AlInP interface [9–11] in spite of its interest due to its applications in high electron mobility transistors (HEMTs) [12], III–V metal-oxide-semiconductor field effect transistors (MOSFET) devices [13], III–V multijunction solar cells [14], etc.

MOVPE is not able to achieve as abrupt interfaces as Molecular Beam Epitaxy (MBE) does. Therefore, it is very interesting to have a procedure to estimate not only the approximate interface thickness but also the origin of gradients in composition at the interface, namely, inter-diffusions, phase separations, etc. Accordingly, the MOVPE samples prepared in this paper were not especially abrupt with the aim of testing the checking procedure. The analysis of III–V interfaces requires techniques which reduce as much as possible the possibility of chemical change in the studied region as

a consequence of the characterization process itself. Accordingly, X-Ray Photoelectron Spectroscopy (XPS) has been selected in this work as an analysis tool since XPS is a versatile technique with a high chemical sensitivity. Two different types of measurements have been carried out, namely, depth profile and angle-resolved XPS. The evolution of the III–V elements concentration and their chemical environments along the whole interfaces has been studied by quantitative depth profiling analysis. However, it must be kept in mind that this information is influenced by the ion bombardment that always produces damage in the solid surface. This damage may be categorised as either physical damage -related to the energetic ions that eventually may destroy the surface structure and produce a large number of defects in the surface- or chemical damage -because sputtering will alter the surface concentrations and chemical states in the surface of many compound materials [15–17]. Moreover, it is quite difficult to obtain reliable information on element segregation, or on the presence of mixed compounds, because they may have been induced by the ion bombardment. These non-desirable effects can be overcome if the interfaces are studied by angle resolved X-ray photoelectron spectroscopy (ARXPS). ARXPS offers the possibility to study compositional changes at different depth amplitudes from the surface, without ion bombardment and its negative consequences. In this case, the distribution of elements and chemical states within the film will be reliable and it would be possible to reach a conclusion about the presence of mixed compounds. However, due to the limited inelastic mean free path (IMFP) of the photoelectrons, ARXPS provides chemical information for ultra-thin layers, which limits its usefulness in the study of real devices.

In order to achieve a reliable picture of the GaAs/GaN and GaAs/AlInP interfaces, both techniques have been combined in this work. In this way, the disadvantages of Ar^+ sputtering for XPS depth profiling will be overcome by ARXPS. Two kinds of interfaces designated as “thin” and “thick” were grown (see details in the EXPERIMENTAL Section). Identical heterostructures of GaAs/GaN and GaAs/AlInP in terms of switching conditions were prepared. The buried interfaces in the thick heterostructures were explored by doing an XPS depth profile analysis where subsequent stages of Ar^+ bombardment progressively revealed the chemistry of the layers along the explored thickness. The GaAs layer is only 5 nm thick in the thin heterostructures. Therefore, the surface-interface distance is on the order of the explored depth using the more energetic outgassing photoelectrons, i.e. those photoelectrons coming from low binding energy core levels. The “thick” interfaces correspond to the structures found in actual III–V multijunction solar cells while the “thin” samples have been specifically designed to have an easier access to the interface. The combination of the information extracted from both types of experiments will allow us to accurately depict the interface chemistry for the GaAs/GaN and GaAs/AlInP interfaces.

2. Experimental

Samples were grown in a commercial horizontal Metal Organic Vapor Phase Epitaxy (MOVPE) reactor, namely, an AIX200/4 (manufactured by Aixtron of Herzogenrath, Germany). The precursors used were AsH_3 and PH_3 for group-V elements and TMGa, TMIIn and TMAI for group-III elements. Samples were grown at 50 mbar using 8 slpm of Pd-purified H_2 as the carrier gas. Growth temperature was 640 °C and growth rate was ~60 nm/min for GaAs and ~50 nm/min for both phosphides. All samples were grown on (100) GaAs substrates with a 2° miscut towards the nearest (1 1 1) plane. The switching between the phosphide and the arsenide was implemented using a growth stop of 10 s where only carrier gas (i.e. pure H_2) was present in the reactor chamber. GaInP and AlInP samples

were grown lattice matched to GaAs (i.e. $\text{GaInP} \sim \text{Ga}_{0.515}\text{In}_{0.485}\text{P}$ and $\text{AlInP} \sim \text{Al}_{0.525}\text{In}_{0.475}\text{P}$) with a lattice parameter adjustment better than 250 arcsecs.

The two heterostructures (GaAs/AlInP and GaAs/GaN) were prepared in two versions that will be named as thick and thin structures hereafter. The adjectives thick and thin refer to the thickness of the GaAs capping layer used. Therefore, thick structures have a top GaAs cap layer of 100 nm for the GaAs/GaN structure and 225 nm GaAs cap layer in the case of GaAs/AlInP device. All the ternary films were 850 nm thick. The two structures were grown on a 350 nm GaAs buffer to optimize the morphology. These thick structures were used for depth profiling XPS analysis. On the other hand, the thin structures have a very thin 5 nm top GaAs cap layer onto the GaInP or AlInP layer, which in this case, are 350 nm thick. These ternary layers were grown on a 350 nm GaAs buffer to optimize the morphology. These samples were designed for the ARXPS analysis of the GaAs/GaN and GaAs/AlInP interfaces.

XPS spectra were obtained using an X-ray photoelectron spectrometer (Physical Electronics, Inc., model PHI 5700) with a 300 W, Mg K α (1253.6 eV) excitation source, at a fixed voltage of 15 kV and the vacuum pressure reaches 10^{-9} Torr in the XPS analysis chamber. The spatial resolution and the spot size are defined by the analyzer aperture which is 720 μm in diameter. ARXPS data from the thin heterostructures were obtained at several angles of emission. Depth profiling analysis was accomplished in the thick heterostructures using Ar^+ ions at 4 kV and the vacuum pressure was kept at 10^{-7} Torr. Sputtering times were 2 and 1 minutes for the GaAs/GaN and GaAs/AlInP interfaces, respectively. No charge compensation was made after every sputtering stage, therefore, slight binding energy variations of the considered peaks in the core level analysis are expected to occur. Core level deconvolution in the several peak components has been made using the XPSPeak software package [18]. Shirley background subtractions have been applied to each analyzed core level and the peak line shapes are Gaussian–Lorentzian (70–30).

3. Results and discussion

In order to provide a general view of the evolution of the layer chemistry of the GaAs/GaN and GaAs/AlInP thick structures, their depth profiles were registered across the interfaces (Fig. 1). Since the layer composition was known due to the epitaxial character of the growing technique (MOVPE), no special attention was paid to the stoichiometry in these measurements and the data are presented in an arbitrary intensity scale. After each ion bombardment stage, several core levels were analyzed in order to monitor the element chemical environment along the structure.

3.1. CAP layer: GaAs

From left to right in the graphics in Fig. 1, the first layer is the outer one, which corresponds to GaAs in both cases, GaAs/GaN and GaAs/AlInP. In these layers, an As preferential sputtering which leads to a surface exposed Ga enrichment is observed [15,16]. Surface concentration variations due to the preferential sputtering and eventual surface structure modification are typical phenomena caused by the ion bombardment. The results of these effects can be observed in the uneven intensity profile of gallium and arsenic core levels [19].

The Ga 3d core level signal has a single contribution at a binding energy compatible with GaAs, 19.0 eV and 19.1 eV for the GaAs/GaN and the GaAs/AlInP samples, respectively (Fig. 2, left, top and bottom). The data shown correspond to an intermediate point of the GaAs layer in both heterostructures. In the Ga 2p $_{3/2}$ core level, there is a dominant contribution centered at 1116.9 eV and

Fig. 1. Depth profile of the thick heterostructures GaAs/GaInP (left) and GaAs/AlInP (right). Black squares: Ga; red circles: As; blue triangles: P; green triangles: In; cyan diamonds: Al. Solid lines are a guide to the eye. Vertical lines mark the interface region. Arrows mark the point where core level analysis was performed at the interface subsection. Note the time axis break in the GaAs layer. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

1116.7 eV for the GaAs/GaInP and the GaAs/AlInP layers, respectively (Fig. 2, right, top and bottom). There are two additional contributions due to the preferential As sputtering as a bombardment effect on the GaAs compound. The bombardment induces the segregation of a very small quantity of elemental Ga, along with the formation of damaged GaAs at the topmost surface. These sub-products will be responsible of the lower and higher binding energy contributions to the Ga $2p_{3/2}$ core level, respectively. The formation of these undesirable subphases is inherent to sputtering effects in these compounds [17,19]. Very recently, studies on the In $3d_{5/2}$ core level in several III-V semiconductors have also demonstrated that after Ar^+ sputtering, the main contribution due to the bulk compound is accompanied by lower binding energy contributions

due to metallic In clusters and/or higher binding energy contributions arising from the reconstructed surface after sputtering [20]. Ga $2p_{3/2}$ photoelectrons provide chemical information of a more superficial region than Ga 3d photoelectrons do. Therefore, their absence in the Ga 3d core level is a proof of its superficial character. Similarly to what has been described for the Ga 3d core level, As 3d core levels (not shown) always exhibit a single component centered at 41 eV, which is a typical binding energy for As in the GaAs coordination.

The structures prepared with a very thin GaAs top layer (with a nominal thickness of 5 nm) are not affected by sputtering artifacts. For these samples the spectra have been acquired at different angles of emission in order to control the chemical environment

Fig. 2. Ga 3d (left) and Ga $2p_{3/2}$ (right) core levels corresponding to the outer GaAs layer in both thick heterostructures: GaAs/GaInP (top) and GaAs/AlInP (bottom). Identification of the different contributions is made on the graphics. The red line is the fitting result. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Fig. 3. As $2p_{3/2}$ core levels corresponding to the thin heterostructures: GaAs/GaInP (left) and GaAs/AlInP (right). Data are presented at two different angles of emission, 30° (top) and 90° (bottom). Identification of the different contributions is made in the graphics. The red line is the fitting result. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

evolution of each element as the explored depth increases. The spectra recorded using this technique do not show the metallic and non-stoichiometric contributions appearing in the Ga $2p_{3/2}$ core level presented in Fig. 2 and allow to confirm the origin suggested for these contributions in the spectra of the thick structures (this item will be properly analyzed in Fig. 4).

The 2p core levels of both Ga and As are the most sensitive to the presence of spurious phases like oxides on surface layers, whose presence is unavoidable due to air exposure. Indeed, Fig. 3 shows the As $2p_{3/2}$ peak corresponding to the thin GaAs/GaInP (left) and GaAs/AlInP (right) structures at two different take-off angles, 30° (top) and 90° (bottom). In the first case, the inelastic mean free path (IMFP) for the outgoing photoelectrons is ~ 0.6 nm, while for the second angle, IMFP reaches ~ 1.2 nm. In all cases, curve fitting results of the As $2p_{3/2}$ peak discloses the presence of four contributions. The signal located at lower binding energy is related to GaAs compound and the following one is due to MOVPE precursor debris. The other two peaks are related to arsenic oxide compounds, namely, As_2O_3 and As_2O_5 . As_2O_3 is the main contribution in the spectra taken at 30° and its intensity is three times that of As_2O_5 , in agreement with what has been previously observed [21]. When the explored depth increases (i.e., measurement at 90°), the main contribution to the global signal corresponds to the GaAs coordination, which is half the total peak intensity in this case. Besides, the oxides and precursor debris contributions are thus decreasing its weight in the global signal as the explored thickness increases. In the As 3d spectra (not shown), there is no signal from precursor debris but only from the GaAs compound and both oxides. The evolution of the peak components with the explored depth is rather similar to what has been observed for the As $2p_{3/2}$ but in this core level, the most intense contribution is that of the GaAs compound at any take-off angle. Both facts can be explained if we consider that the explored depth in this core level is in the order of ~ 1.8 nm for the data taken at 30° , and around 3.7 nm for the spectra taken at 90° .

The Ga $2p_{3/2}$ spectra corresponding to the thin heterostructures present three bands (Fig. 4). From high to low binding energy, they correspond to precursor residues – presumably Ga(CH $_3$) $_3$ –, Ga $_2$ O $_3$

and GaAs, all of them with the same FWHM. As stated for the As $2p_{3/2}$ peak, the signals of the oxide and precursor diminish as the explored depth increases, while that of the GaAs increases. However, due to the superficial character of the photoelectrons that give rise to this peak, the largest contribution at any explored depth is that from the Ga oxide. There are no signals of the two contributions seen on the Ga $2p_{3/2}$ spectra of the thick structures corresponding to sputtering effects and elemental Ga. Therefore, these last ones should be directly related to bombardment effects. The Ga 3d core level is very close to the In 4d core level, and due to the very small thickness of the GaAs layer in these samples (5 nm), they both give rise to a broad peak showing a rather complicated structure where contributions from Ga and In are mixed.

3.2. Interface

Revisiting Fig. 1, where the depth profile analysis is depicted for both thick samples, the interfaces seem to be far from abrupt. In Fig. 1, the GaAs/GaInP interface spreads over a shorter sputtering time interval than the GaAs/AlInP interface. Therefore, the latter would have a longer thickness. A rough estimation of the interface widths revealed rather large values: ~ 26 nm for the GaAs/GaInP interface and ~ 32 nm for the GaAs/AlInP interface. Such high values account for intrinsic interface features, like In segregation, that can spread up to 10 monolayers across the interface [22], but also for sputtering effects like preferential sputtering that would enlarge the interface width. The way the concentration of the top layer constituents (Ga and As) diminishes across the interface is not linear. Rather, it depicts a decreasing exponential-like curve. A similar conclusion could be derived from the shape of concentrations of the bottom layer elements (Ga, In, P and Al), namely, its shape resembles that of an exponential growth function. Even though, XPS is a powerful chemical analysis tool, damage induced by the ion sputtering limits its applicability to superficial characterization and to determine qualitative depth profiles.

The Ga $2p_{3/2}$ core level spectra show very similar features to those presented by the GaAs outer layer for both GaAs/GaInP and

Fig. 4. Ga $2p_{3/2}$ core levels corresponding to the thin heterostructures: GaAs/GaInP (left) and GaAs/AlInP (right). Data are presented at two different angles of emission, 30° (top) and 90° (bottom). Identification of the different contributions is made on the graphics. The red line is the fitting result. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

GaAs/AlInP heterostructures across the whole interface (see Fig. 2). As observed for the GaAs outer layer, there are two additional contributions accompanying the GaAs signal at lower and higher binding energies. They have the same binding energy and their intensities are equivalent to what has been found in the GaAs layer. Therefore, their origin should be again caused by bombardment effects. The deconvolution of the Ga $2p_{3/2}$ core level spectra is very similar along the whole interface for both heterostructures, even when the core level signal is very weak in the final stages of the GaAs/AlInP interface depth profile analysis.

On the other hand, the decreasing intensity of As was monitored through the As3d core level signal in both interfaces. No extra contribution was found in any stage of the depth profile analysis. Thus, the only As contribution would correspond to the chemical environment in the GaAs coordination.

Indium is the first element appearing in the depth profile analysis for both structures. It thus means that, after GaInP and AlInP layer growth, the In carry-over effect takes place and In atoms tend to segregate at the surface, in such way that they will likely incorporate into the GaAs outer layer. This is a well-known phenomenon described by several authors for the interface GaAs/GaInP [4,6,22,23]. According to our results, In atoms in the GaAs/AlInP interface would exhibit the same behavior. The In 3d core level signals are very similar in both GaAs/GaInP and GaAs/AlInP interfaces. In Fig. 5, only data from GaAs/GaInP interface in the thin and the thick heterostructures are shown. They always consist of two contributions. The main one comes from In cations in cubic coordination, like in the GaInP crystalline structure. The one at higher binding energy has two possible origins, depending on the tool used to explore the interface. When the interface has been explored after the sputtering of the GaAs layer, there is an undesired bombardment effect due to the preferential evaporation of anions (Fig. 5, top) that would give rise to the presence of a cation-rich-layer at the topmost surface and to the surface reorganization that takes place after sputtering [20]. The same effect has been detected for Ga cations and it has already been described in Section 3.1 and

Fig. 2. The intensity of this contribution maintains a rather constant value across the whole interface, like those in the Ga $2p_{3/2}$ core level. In the samples where the interface has been studied by ARXPS through a very thin GaAs layer, the presence of cation oxides is unavoidable (Fig. 5, bottom). This oxide contribution diminishes its intensity as the explored depth increases, which is a proof of the assigned origin. Besides, there are two small peaks (dashed lines) due to the non monochromaticity of the X-ray source, which appear in the low binding energy side of the $3d_{5/3}$ doublet constituent.

Al 2p core level signal looks very different when the interface GaAs/AlInP is explored through depth profiling (Fig. 6, top) or ARXPS (Fig. 6, bottom). In the first case, the signal consists of only

Fig. 5. In 3d core level deconvolution from the GaAs/GaInP interface. Top: data from the thick heterostructure taken after depth profiling. Bottom: data from the thin heterostructure taken at take-off angle 60° . Different contributions are identified in the figure. The red line is the fitting result. In both cases, dashed line corresponds to a satellite peak due to the non-monochromaticity of the incident radiation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Fig. 6. Al 2p core level deconvolution at the interface GaAs/AlInP. Top: data from the thick heterostructure taken after depth profiling. Bottom: data from the thin heterostructure taken at a take-off angle of 70°. Different contributions are identified in the figure. The red line is the fitting result. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

one contribution. Its binding energy is compatible with the ternary AlInP compound and the signal is identical to the one found in the AlInP layer. In the signal obtained from ARXPS, there is a low binding energy signal centered at 74 eV, which dominates the global signal. However, three more contributions have to be included. According to their binding energies and following electronegativity arguments, they would come from Al hydroxide, Al oxide and the highest binding energy contribution has been assigned to precursor debris (TMAI). The presence of these residues has been detected also for some other elements in these samples, like Ga and As. The relative intensity of the contributions accompanying the principal one diminishes as the explored depth increases. The presence of oxidized Al is probably due to the fact that the GaAs layer in the thin GaAs/AlInP heterostructure is not completely homogeneous, mainly due to the layer oxidation and the presence of Ga and As precursors. From these experimental results, it seems evident that Al cations do not form any other compound than AlInP at the interface GaAs-AlInP.

Concerning the As/P anion exchange at both interfaces, the study of the P 2p energy level included in Fig. 7 will give us relevant information. ARXPS analysis of the thin heterostructures is hindered by the As 3p signal, which is very close in the high binding energy side of the P 2p core level. Data taken at the angles of emission 60°, 75° and 90° from the thin GaAs/GaInP heterostructure show P 2p photoelectrons leaving out the sample through the nominal 5 nm thick GaAs layer. For the three angles, there is just one contribution, a doublet pair $2p_{3/2}$ and $2p_{1/2}$, located at 129.18 eV (Fig. 7, top left shows data for 75°), which should be related to P anions in the GaInP coordination. The data taken at 60° and 90° (not shown here) depict the same scenario. The GaAs/GaInP interface examined after depth profiling in the thick heterostructure has an extra contribution due to the sputtering effect (Fig. 7, top right), as it has been already observed in the cations signal. This point will be confirmed in the next subsection, where the GaInP and AlInP layers are described. No other extra contribution appeared in the GaAs/GaInP interface region.

The P 2p spectra along the interface of the GaAs/AlInP heterostructures look rather different (see Fig. 7, middle and bottom curves). In this case, the ARXPS analysis of the thin GaAs/AlInP structures is shown here for the angles of emission 60° and 85°. They both reveal the presence of two contributions: one located at lower binding energy (129.11 eV) related to AlInP compound, and another one at higher binding energies (131.74 eV) (Fig. 7, middle and bottom left). The relative intensity of this last contribution

decreases with explored depth (Fig. 7, bottom left). The presence of this extra contribution is confirmed in the depth profile analysis of the thick GaAs/AlInP structure. Fig. 7 (middle and bottom right) shows the deconvolution of the P 2p core level in two different points along GaAs/AlInP: one at the middle of the interface (Fig. 7, middle right) and at the end of the interface (Fig. 7, bottom right). In both cases, three contributions can be distinguished. The most intense one, at lower binding energy corresponds to P anions in the AlInP coordination. The middle one is related with sputtering effects and is the equivalent to that already described for the GaAs/GaInP interface. The one at higher binding energy is the extra contribution also detected in the ARXPS analysis (Fig. 7, middle and bottom left). The intensity evolution of the extra band appearing at high binding energies diminishes rather fast with depth profiling progress, and it is not detected in the last stage of the interface analysis. This extra contribution has not been detected in the GaAs/GaInP interface and it would correspond to phosphorous clusters not incorporated in the AlInP lattice.

Studies of the GaAs/GaInP interface have revealed the formation of GaInAs, mainly caused by the incorporation of In atoms into the subsequent GaAs layer [6,7]. The presence of quaternary phases like GaInAsP is also feasible; however XPS is not able to assert its presence since Ga 2p, As 3d, In 3d and P 2p core levels do not show contributions different to those appearing in the GaAs and the GaInP layers. The formation of this kind of compounds has been detected in the GaAs/GaInP interface when studied by other techniques [4,5]. The As/P exchange does not seem to induce the formation of phases with different symmetry than that of GaAs since As atoms easily replace P atoms in the GaInP surface [24]. Therefore, our results agree with previous reports in the literature.

On the other hand, GaAs/AlInP interface reveals a more complicated chemistry. Ga, As, and In core levels do not show distinct features as those in the GaAs/GaInP interface. Al shows a single coordination environment along the interface, which is identical to the one appearing for the inner AlInP layer. However, the P 2p core level is different to what has been described in the GaAs/GaInP interface since an additional contribution accompanies that of the AlInP coordination, appearing in both the thin and the thick heterojunctions. Its relative intensity diminishes as the explored depth increases. The appearance of this contribution may be indicative of the formation of an undesired phase at the top of the GaAs/AlInP interface. Its composition and stoichiometry is uncertain but its binding energy suggests it could be related to P-P bonds. Nagao and co-workers reported the substitution of a few percent of P atoms into As atoms for an AlInP surface exposed to an As beam [9]. These P atoms would organize as P-P clusters giving thus rise to the higher binding energy contribution in the P 2p core level signal. It is worth mentioning that there is not only an anion exchange (As/P) in this interface but also a total cation replacement (Ga/Al-In), while in the GaAs/GaInP interface, there is just a partial cation replacement (Ga/Ga-In). Undoubtedly, the differences among the three cation sizes could certainly be an additional inconvenience in the cations and anions exchange.

3.3. Inner layers: GaInP and AlInP

Regarding the inner GaInP and AlInP layers, the core level data analysis from depth profiling demonstrates a stable composition in both cases. Concerning the GaInP layer, Ga $2p_{3/2}$ and In 3d core levels, as well as the P 2p core level, do not show any other component, except for those already discussed for the cap layer or the interface as a result of sputtering. Fig. 8 (top) shows the P 2p core level signal for the GaInP layer (top). The sputtering effect induces the extra component in the high binding energy side of the main peak as it has been already discussed for the interface data. Regarding the AlInP layer, Al 2p and In 3d core levels exhibit the same features already

Fig. 7. P 2p core level corresponding to the thin (left) and the thick (right) heterostructures at the interfaces. In both cases, the graphics in the top correspond to GaAs/GaInP interface and middle and bottom graphics correspond to GaAs/AlInP interface. To show the intensity variation of the higher binding energy contribution in the GaAs/AlInP interface, data are shown for two explored depths (left) for the thin GaAs/AlInP heterostructure, and two different points at the point marked with an arrow in Fig. 1 (middle) and the end (bottom) of the interface for the thick GaAs/AlInP heterostructure.

Fig. 8. P 2p core level deconvolution corresponding to GaInP (top) and AlInP (bottom) layers. The red line is the fitting result. The lower binding energy contribution corresponds to P in GaInP and AlInP coordination, while the higher binding energy feature is a sputtering effect. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

described in the interface section. The P 2p core level corresponding to the AlInP layer is shown in Fig. 8 (bottom). The only difference between the top and bottom graphics concerns the relative intensity of the contribution related to sputtering effects respect to the stoichiometric one, which is larger in the AlInP layer. This could be related to the preferential sputtering of the Al cation in this layer. In fact, the Al 2p core level displays just one contribution, as in the GaAs/AlInP interface (Fig. 6, top). Al is the lightest element in the layer, and consequently is the one more easily sputtered during the

depth profile analysis, leaving thus an enriched In and P surface. No traces of any spurious phase involving P anions have been found in the inner AlInP layer. As a summary of this section, it can be concluded that for both inner layers, there are not any other phases than the nominal ones, GaInP and AlInP.

4. Conclusions

The study of GaAs/GaInP and GaAs/AlInP interfaces grown by MOVPE has been accomplished by means of XPS analysis tools. Our results prove that the combined use of ARXPS and depth profile XPS for the study of buried interfaces provides more accurate results than each separate technique. ARXPS could help to discern contributions due to sputtering effects in the core level signals, and depth profile data are not affected by the presence of oxides due to ambient exposure.

According to the depth profile analysis, GaAs/AlInP interface thickness is longer than that of GaAs/GaInP. According to the depth profile analysis of the thick heterostructures, As and Al suffer preferential sputtering in their respective layers. The depth profile sputtering assisted analysis induces the appearance of artificial contributions in the Ga 2p_{3/2}, In 3d and P 2p core levels. As it has been previously reported, In has demonstrated its tendency to segregate at the growing surface, which probably gives rise to mixed phases like GaInAs at the interfaces between GaAs and GaInP and also between GaAs and AlInP. Our results are also compatible with the presence of some other phases like quaternary GaInAsP at both GaAs/GaInP and GaAs/AlInP interfaces. An additional phase, probably related to the presence of P clusters, has been detected only in the GaAs/AlInP interface. This spurious phase would tend to concentrate at the top of the interface region.

Acknowledgements

Authors acknowledge financial support from Spanish Ministerio de Economía y Competitividad through projects

TEC2011-28639-01 and -02, TEC2014-54260-C3-01 and -03, and from Madrid local government under contract S2013/MAE-2780 (MADRID-PV). S.P. thanks Spanish Ministerio de Ciencia e Innovación for a Ramón y Cajal fellowship.

References

- [1] A.S. Gudovskikh, N.A. Kalyuzhnyy, V.M. Lantratov, S.A. Mintairov, M.Z. Shvarts, V.M. Andreev, Properties of interfaces in GaInP solar cells, *Semiconductors* 43 (2009) 1363–1368.
- [2] A.S. Gudovskikh, J.P. Kleider, N.A. Kalyuzhnyy, V.M. Lantratov, S.A. Mintairov, Band structure at heterojunction interfaces of GaInP solar cells, *Solar Energy Mater. Solar Cells* 94 (2010) 1953–1958.
- [3] J.P. Samberg, H.M. Alipour, G.K. Bradshaw, C.Z. Carlin, P.C. Colter, J.M. LeBeau, N.A. El-Masry, S.M. Bedair, Interface properties of Ga(As,P)/(In,Ga)As strained multiple quantum well structures, *Appl. Phys. Lett.* 103 (2013) 071605.
- [4] C.Y. Tsai, M. Moser, C. Geng, V. Härle, T. Forner, P. Michler, A. Hangleiter, F. Scholz, Interface characteristics of GaInP/GaAs double heterostructures grown by metalorganic vapor phase epitaxy, *J. Cryst. Growth* 145 (1994) 786–791.
- [5] C. Frigeri, G. Attolini, M. Bosi, C. Pelosi, F. Germini, Detection of the interlayer at the GaAs-on-InGaP interface in MOVPE InGaP/GaAs by the dark field method, *J. Mater. Sci.: Mater. Electron.* 19 (2008) S107–S110.
- [6] Y. Dong, R.M. Feenstra, M.P. Semtsiv, W.T. Masselink, Cross-sectional scanning tunneling microscopy and spectroscopy of InGaP/GaAs heterojunctions, *Appl. Phys. Lett.* 84 (2004) 227–229.
- [7] Y. Dong, R.M. Feenstra, M.P. Semtsiv, W.T. Masselink, Band offsets of InGaP/GaAs heterojunctions by scanning tunneling spectroscopy, *Appl. Phys. Lett.* 103 (2008) 073704.
- [8] S. Dhellemmes, S. Godey, A. Wilk, X. Wallart, F. Mollet, As-P interface-sensitive GaInP/GaAs structures grown in a production MBE system, *J. Cryst. Growth* 278 (2005) 564–568.
- [9] S. Nagao, M. Takashima, Y. Inoue, N. Katoh, H. Gotoh, Abruptness of GaAs/AlInP hetero-interfaces grown by GS-MBE, *J. Cryst. Growth* 111 (1991) 521–524.
- [10] J.M. Kuo, H.C. Kuo, J.Y. Cheng, Y.C. Wang, Y. Lu, W.E. Mayo, Interface optimization of AlInP/GaAs multiple quantum wells grown by gas source molecular beam epitaxy, *J. Cryst. Growth* 158 (1996) 393–398.
- [11] P.E. Smith, M. Lueck, S.A. Ringel, L.J. Brillson, Atomic diffusion and electronic structure in $\text{Al}_{0.52}\text{In}_{0.48}\text{P}/\text{GaAs}$ heterostructures, *J. Vac. Sci. Technol. B* 25 (2007) 1916–1921.
- [12] W.E. Hoke, P.J. Lemonias, T.D. Kennedy, A. Torabi, E.K. Tong, K.L. Chang, K.C. Hsieh, Molecular beam epitaxial growth and characterization of strain-compensated $\text{Al}_{0.3}\text{In}_{0.7}\text{P}/\text{InP}/\text{Al}_{0.3}\text{In}_{0.7}\text{P}$ metamorphic-pseudomorphic high electron mobility transistors on GaAs substrates, *J. Vac. Sci. Technol. B: Microelectron. Nanometer Struct.* 19 (2001) 1519–1523.
- [13] X. Li, Y. Cao, D.C. Hall, P. Fay, B. Han, A. Wibowo, N. Pan, GaAs MOSFET using InAlP native oxide as gate dielectric, *IEEE Elect. Dev. Lett.* 25 (2004) 772–780.
- [14] C. Algorta, I. Rey-Stolle, The interest and potential of ultra-high concentration, in: A.B. Cristóbal López, A. Martí Vega, A. Luque López (Eds.), *Next Generation of Photovoltaics*, Springer Series in Optical Sciences, 2012, pp. 23–60.
- [15] J.L. Sullivan, W. Yu, S.O. Saied, A study of the compositional changes in chemically etched, Ar ion bombarded and reactive ion etched GaAs(100) surfaces by means of ARXPS and LEIS, *Appl. Surf. Sci.* 90 (1995) 309–319.
- [16] G. Padeletti, G.M. Ingo, Factors determining preferential sputtering in InGaAs system: angle-resolved small-area XPS investigation, *Surf. Interface Anal.* 34 (2002) 266–270.
- [17] G. Padeletti, G.M. Ingo, Small-area XPS investigation on ion-induced chemical modifications during depth-profiling of an $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ structure, *Surf. Interface Anal.* 22 (1994) 31–35.
- [18] XPSPeak 4.1, <http://xpspeak.software.informer.com/4.1/>.
- [19] W. Yu, Ion bombardment induced compositional changes in compound semiconductor surfaces studied by XPS combined with LEIS, Ph.D. Thesis, The University of Aston in Birmingham (1995).
- [20] J. Mäkelä, M. Tuominen, M. Kuzmin, M. Yasir, J. Läng, M.P.J. Punkkinen, P. Laukkanen, K. Kokko, K. Schulte, J. Osiecki, R.M. Wallace, Line shape and composition of the In $3d_{5/2}$ core-level photoemission for the interface analysis of In-containing III–V semiconductors, *Appl. Surf. Sci.* 329 (2015) 371–375.
- [21] L. Geelhaar, R.A. Bartynski, F. Ren, M. Schnoes, D.N. Buckley, Photoluminescence and X-ray photoelectron spectroscopy study of S-passivated InGaAs (001), *J. Appl. Phys.* 80 (1996) 3076–3082.
- [22] M. Mesrine, J. Massies, C. Deparis, N. Grandjean, E. Vanelle, Real time investigation of In surface segregation in chemical beam epitaxy of $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ on GaAs (001), *Appl. Phys. Lett.* 68 (1996) 3579–3581.
- [23] M. Mesrine, J. Massies, E. Vanelle, N. Grandjean, C. Deparis, Photoluminescence energy and interface chemistry of GaInP/GaAs quantum wells, *Appl. Phys. Lett.* 71 (1997) 3552–3554.
- [24] K. Ouchi, T. Mishima, Preferential group-V replacement at InGaP/GaAs interfaces grown by gas-source MBE, *J. Cryst. Growth* 209 (2000) 242–246.