

XPS study of Ti/oxidized GaAs interface

R. V. GHITA*, C. LOGOFATU, C. NEGRILA, A. S. MANEA, M. CERNEA, V. CIUPINA^a, M. F. LAZARESCU

National Institute of Materials Physics P.O. Box MG 7, Magurele, Bucharest, Romania

^aDepartment of Physics, "Ovidius" University of Constanta, RO-8700, Constanta, Romania

X-Ray Photoelectron Spectroscopy (XPS) analysis was performed on Ti/oxidized GaAs. This interface is prepared by chemical etching in a mixture of reagents, followed by a vacuum deposition of a nanometer Ti layer. The surface sensitivity of XPS (typically 40-100 Å), makes the technique ideal for the measurements of oxidation states and oxide layer thickness on III-V compounds. The study of Ti/oxidized GaAs put into evidence a lack of stoichiometry at the semiconductor surface due to the presence of a volatile element (As). At the interface Ti/Oxide/n-GaAs common oxides are present: Ga₂O₃, As₂O₃ and As₂O₅, together with titanium oxide. The XPS spectra recorded on the sample surface sputtered with 5 keV Ar⁺ ions (in two steps: t = 15 min, t = 45 min) were analyzed using SDP subroutines program facilities. The As signal at the interface after t = 15min plasma etching is related to GaAs, As₂O₃ and over 40% from a GaAs oxidation complex or due to inter-metallic oxide of Ti. After the last plasma etching at the surface of GaAs the stoichiometry was demonstrated: the signal of As and Ga arises commonly from GaAs. It was remarked a broader titanium line profile, which arises from titanium oxide and from different intermediate states at the interface.

(Received October 14, 2005; accepted January 26, 2006)

Keywords: X-Ray photoelectron spectroscopy, Chemical etching, Oxidation states, Plasma etching

1. Introduction

Soft X-ray Photoelectron Spectroscopy is one of the most important techniques for the study of metal/semiconductor contacts. One of its greatest assets is that it allows sampling of both the composition and the electronic structure of an interface in the same experiment. Soft X-ray Photoelectron Spectroscopy is one of the most important techniques for the study of metal/semiconductor contacts. The surface sensitivity of XPS, which is typically 40-100 Å, makes the technique ideal for measurements of oxidation states and oxide layer thickness on III-V compounds and other semiconductor materials.

From a basic point of view the XPS works by sending massive amounts of photons toward the sample to produce a large number of photoelectrons and comparing the kinetic energy with the initial energy of the photon. The difference is accounted for the amount of attraction the electron has with the nucleus to remove it (binding energy) and the amount of energy the particle loses in transit from the sample to the analyzer (work function). The electrons of atoms that are photo emitted remain within a range of binding energies to help identify the specific element within the sample. Different types of bonds affect where in the range these binding energies fall, creating a "chemical shifts" which acts as another part of the compound's fingerprint. Comparing the results of an unknown sample to those of other known standards leads to the identification of a compound or at least an idea of what sort of structure is present.

Gallium arsenide is perhaps the most popular compound semiconductor material, and it does not have a natural oxide. Also, the vapor pressure of arsenic oxides is much larger than those of Ga, hence oxidation in GaAs is much more complicated than in silicon. From this point of

view, Spicer [1] has argued that the simple process used to passivate silicon is the exception rather than the rule in semiconductor surface passivation chemistry, and he suggests that a more elaborate procedure may be required for the passivation of compound semiconductors. The interface between compound semiconductors such as GaAs and its oxides could exhibit a large number of chemical and structural configurations [2].

In a previous work [3] we have investigated the rectifying contact Au-Ti/GaAs (SI) deposited by thermal evaporation. Titanium lies on the top of GaAs and the chemical interaction between Ti and substrate suggests that titanium forms inter-metallic compounds with As and Ga.

The present work is concerned with the characterization of GaAs:Ti oxidized surface and the interface obtained by Ti thin film deposition on this wafer. The practical goal is to obtain a good Schottky contact for Ti/GaAs(SI). The elemental oxides of GaAs have different heats of formation, chemical potential, diffusion rates, solid solubility and volatility [4]. These factors interact in a complex way during the growth of oxide layer and the metal/oxide/interface region [4]. The oxides and interfaces of GaAs change considerably with the method of oxidation, e.g. the electrical properties of the thermal oxide of GaAs and anodic oxide on GaAs. The oxide characterization employs acquisition of high energy resolution spectra of Ga and As photoelectron peaks plus the application of mathematical curve separation routines. When combined with reference data, the relative percentages of species as GaAs, Ga₂O₃, As₂O₃ and As₂O₅ on the surface can be determined. The form of Ga-As bonding in the oxide, could be important in determination the insulating quality of the oxide [4].

Surface midgap states in GaAs are known to pin the Fermi level and therefore impede the performance of metal

oxide semiconductor devices [5]. Bare arsenic atoms are thought to be one of the species present within the native oxide responsible for pinning the Fermi level [5]. Both As_2O_3 and Ga_2O_3 will form when a clean GaAs surface is exposed to oxygen and light. However, the formation of Ga_2O_3 is thermodynamically favored, leaving bare arsenic atoms embedded within the oxide near the oxide/GaAs interface. The As_2O_3 is also mobile at grain boundaries, resulting in a non-uniform oxide in which an As_2O_3 -rich layer is found near the oxide/air interface, and the bare arsenic atoms are found embedded within the Ga_2O_3 -rich layer near oxide/GaAs interface. Surface midgap states in GaAs are known to pin the Fermi level and therefore impede the performance of metal oxide semiconductor devices. Bare arsenic atoms are thought to be one of the species present within the native oxide responsible for pinning the Fermi level [6]. Both As_2O_3 and Ga_2O_3 will form when a clean GaAs surface is exposed to oxygen and light. The complicated chemistry of the GaAs native oxide has prevented the development of a simple and robust surface passivation scheme for this surface. XPS is a surface analysis tool that is well qualified to characterize cleaning processes. After cleaning in organic solvents and chemical etching in reagents the surface of GaAs:Ti (100) is contaminated with carbon. The air-oxidation for GaAs surfaces causes a large amount of defects and till now, there has been no report on the successful fabrication procedure for effective interface state, i.e free of detectable interfacial compounds [6]. The defective states are due to two different causes: i)-air oxidation of GaAs surface before Schottky metallization and ii) interfacial reaction during metallization.

2. Experimental procedure

The samples used in this experiment were (100) oriented, n-GaAs wafers uniformly doped with Te, with a carrier concentration of $\sim 10^{18}$ - 10^{19} cm^{-3} . Prior to metal deposition the GaAs was degreased employing a standard cleaning process using trichloroethylene and acetone. The wafer was chemical etched in $\text{HCl}:\text{H}_2\text{O}$ (1:1) for 30 sec and successively rinsed in deionized water for 1 minute. The result is the development of an oxidized interface at the contact surface of GaAs of the chemical reagents.

The metal (Au/Ti)/n-GaAs interface was fabricated by thermal vacuum deposition of Ti and Au on the top of the sample. The evaporation took place in high vacuum (8×10^{-5} Torr) in a geometry source-sample as follows: $R_{\text{Au}}=10^{-1}$ m, $R_{\text{Ti}}=4 \times 10^{-2}$ m. The samples were annealed in a furnace at low vacuum (10^{-1} Torr) in the temperature range 310 - 330 °C for $t \sim 10$ s. The thickness of Au-Ti deposited films was in the range of 30 nm for Ti and 200 nm for Au. Prior to XPS analysis the Au/Ti/n-GaAs was treated in $\text{KI}+\text{I}_2+\text{H}_2\text{O}$ for 80 min. and the result was an excellent image of Ti/GaAs clean interface. The XPS analysis was performed on a VG ESCA 3 MK II installation with X-rays emitted by an anti-cathode of Al at $E(K_{\alpha})=1486.7$ eV). The analysis chamber was maintained at ultra high vacuum ($p=3 \times 10^{-9}$ Torr) and the sample position was oriented at $\theta=45^\circ$ in respect to the analyzer. The XPS

registered spectrum involved a energy window $w=20$ eV with the resolution $R=50$ eV, and with 256 recording channels. The XPS registered spectra were processed using Spectral Data Processor v2.3 (SDP) software. In its structure the SDP soft uses for the deconvolution of the XPS line a specific ratio between the Lorentzian shape and Gaussian shape, and this characteristic ensures a good fit of experimental data. The Au/Ti/n-GaAs was exposed to plasma etching in a preparation chamber at the argon vapors pressure of $p(\text{Torr}) = (5 \times 10^{-6} - 3.5 \times 10^{-6})$, accelerated voltage for argon ions $E=(4-5)$ kV, focusing voltage $U_f = (3.4 - 5.2)$ kV, etching time $t = (15+30)$ min. The XPS analysis was performed after chemical etching of Au/Ti/n-GaAs and after plasma etching (PE) for the same sample.

3. Results and discussion

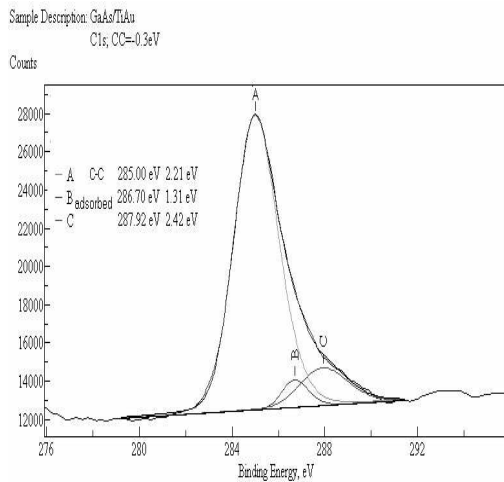
The XPS spectra recorded in ultra high vacuum give information regarding the nature of compounds in the interface region as well as the type of chemical bond taking into account the level for the photo-emitted electrons. The recorded signal has as a calibration line, the carbon 1s line of the energy 285 eV corresponding to C-C bond in an 83.6% proportion and in the proportion of 16.4% for the energy of 287 eV.

The energetic shifts in XPS spectrum indicates that Ga in GaAs has a positive charge while As has a negative charge in respect with elemental Ga and As. The chemical etching of n-GaAs in $\text{HCl}:\text{H}_2\text{O}(1:1)$ leaves behind an intense contaminated surface that contains two forms of As-excess, one As-elemental, the other oxidized. Due to this fact is important to establish the concentration ratio Ga/As in the oxide bulk.

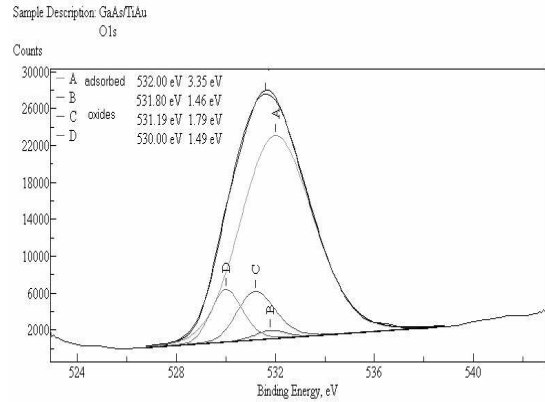
The migration of Ga to the surface implies that elemental As is left behind near the interface region, between the surface oxide layer and not-oxidized GaAs substrate [2]. The HCl solution dissolves the oxidized GaAs, exposing the excess of As at the interface. The aqueous solution then sequentially oxidize and dissolve the As in this region [2]. The reason for more nearly stoichiometric surfaces (i.e equal Ga and As concentrations) is at least partly related to the nearly equivalent solubilities of Ga and As oxides in HCl basic solution. Before the XPS analysis, there was deposited the Au-Ti film by thermal vaporization on clean surface of n-GaAs (100) wafer in the section Au/Ti/Oxidized GaAs.

The valence-band region, present in the range (0-17) eV, is composed of Ga and As derived 4s and 4p bands. The shape of these features serves as a convenient fingerprint for identifying bulk GaAs [2]. In order to identify the chemical nature of the surface species it is important to determine their oxidation states. The XPS spectra were recorded in the range of C(1s), O(1s), As(3d), Ga(3d) and Ti(2p) core-level photo-emission lines for the as prepared sample. The C(1s) peak shapes are complex as presented in Fig.1a and different carbon species being located at 285 eV-predominant peak for BE calibration, C-C bond, and two peaks at 286.7 eV and 287.92 eV

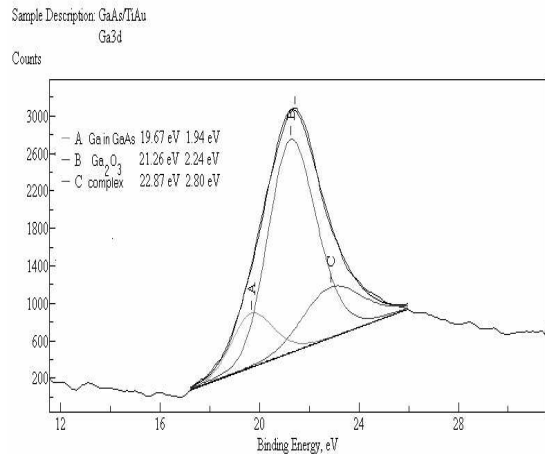
attributed to adsorbed species. The deconvoluted spectrum of O(1s) is presented in Fig.1b and it is based on four peaks, namely: first at BE 532 eV attributed to adsorbed oxygen to the surface in a 79.3% ratio and the others at BE 531.19 eV, 531.80 eV, 530 eV attributed to oxygen in oxides (O in Ga₂O₃ and O in arsen oxides) in a 20.7% ratio. From As(3d) and Ga(3d) spectra we found the contribution presented in Fig.1c and Fig.1d. The 41.61eV attributed to elemental As from GaAs (9%) and at higher BE peak of 44.32 eV attributed to As₂O₃ (11%) and As₂O₅(45.86 eV)-proportion ratio 80%. The 19.57 eV peak is attributed to elemental Ga in GaAs (35%) and at higher BE peak 21.26 eV Ga in Ga₂O₃ (51%), also at BE 22.87 eV an unknown compound, probably Ga-Ti complex in a 14% proportion ratio. The Ti (2p_{3/2}) and Ti(2p_{1/2}) spectrum is characteristic for the asymmetry of a transition metal and has the following proportions: BE:459.08 eV (65.6%-2p_{3/2}), BE:464.73 eV (34.4%-2p_{1/2}). The surface of GaAs substrate has been prior to Ti vacuum deposition chemical etched in HCl:H₂O, the oxidized species developed at Ti/GaAs interface contain elemental As and Ga as detected by XPS. The oxidized surfaces species being an insulator may not be in an electrical equilibrium with the semiconductor substrate i.e. their Fermi levels (really quasi-Fermi levels, one for electrons and one for holes) need not be aligned. The elemental As from the crystal may be a semimetal (crystalline phase) or a semiconductor with a gap 1.1 eV (amorphous), so the elemental As at the interface oxide/GaAs is not necessarily a metallic form that introduce the interface states at the middle of the gap (E_g). The elemental oxides of oxide/GaAs interface have different heats of formation, chemical potentials, diffusion rates and solubilities. These factors interact in a complex way during the development of oxide layer and metal/oxide interface region /3/. In XPS analysis the X-ray beam causes a small damage of the sample, but the electrons that escape cause a electrical charge of the insulating oxide films.



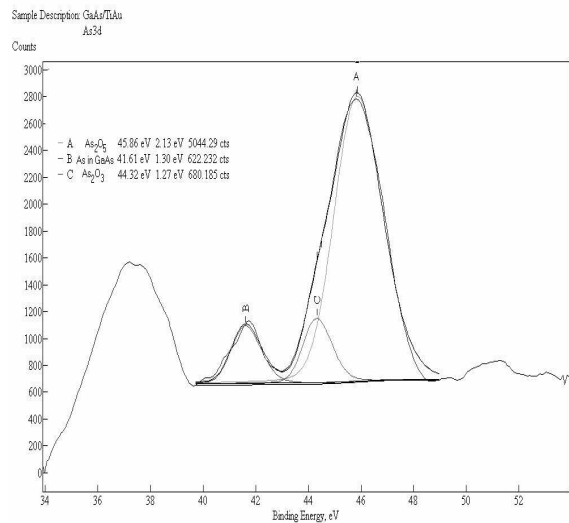
a



b



c



d

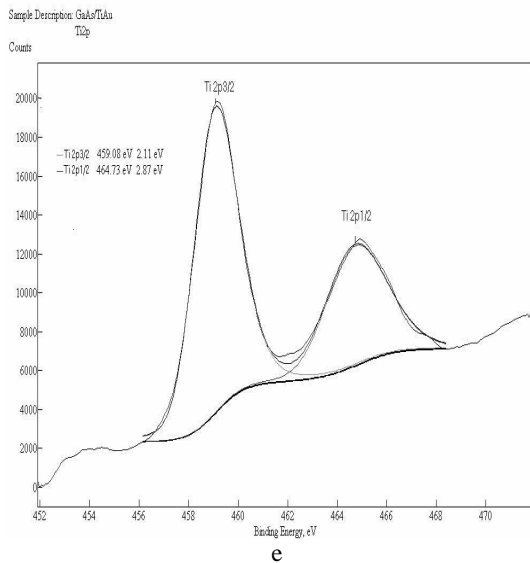
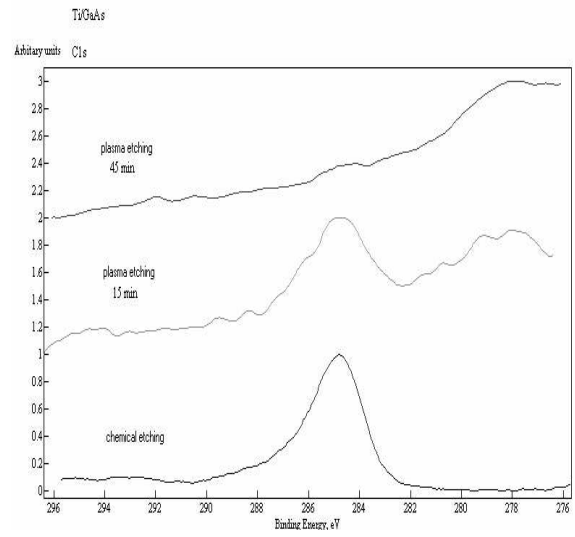
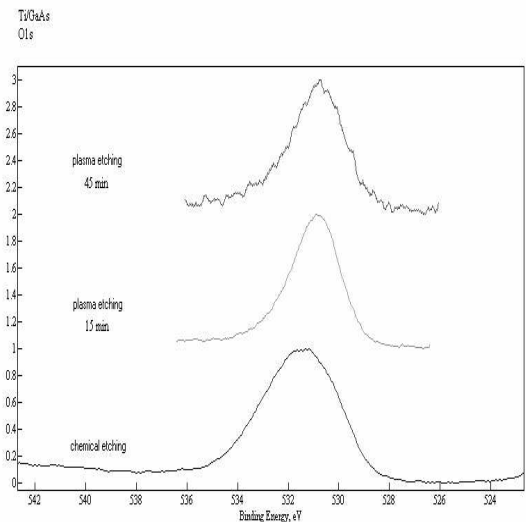


Fig. 1. XPS spectra of C(1s), O(1s), As(3d), Ga(3d), Ti(2p) as registered and after SDP deconvolution.

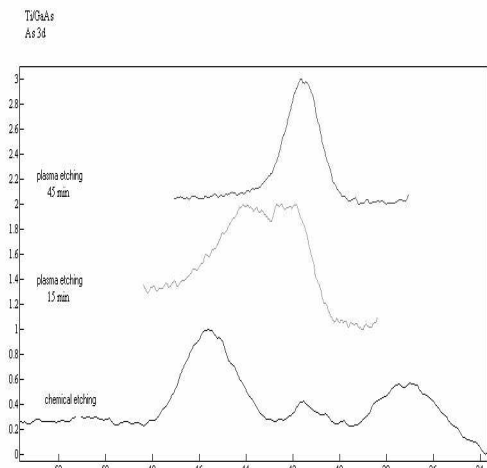
In Fig. 2, there are presented the superimposed normalized spectra for Ti/oxidized GaAs after plasma etching in two steps of 15 and 45 minutes. For the XPS normalized spectrum in the case of Carbon line, it is observed a decrease of signal intensity that corresponds to a decontamination of the surface for the main bond C-C. The analysis for the normalized spectra for Oxygen indicates that after 15 PE the adsorbed oxygen is in the ratio of 29%, the oxygen bounded to As is in the ratio of 35% and Oxygen bounded to Ga is in the ratio of 37%. After 45 minutes of PE the corresponding signals indicate 52% oxygen bounded to As and 48% Oxygen bounded to Ga, in this stage it disappears the adsorbed species. For As (3d) signal after 15 minutes of PE the composition indicates the presence of 33% As in GaAs, 25% As in As_2O_3 and for the lines of 42.7 eV and 43.8 eV, in proportion of 19% and 23% respectively, there exists a complex oxide as $GaAsO_3$ or inter-metallic oxide of Titanium. After 45 minutes of PE As signal arise only from GaAs. For the Ga(3d) signal, after 15 minutes of PE the composition indicates the presence of 14% Ga in GaAs, 66% Ga in Ga_2O_3 and the proportion of 20% arise from an unidentified specie. After 45 minutes of PE Ga signal is due only to GaAs. In the case of Titanium signal (2p) for the as-deposited sample the signal is due in proportion of 66% from TiO_2 . After 15 minutes of PE there appear some oxidized interface states, possibly inter-metallic oxidized compounds, and after 45 minutes of PE 63% is the signal of TiO_2 , and the remaining is due to the oxide compounds. Regarding the general signal of titanium (as observed in Fig. 2) we remark a relative increase of concentration and a broader signal profile is broader. As a general remark the titanium signal is related to different oxides compounds, and the reaction for leading to a stable TiAs compound does not take place.



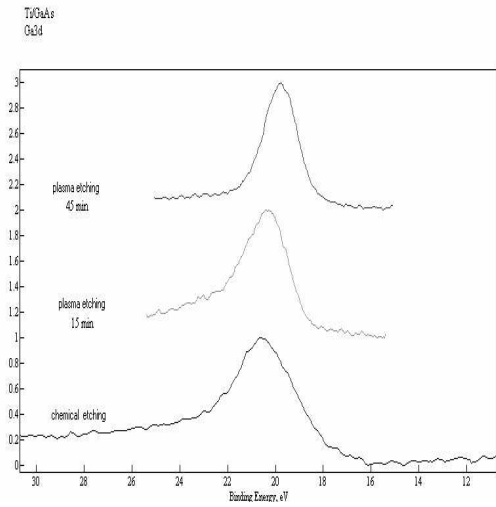
a



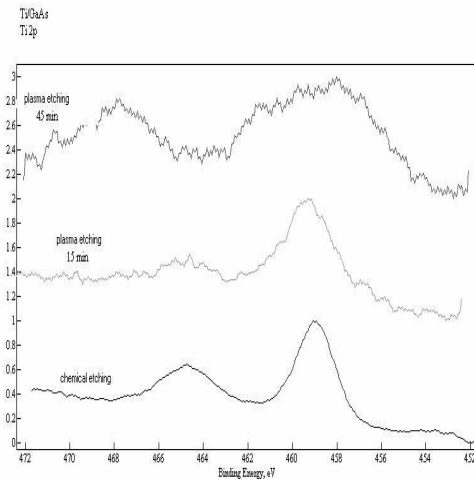
b



c



d



e

Fig. 2. The superimposed XPS spectra for C(1s), O(1s), As(3d), Ga(3d), Ti(2p) before and after plasma etching.

In Table 1 there is presented the initial surface composition for the as deposited Ti/GaAs, then it follows the composition after plasma etching (PE) for 15 minutes and 45 minutes. The first initial surface composition indicates a lack of stoichiometry in the ratio Ga/As probably due the volatile behavior of As, the ratio is near one after 15 minutes PE and is around 2 after 45 minutes PE, indicating a loss of As at the etched surface.

Table 1. Surface composition ratio Ti/GaAs.

	Ga, (%at.)	As, (%at.)	Ti, (%at.)	O, (%at.)	Ga/As
as prepared	13.4	6.5	8.1	72	2.06
15 min PE	14.8	11.9	18.3	54	1.244
45 minPE	18.3	10.6	46.6	24.5	1.726

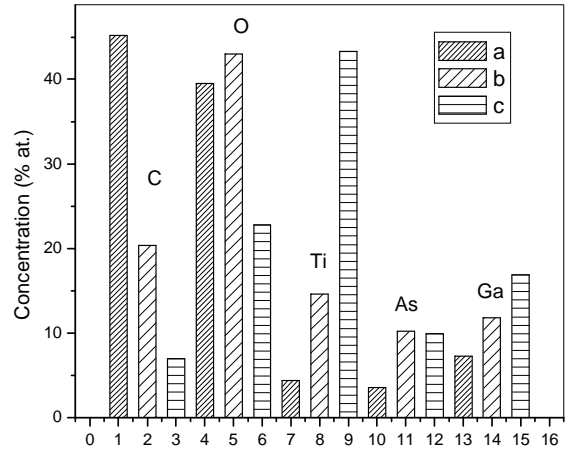


Fig. 3. The histogram of surface concentration. a - after chemical etching b - plasma etching: 15 min. c - plasma etching: 45 min.

The histogram for composition ratios in Ti/Oxidized GaAs is presented in Fig. 3. It is remarkable for the three cases (a, b, c) a constancy in As concentration after PE, and an increasing tendency for Ga concentration at the surface. The Ti concentration is increasing at the surface from the moment of deposition to last PE. The oxygen concentration is relatively constant for case 'a' and 'b', and is decreasing in the case 'c' as the oxides on the surface disappear due to plasma etching. The C concentration indicates a decontamination of the surface due to plasma etching.

4. Conclusions

It is known that XPS analysis provides important information on Ti/oxidized GaAs interface. The data regarding the nature of chemical bonding provided by XPS are essential to the determination of chemical state of the interface. The Ga 3d and As 3d photo lines at binding energies of 19.67 eV and 41.61 eV respectively also serve as convenient signatures for bulk GaAs. The energetic shifts in XPS spectrum indicates that Ga in GaAs has a positive charge while As has a negative charge in respect to elemental Ga and As. The relative percentage of species as Ga₂O₃, As₂O₅, As₂O₃ on the surface can provide useful information on the surface stoichiometry. At the interface Ga/As ratio is far from stoichiometry. For Titanium the 2p principal signal is related to oxidize species as it follows: 459.08 eV (TiO₂), in a concentration ratio of 66%, and 464.73 eV for other oxides species. The interface Ti/oxidized GaAs was exposed to plasma etching (PE) in argon atmosphere, and the result was the establishment of a ratio Ga/As near 2 at the interface together with a broader titanium line profile corresponding to an increase of titanium concentration at the surface. After PE the Ti signal indicates the possible existence of inter-metallic oxidized compounds.

References

- [1] W. E. Spicer, A. M. Green, *J. Vac. Technol. A* **11**, 1061 (1993).
- [2] C. C. Chang, P. H. Citrin, B. Schwartz, *J. Vac. Sci. Technol* **14**(4), 943 (1977).
- [3] R. V. Ghita, C. Logofatu, C. Negrila, A. S. Manea, M. Cernea, M. F. Lazarescu, *J. Optoelectron. Adv. Mater.* **7**(6), 3033 (2005).
- [3] C. W. Wilmsen, R. W. Kee., *J. Vac. Sci. Technol* **15**(4), 1513 (1978).
- [4] Ting Hou, C. Michael Greenlief, Steven W. Keller, Louis Nelen, John F. Kauffman, *Chem. Mater* **9**, 3181 (1997).
- [5] Min-Gu Kang, Ji-Wan Kim, Hyung-Ho Park, *Jpn. J. Appl. Phys.* **39**, 7003 (2000).

* Corresponding author: ghitar@infim.ro