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XPS analysis of n-GaP(111) native and etched surfaces

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The obtaining of a good ohmic contacts on the semiconductor material surfaces is strongly depending on the ability of the cleaning procedures to remove the native oxides and also, in the case of the compounds, to keep the surface stoichiometry. In this work, the XPS technique has been used in order to compare the efficiency of both, chemical etching and the Ar^+ ion sputtering methods as to be suitable cleaning procedures in the case of n-GaP semiconductor compound surfaces preparation for the optoelectronic devices obtaining. The results have revealed some differences in the final surface composition/stoichiometry. The atomic ratio P/Ga within the outer layer of the single crystalline sample (~ 100 Å) has been evaluated. The presence of residual of surface oxides was recorded after performing the chemical cleaning.

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1. Introduction

Solid/solid interfaces could play an important role in the field of microelectronic device technologies development. The deposition of metallic layers on clean semiconductor surfaces in order to obtain good ohmic contacts it is an important task for the structures and related devices preparation. The surface of III-V semiconductor compounds which is exposed to the ambiental conditions is usually covered with native oxide layers. The III-V surface oxides are chemically unstable in air. Various techniques for performing the surfaces cleaning process are used (chemical etching, plasma etching, “in situ” ion sputtering etc.) according to the specific properties of the experimental system. In the cases presented in this paper, both chemical etching and low energy (<5 keV) Ar^+ ion sputtering techniques were used with the aim to remove the native oxides from n-GaP single crystalline sample surfaces.

The main goal of this work is to compare the effects of both mentioned surface cleaning procedures on the GaP surface preparation. The evaluation has been carried out by the XPS (X-ray Photoelectron Spectroscopy) analysis, for two values of the incident/emergent radiation angle.

2. Experimental

N-type GaP(111) samples were cleaned as follows: degreasing in boiled pure trichloroethylene, rinsing in acetone at room temperature and rinsing in deionized water (DIW) 10^{18} MΩ, for t=2 min. at room temperature. The growth rate for the oxide in DIW could be approximated at 30 Å/2h. In air, the thickness of the reconstructed layer is maximum 10 Å [1]. After these preliminary steps the XPS measurements were carried out by the use of a VG Scientific ESCA3 MKII spectrometer with a Mg Kα X-ray source (1253.6 eV photons energy) operated at 250 W (12.5 kV, 20 mA). The XPS analysis was performed on native oxidized surfaces of GaP samples and then, on surfaces modified by both treatment variants, chemical etching and also under Ar^+ ion bombardment cleaning.

The XPS measurements were carried out at 20° and 55° TOA (take-off angles). TOA is defined as well as its description in the ASTM E 673-98 related to standard terminology regarding the surface analysis. TOA represents the angle between the beam of emitted photoelectrons and the sample surface.

The XPS measurements were performed along four experimental steps on :

- GaP surfaces covered with native oxide,
- GaP surfaces after H_3PO_4 (85%) chemical etching at room temperature,
- GaP surfaces after H_2SO_4:H_2O_2:H_2O (3:1:1) etching at room temperature,
- GaP surfaces after the “in situ” ion gun Ar^+ cleaning treatment with (1-3-5) keV accelerating ion voltage, ion beam current: I=25-50-100 μA and, focus voltage: 3 kV. Sputtering time was: 5 minutes. The pressure of the argon gas was about 5×10^{-6} Torr.

The evolution of the atomic ratio $C_{P\ total}/ C_{Ga\ total}$ has been studied within the surface region for two values of TOA (20° and 55°). Several phenomena, as there are: the tendency of P or Ga dissociation from the compound, chemical reactivity of surface, and the influence of the cleaning procedures were approximated. As usually, because it exists the possibility to detect the compositional changes within few layers depth from the surface, the most sensitive angle to the surface compositional change was the take-off-angle TOA=$20^°$.

3. Results and discussion

As regards the GaP surfaces analysis, the XPS spectra were recorded at TOA=20° and respectively at TOA 55° in

the range of C 1s, O 1s, Ga 3d, P 2p core-level photoemission lines. The Ga 3d and P 2p lines could offer information about the presence of Gallium and Phosphorous oxides on the surface. The XPS spectra obtained for Ga 3d, at TOA=20º (Fig. 1) and TOA=55º (Fig. 2) on GaP native surface confirm both contributions, one from elemental Gallium and the second one from Ga_2O_3.

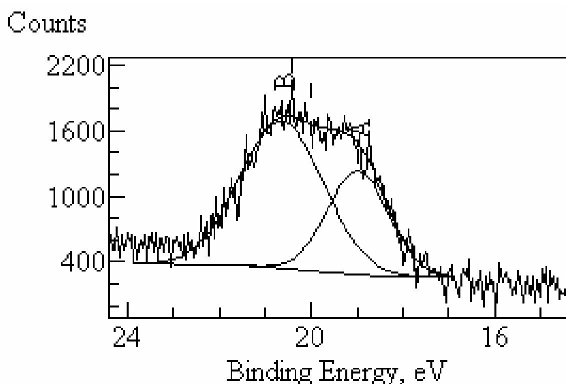

Fig. 1. XPS spectrum in the Ga 3d region at TOA=20º for GaP native oxidized surface: (A)- Ga 3d line: 19 eV, (B)- Ga_2O_3 3d: 20.64 eV.

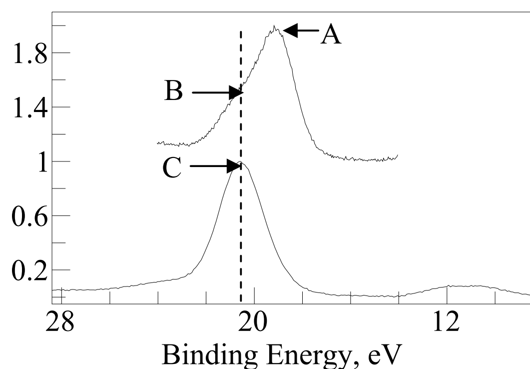

Fig. 2. XPS spectra in the Ga 3d region at TOA=55º for GaP native oxidized surface: (A)-Ga: 19 eV, (B)-Ga_2O_3: 20.49 eV, (C)-Ga_2O_3: 20.5 eV.

In Fig. 2, the curve (C) represents the result of an "in situ" measurement on Ga_2O_3 (99.99% purity) additional powder sample. This measurement was performed with the aim to compare the fitted curves (from A and respectively, B cases) with the signal of pure Ga_2O_3..

The lines could be fitted with two Gaussian peaks with FWHM of 1.61 ±0.1 eV for Ga 3d in GaP and with FWHM of 2.1 ±0.1 eV for Ga_2O_3, respectively

It should be noted that quite different values, in the range of 19.6 eV to 21 eV, have been reported in the literature for the BE of Ga-O in Ga_2O_3 [2,3].

As regards the P 2p1 and P 2p3 core-levels the XPS spectrum for native oxidized sample (Fig. 3) (TOA=20º) shows two fitted Gaussian lines for phosphorous oxide core-levels with FWHM of 1.7±0.1 eV and 2.0±0.1 eV, respectively

As well in the case of Ga_3O_3, the XPS signal from the P_2O_5 pressed powder sample, in the P 2p region was recorded. The peak of pure P_2O_5 powder was compared too with the line of phosphorous oxide on the surface of GaP (Fig. 4).

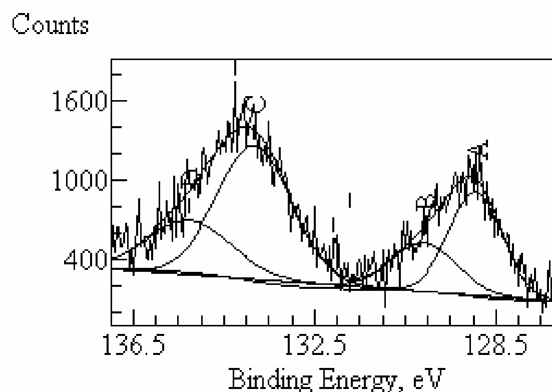

Fig.3. XPS spectrum in the P 2p region at TOA=20º for GaP natively oxidized surface: (A)-P 2p3/2: 128.94 eV, (B)-P 2p1/2:130.08 eV, (C)- P_2O_5 2p3/2:133.83 eV, (D)- P_2O_5 2p1/2:135.26 eV.

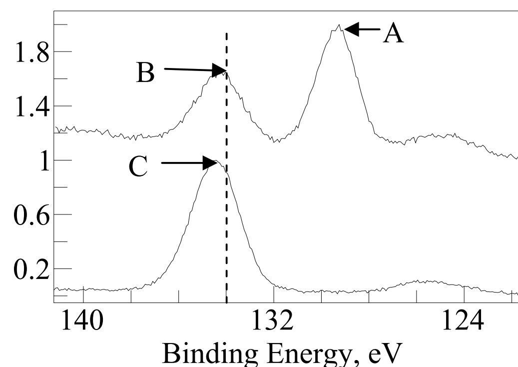

Fig. 4. XPS spectra in the P 2p region at TOA=55º for GaP native oxidized surface: (A)-P 2p3/2: 129.09eV, (B)- P_2O_5 2p3/2: 133.99 eV and for P_2O_5 powder (99.99% from Merck): (C)-P_2O_5 2p3/2: 134.2 eV.

In the case of P_2O_5 powder (Fig. 4) the main peak (C) at 134.2 eV (FWHM=2.0±0.1 eV) is assigned to 2p3 core-level in P_2O_5 and a second peak at 135.3 eV (FWHM=2.0±0.1 eV) that broadens the peak (C) is attributed to 2p1 core-level in P_2O_5.

Table 1 presents the atomic P/Ga ratio on GaP surface after chemical etching with H_2SO_4:H_2O_2:H_2O (3:1:1) and after etching by H_3PO_4 (85%).

Table 1. P/Ga ratio before and after chemical etching.

XPS	P_{total} / Ga_{total} ratio		
TOA (°)	Native surface	H_2SO_4:H_2O_2:H_2O (3:1:1)	H_3PO_4 (85%)
20	0.95	0.84	1.13
55	0.80	0.77	0.88

The Gallium 3d signal arises at 19 eV (from GaP) and at 20.5 eV (from Ga_2O_3). On the other hand the Phosphorous 2p signal arises from GaP and P_2O_5. The P/Ga atomic ratio on the semiconductor compound surface has a value near to near stoichiometry. In the case of the native oxidized sample (see Table 1) these values (of P/Ga ratio) have revealed the contribution of P and Ga from native oxides contained in the surface layers. As easily observed, the concentration of Ga(III) oxide is greater than that of P(V) oxide.

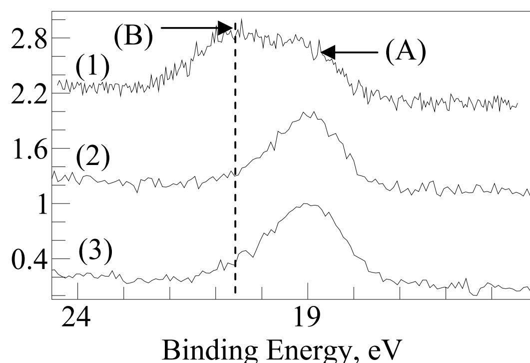

Fig. 5. XPS spectra for Ga 3d from GaP: (1)-native oxidized, (2)-chemical etched with H_3PO_4, (3)-chemical etched with H_2SO_4:H_2O_2:H_2O, peak (A) is Ga 3d and peak (B) is Ga_2O_3 3d for TOA=20°.

This Ga enrichment in the air-exposed GaP surfaces was also put in evidence in [4].

After the performing of the chemical etching procedure (H_3PO_4 85%), the atomic ratio of P 2p to Ga 3d indicates a P- riched surface layers formation (P/Ga atomic ratio is bigger than 1.0).

Three naturally oxidized GaP(111) samples were cleaned by Ar^+ ion sputtering, (5 minutes) with 1÷5 keV energies (Fig. 6).

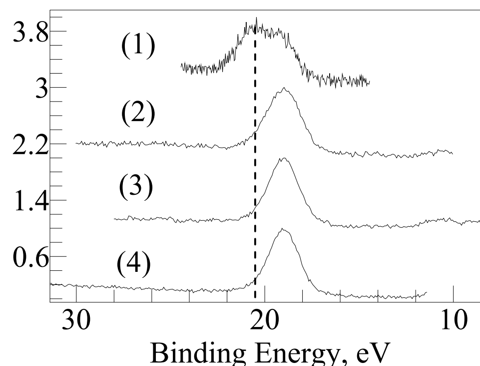

Fig. 6 XPS offset superimposed normalized spectra for Ga 3d lines from GaP surfaces: (1)-native oxidized and after Ar^+ ion sputtering: (2)-1 keV, (3)-2 keV, (4)-3keV TOA=20°

Fig. 7 shows the P 2p lines of native oxidized surface and also the lines corresponding to the chemically etched

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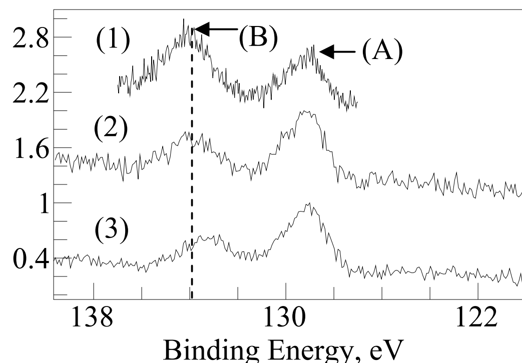

Fig.7. XPS spectra of P 2p lines from GaP surfaces: (1)- native oxidized and chemical etching surfaces: (2)-H_3PO_4, (3)-H_2SO_4:H_2O_2:H_2O for TOA=20°

From Fig. 7 and 8 results that the (A) peaks corresponding to P 2p1/2, P 2p3/2 lines are broader (FWHM≈1.8±0.1 eV) for native oxidized GaP than P 2p1/2, 2p3/2 lines (FWHM≈1.6±0.1eV) of etched or sputtered GaP surfaces for TOA=20°. A decrease of the signal arising from oxide (peaks (B)) it is observed after the chemical etching or Ar^+ ion sputtering with (1÷5) eV energies.

From Fig. 7 we can conclude that chemical etching removes the native GaP oxide. However, complete removal of the oxide cannot be achieved even after long time etching. The wet etching can remove the native oxide layer and leave a bare GaP surface, but as soon as the sample is exposed to air, an oxide regrows on the semiconductor surface. The disappearance of the signal from P oxide after Ar^+ ion sputtering is observed at 5 keV energy (Fig.8) in high vacuum conditions.

Fig. 8 presents the XPS recorded signal at TOA=20º, from GaP surface after carrying out the ion sputtered surface treatment.

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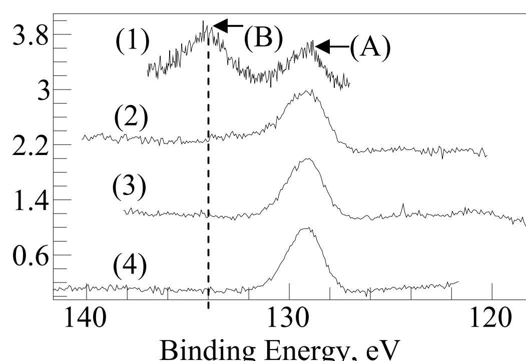

Fig.8. XPS offset superimposed normalized spectra of P 2p peaks from GaP (1)-native oxidized and after Ar^+ ion sputtering (2)-1 keV, (3)-2 keV, (4)-3keV for TOA=20°

The oxide over-layer was removed by sputtering and the changes in both core-level signals of Ga and P illustrate that the Ar^+ ion sputtering causes P depletion in GaP surface.

The Ar^+ ions plasma sputter rates for GaP, GaAs, InP, InGaAs are relatively slow (<250 nm/min) [1].

The Ar^+ ions bombardment generates a near-surface layer depleted of ”volatile atoms”. Also, since altered layers were found to extend far beyond the depth of origin of sputtered atoms, compositional changes generated by preferential sputtering were assumed to propagate into the bulk by diffusion process.

The distribution of Ga and P atoms in outer layers can be explained by the competition between the preferential sputtering of P versus Ga and radiation-enhanced surface diffusion/Gibbson segregation (analog with the distribution mechanism for Ga and As [6,7]).

Atomic concentration ratio P/Ga is computed after [3] by:

$$\frac{C_P}{C_{Ga}} = \frac{I_P F_{Ga} \sigma_{Ga} \lambda_{Ga}}{I_{Ga} F_P \sigma_P \lambda_P} \qquad (1)$$

where:
I_P, I_{Ga} are measured line intensities for P 2p, respectively Ga 3d.

F_{Ga}, F_P are values of spectrometer transfer function for Ga 3d and P 2p evaluated with NPL (National Physical Laboratory) procedure (F_{Ga}=414, F_P=464), σ_{Ga}, σ_P are photoionisation cross sections (Scofield factors) for Ga 3d line (1.193), respectively for P 2p line (1.25) [3]. λ_{Ga}, λ_P are electron inelastic mean free paths (IMFP) from Ga in GaP and in a mixture of Ga_2O_3 and P_2O_5, respectively from P in GaP and in a mixture of oxides [8, 9]. The values considered were 26.54 Å for photoelectrons from Ga in GaP and 24.68 Å for photoelectrons from P in GaP because there were small differences between the values for IMFP from GaP and the values for IMFP from oxides.

Then eq. (1) leads to:

$$\frac{C_P}{C_{Ga}} = 0.9158 \frac{I_P}{I_{Ga}} \qquad (2)$$

The composition of the native surface namely $C_{Gatotal} > C_{Ptotal}$ indicates a gallium oxide rich initial surface layer. After chemical etching a Ga rich surface is obtained and the ratio $C_{Ptotal}/C_{Gatotal}$ tends slightly to stoichiometry from values under unit.

In the ion sputtering phase, Ar^+ ions have a large screened Coulombic interaction cross-section with the surface atomic nuclei causing a cascade through neighborhood atoms [5].

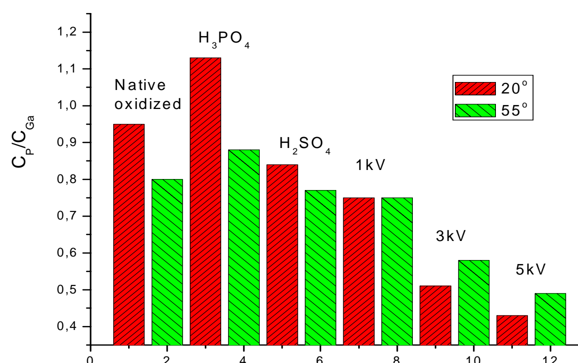

Fig. 9. C_P/C_{Ga} ratio histogram before and after chemical etching or Ar^+ ion sputtering (1÷5 keV) for TOA=20° (odd columns) and 55º (even columns).

When the collision cascade intersects with the surface, top layer atoms are rejected. The various elemental constituents aren't sputtered at the same rate. Thus this sputtering process is preferential. The resulted surface composition differs appreciably from the stoichiometric bulk composition. The observed higher depletion of group V species from surface is related to a sublimation energy of P or As smaller than that of Ga [6]. There will be a significant damage to the surface and sub-surface region [10]. The results from Fig. 9 correspond to a final composition in the investigated surface region. The preferential sputtering of phosphorus and phosphorous oxide-P_2O_5 in the outer layer is responsible for the

decrease of P/Ga ratio under 0.5 following Ar^+ sputtering with 1÷5 keV for 5 minutes. The analysis is more sensitive for the minimum escape depth of the photoelectrons [11] that corresponds to a small TOA related to a small sampling depth.

In the energy range 1÷5 keV, the ratio $C_{P\ total}/C_{Gatotal}$ indicates a preferential sputtering of P. Consequently, there is a Ga rich surface.

After the performing of an "in situ" Ar^+ ion sputtering at 3 keV the ratio $C_{Ptotal}/C_{Gatotal}$ became 0.51, measured at TOA=20°, on GaP surface.

The chemical etching with H_2SO_4:H_2O_2:H_2O (3:1:1) removes both Ga and P, but more Ga than P, because P/Ga ratio is greater in outer layer (TOA=20°) than in the sub-surface region. Thus, the chemical etching removes rather the atoms of the element with metallic feature well established (group III).

The Ar^+ ion sputtering procedure is more efficient than the chemical etching for the removal of the oxides from surface. The chemical etching and the exposure to air involve the growth of oxides on chemically unstable semiconductor surfaces.

The atomic ratio P/Ga in GaP(111) surface does not change significantly after Ar^+ ion sputtering process in the energy range (3÷5) keV. The stoichiometry is restored by successive chemical etching (e.g. H_3PO_4 85%) and light Ar^+ ion sputtering (1 keV energy) (Fig. 9).

4. Conclusions

The XPS analysis was performed on native oxidized, chemical etched and Ar^+ ion sputtered n-GaP surfaces in order to detect the effects of the cleaning procedures on the atomic composition of surfaces.

There were investigated only the outer chemically altered layers by evaluation of P/Ga ratio.

A native oxide layer is always present on the surface of the naturally stored GaP sample. The surface native oxide is composed a mixture of Ga_2O_3 and P_2O_5 phases. The concentration of Ga oxide is greater than that of P oxide and as a consequence it results a Ga enrichment of the air-exposed GaP surface. The Ar^+ ion sputtering in the energy range 1÷5 keV for a time t=300 seconds removes more efficiently the oxides from the semiconductor surface than the chemical etching. Above 3 keV Ar^+ ion energy the oxide layer is roughly totally removed and sputtering procedure is less justified.

The experiments of Ar^+ ion sputtering indicate that in the outer layer the concentration ratio $C_{Ptotal}/C_{Gatotal}$ tends to decrease bellow 0.5, as a consequence of the Ga enrichment of the surface because of the preferential removing of the Phosphorus from GaP surface.

The chemical etching procedure using H_2SO_4:H_2O_2:H_2O (3:1:1) for t=300 seconds removes the oxide layer from the GaP(111) surface. The oxide layer of GaP native surface is Ga-rich, and consequently the surface after the outer layer has been removed is P-rich. The etching rate of the acid (1 μm/5 min) [12] is generally high, hence both the oxide layer and the P–rich region will be removed during wet etching process.

After the etching (H_3PO_4) 85%, the P oxide is removed from surface oxide layer less than in the case of etching with H_2SO_4:H_2O_2:H_2O (3:1:1).

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