

Evolution of surface oxides on GaAs

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A real GaAs surface is covered with a relatively thick layer (a few nanometers) of native oxide. As_2O_3 , As_2O_5 , and Ga_2O_3 will form when a clean GaAs surface is exposed to air and light. It was put into evidence the presence of a Ga-As-O precursor oxide in an XPS measurement on native oxide at room temperature. An extended ARXPS study on native oxide on GaAs was performed for native oxides. The influence of thermal treatment on native oxides was put into evidence by an ARXPS study from Room temperature to 700°C. In the thermal evolution of As and Ga oxide is observed the disappearance of As oxide at 400°C and the Ga oxide at 700°C. The spectral data in ARXPS analysis indicated the same evolution for As and Ga oxides.

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1. Introduction

Among the III-V semiconductor compounds, GaAs is one of the most studied due to its importance in modern microelectronics and optoelectronics applications. As a result of its success in the production of infrared and visible semiconductor lasers, this material has opened up potentially huge markets in optical communications, compact disc and related data storage, lighting and display technologies [1]. It was thought in the '70-'80 that lattice matching was fundamental in making lasers, but at the beginning of '90 [2, 3] it was shown that the layered structures with an important lattice mismatch (>1%) have advantages in semiconductor strained-layer superlattices and conducted to even better lasers. The properties of these characteristic structures depend on the composition of the layers, but the composition changes in particular in the surface region as a result of processing as chemical cleaning, plasma etching, and ion beam sputtering.

The GaAs surfaces have been studied for a long time, but the difficulties in the interpretation of these compositional changes still exist. A real GaAs surface is covered with a relatively thick layer (few nanometers) of native oxide which generates a high density of surface states $N_{SS} \sim 10^{12} \text{ cm}^{-2}$ pinning the surface Fermi level within the band gap of the semiconductor. On GaAs surface both As_2O_3 and Ga_2O_3 are formed when a clean GaAs wafer is exposed to air and light as is stated in literature [4]. The formation of Ga_2O_3 is thermodynamically favored [5] and results in the reaction:



leaving bare arsenic atoms embedded within the oxide near the oxide/GaAs interface. The arsenic oxide As_2O_3 is also mobile at grain boundaries [6.7] 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 the oxide/GaAs interface. The Ga_2O_3 and As_2O_3 are somewhat soluble in water, and their solubilities are dependent on pH. The complicated chemistry of the Ga and As oxides has prevented the development of a simple and robust surface passivation scheme for this surface.

The effect of the variation of Ga/As ratio on GaAs (100) starts from a previous attempt [8]. As it was observed [9] in the case of chemical etching, the surface is enriched in As atoms and Ar^+ ion sputtering has a reverse effect of depletion the surface in As atoms. As a result, the combination of these two etching techniques will conducted to a nearly stoichiometric surface but with a high degree of disorder.

This paper presents an extended Angle-Resolved X-Ray Photoelectron Spectroscopy (ARXPS) on native oxide on GaAs including the study of thermal treatment for GaAs at relatively high temperature (100- 650)°C.

This attempt is related to the possibility of using GaAs wafers as "epiready" substrates meaning that GaAs substrates can be used for device processing with no further treatment. The study of GaAs oxides evolution on the surface is a part of the effort in literature [10, 11] to understand a non-stoichiometric final surface with a Ga excess. The stoichiometric surface is a requirement for preparing the wafer before use, and includes degreasing, etching, rinsing and drying. The GaAs surface has to be deoxidised and annealed before growth process. The GaAs storage in laboratory condition is affected by an increase of the oxide thickness with time that can affect the operation condition for a device (e.g. laser diode device where the mirror of GaAs affects the operating power by facet oxidation [12]).

In this paper there is presented a protocol of experiments for deoxidation of GaAs using chemical etching in HCl (that removes As_2O_3 and Ga_2O_3 from the wafer) and thermal treatment up to 650°C. In this view is presented an extended Angle-Resolved X-Ray

Photoelectron Spectroscopy (ARXPS) on native oxide on GaAs including the study of thermal treatment as mentioned for GaAs at relatively high temperature range (100- 650)⁰C.

2. Experimental

The experiments were performed on n-GaAs(100) Te doped ($n \sim 10^{18} \text{ cm}^{-3}$) wafers. Prior to XPS analysis the GaAs wafers were washed in alcohol and rinsed in deionised water (DIW). The n-GaAs(100) maintained the initial aspect of the optical polished front surfaces. The wafers suffered a thermal treatment in ultra high vacuum (10^{-9} mbar) in the temperature range (room temperature-700⁰C) maintained at each temperature step for $t=30$ min. and then, they were measured after cooling at room temperature in a XPS system. At a take-off angle $\text{TOA}=30^0$ it was followed the effect of heating upon the native surface oxides on GaAs.

In order to understand the evolution of native oxides on GaAs *n* and *p* surfaces the as received wafers were subjected to a XPS analysis, then the wafers were exposed to a chemical etching in HCl:H₂O (DIW) for 5 and 15 seconds, and then, to a thermal treatment at 350⁰C in high vacuum (10^{-8} torr).

Measuring the thickness of the native amorphous oxide layer on top of semiconductor GaAs wafer may be achieved by transmission electron microscopy (TEM) imaging on a cross-section specimen cut from the wafer. A cross section specimen has been prepared from a GaAs(100) wafer by mechanical grinding and lapping on the two sides of the assembled sandwich followed by ion milling at low incidence angle (7 degrees) and 4 kV ion accelerating voltage in a Gatan PIPS installation. The ion milling procedure has been ended with a fine milling step at low voltage (2 kV) in order to remove the ion milling induced amorphous layer enveloping the surfaces exposed to ion beams. The TEM observation of the prepared specimen has been performed on a JEOL 200CX electron microscope operated at 200 kV.

The XPS recorded spectra were obtained using a SPECS XPS spectrometer based on Phoibos analyzer with monochromatic X-rays emitted by an anti-cathode of Al (1486.7 eV). The hemispherical analyzer operated in the constant-energy mode with a pass energy of 5 eV, giving an energy resolution of 0.4 eV, which was established as FWHM (full width half maximum) of the Ag 3d_{5/2} peak. The analysis chamber was maintained at ultra high vacuum conditions ($\sim 10^{-9}$ mbar). The recorded XPS spectra were processed using Spectral Data Processor v 2.3(SDP) software. The good fit of experimental data is ensured by a specific ratio between a Lorentzian and Gaussian shape in the deconvolution of XPS peaks. The TOA angles in the ARXPS measurement varied from 90⁰ to 15⁰ and as a result the surface sensitivity was increased, together with the analysis of surface oxides on GaAs.

3. Results and discussions

In Fig.1(a-b) is presented the cross-section TEM images of GaAs surface obtained at different magnifications and for a better observation of the amorphous surface layer, the cross-section specimen has been tilted in the microscope so that the crystalline sample shows a strong diffraction contrast. This way, one can clearly notice the interface between the crystalline GaAs and the amorphous layer on the surface. One can notice the roughness of the crystalline GaAs wafer and the amorphous band (arrowed in the images) with a rather constant thickness (about 2 ± 0.3 nm) running along the surface.

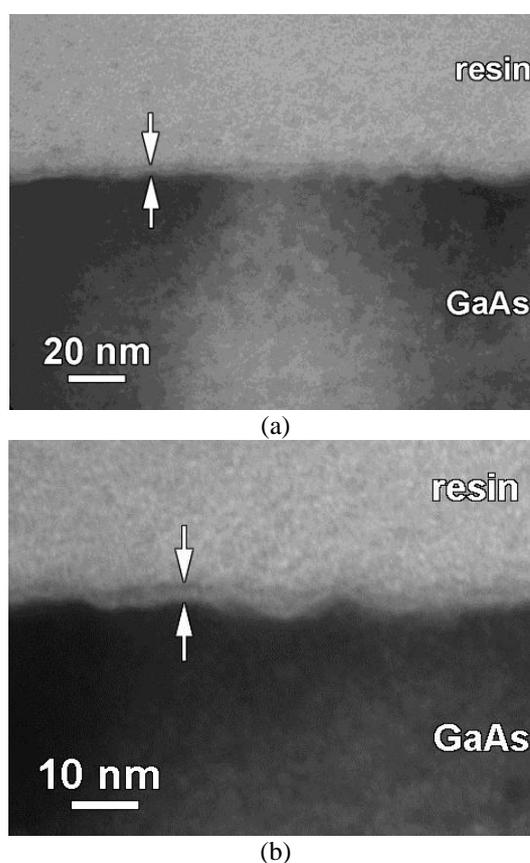


Fig. 1. Cross-section TEM images of the GaAs surface at lower (a) and higher (b) magnifications showing the presence of an amorphous layer on the surface (indicated by the vertical arrows).

The roughness of the surface native oxides on GaAs is presented in an Atomic Force Microscopy (AFM) analysis as it was performed on native sample of p-GaAs (100), cleaned wafer, chemical etched wafer and thermal treatment wafer at 500⁰C. The AFM images are as follows in Fig. 2 (a-d)

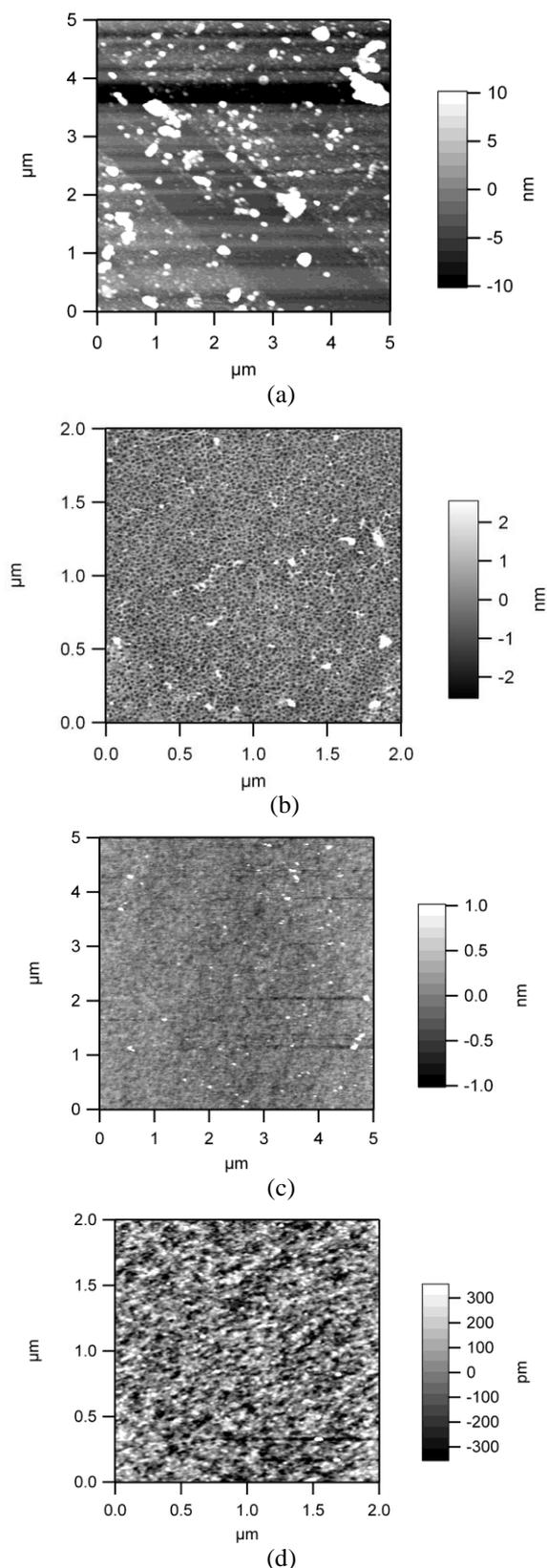


Fig. 2 AFM images for p-GaAs(100): (a)-as received surface; (b)-cleaned in organic solvents; (c)-chemical etched; (d)-thermal treated at 500°C

The characteristics of AFM analysis are : (a) –surface area -25.6 μm^2 , RMS-11.7 nm; (b)-surface area-4.0 μm^2 , RMS-1.03 nm; (c)-surface area-25 μm^2 , RMS-284.3 pm; (d)-surface area-4.0 μm^2 , RMS-207.1 pm. As can be observed the quality of the surface is improved as long as the native oxides on the surface are removed.

In the Fig.3 (a-b) there are presented the main peaks of As 3d and Ga 3d as they have been recorded on a native oxidized sample of GaAs(100) at room temperature(RT) and at a TOA=30°. As can be observed for As 3d the deconvolution curves are as follows: 1-BE:40.79 eV As 3d5/2 corresponding to As in GaAs; 2-BE:41.55 eV As 3d3/2 corresponding to As in GaAs; 3-BE:42.19 eV corresponding to As-Ga-O an oxide precursor; 4-BE:44.12 eV corresponding to As₂O₃; 5-BE:45.07 eV corresponding to As₂O₅. The deconvolution curves for Ga 3d are as follows: 1-BE: 19.32 eV Ga 3d3/2 corresponding to Ga in GaAs; 2- BE: 20.13 eV corresponding to Ga-As-O an oxide precursor; 3- BE: 20.81 eV corresponding to Ga₂O₃. For the signals of 3d electrons the free medium pass is around 30Å and at the most favorable TOA are coming out from a deep pass of 100Å, it is interesting to observe that 10% of XPS signal is coming out from a Ga-As-O form of an oxide precursor.

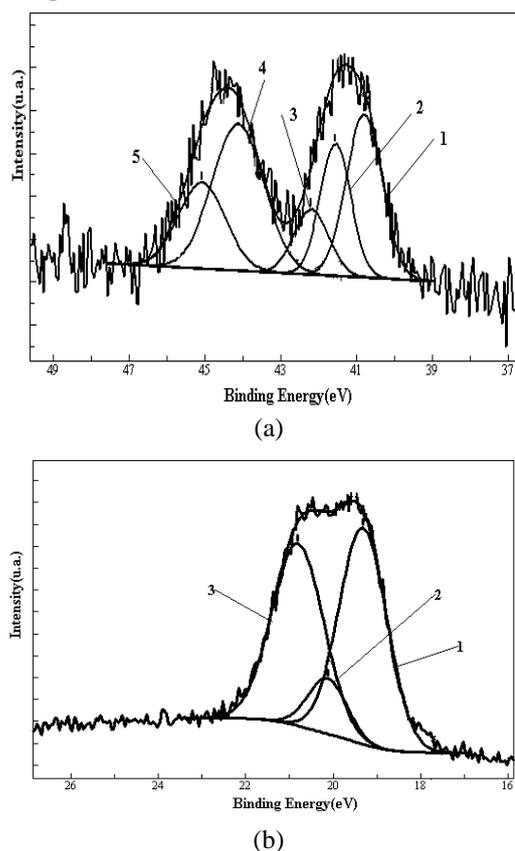


Fig.3 a-As (3d) signal and b- Ga (3d) signal on native oxidized GaAs

In Fig.4 we present the results of ARXPS spectra regarding the overall concentrations of C, O, Ga_{total} and As_{total} for the native oxide at RT. As can be observed at TOA=15° the surface information is the most sensitive, that means the signal for Carbon contamination is really

high and the As and Ga oxides have almost the same concentration of Carbon.

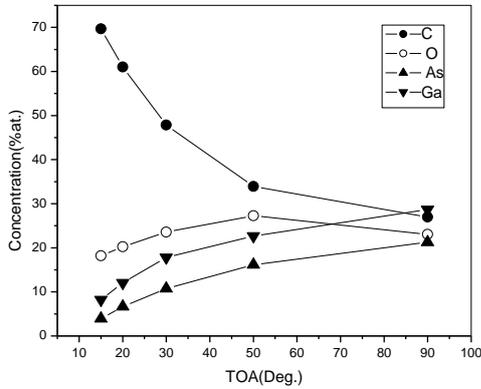
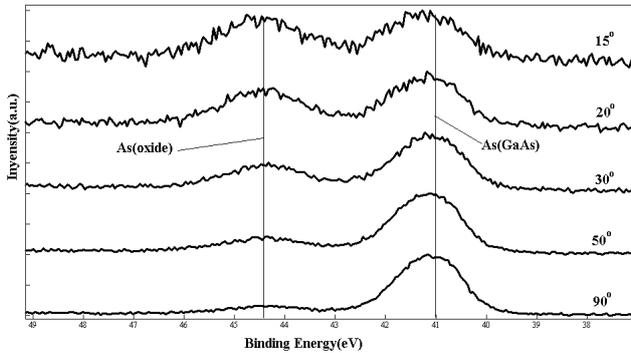


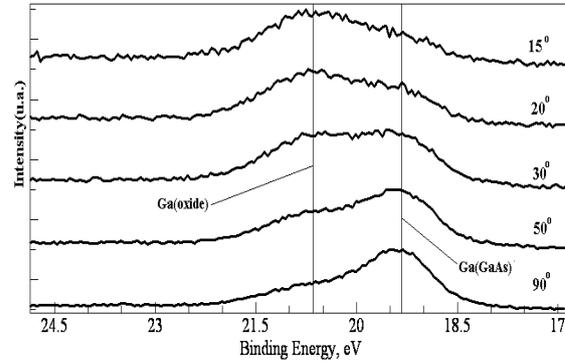
Fig.4 –Concentration for C (1s), O(1s), As (3d), Ga(3d) in native oxide on GaAs

In Fig.5 (a, b) there are presented the super imposed spectra for As 3d and Ga 3d for different TOA . As can be observed at TOA=90° the As and Ga signal came from the bulk GaAs, and as the sensitivity is rising to the surface (TOA=15°) the signals from the As and Ga oxides are present and powerful.

In Fig.6 we present the evolution of As 3d and Ga 3d superimposed spectra with the temperature of thermal treatment at TOA=30°. For As 3d the XPS spectra starts at room temperature with a signal from As oxides and As from GaAs, as the temperature is rising the As oxide disappears, and at 400°C the signal is completely missing. At the last treatment temperature, namely 700°C, the only XPS signal is from As in GaAs. For Ga 3d the XPS spectra starts also from RT with a signal from Ga oxides and Ga from GaAs and as the temperature is rising the Ga oxides disappear and at the last thermal treatment temperature-700°C the only XPS signal is from Ga in GaAs.

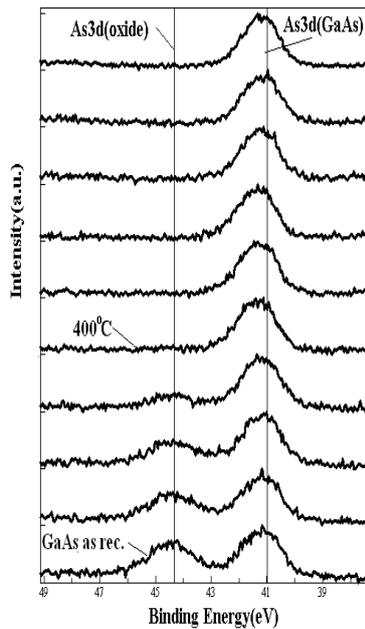


(a)

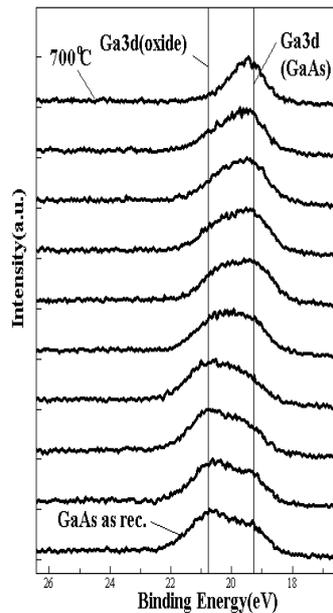


(b)

Fig.5 Evolution for ARXPS As (3d) and Ga (3d) spectra for GaAs and GaAs oxides



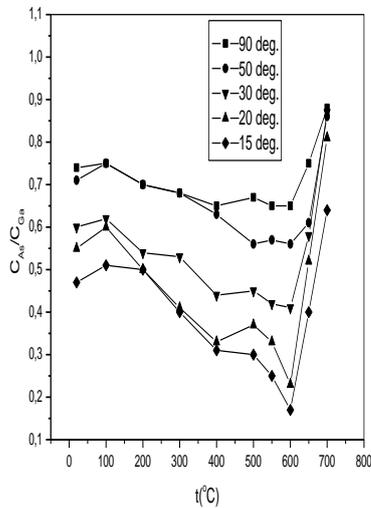
(a)



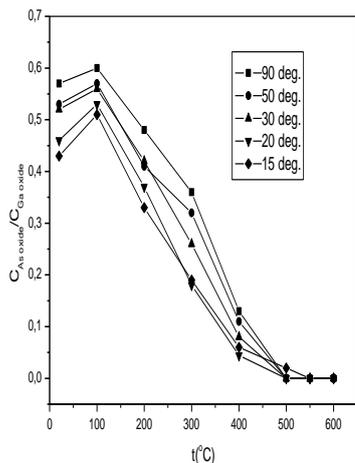
(b)

Fig.6- Temperature evolution for As (3d) and Ga (3d) spectra arising from oxides at TOA=30°

In Fig.7 (a) we present the evolution for Ga/As ratio with temperature and TOA. At the surface (TOA=15°) is present a slight enrichment in Ga atoms ($C_{As}/C_{Ga}=0.45$) and as the temperature is rising it appears a continuum lost of As atoms and at 600°C we have a strong evaporation of As and at 700°C the surface is enriched in Ga ($C_{As}/C_{Ga}=0.65$). The evolution presented is in the limit of experimental errors the same for the other recorded TOA. In Fig.7 (b) we present the evolution of the ratio $C_{As\ oxide}/C_{Ga\ oxide}$ for different TOA, at various temperatures. At the surface (TOA=15°) we have a Ga oxide ($C_{As\ oxide}/C_{Ga\ oxide} \sim 0.45$) and at 100°C we have a slight increase in As oxide and then it follows a continuum decrease in As oxide and at 500°C the As oxides is evaporated. In the experimental curves it is observed the same evolution for all the TOA of the XPS recorded spectra.



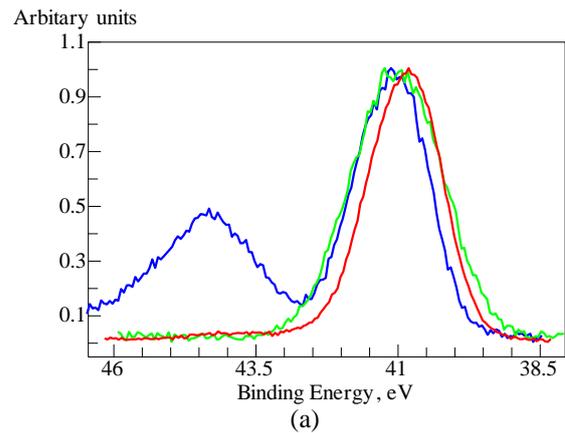
(a)



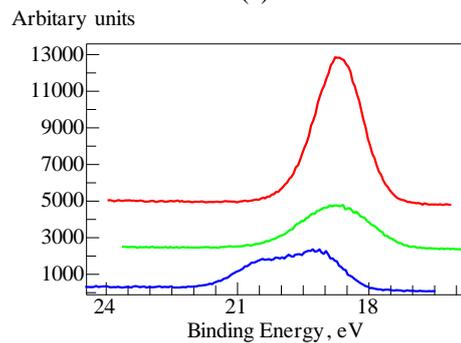
(b)

Fig.7 Temperature evolution for different TOA for (a) C_{As}/C_{Ga} and (b) $C_{As\ oxide}/C_{Ga\ oxide}$ (recorded As (3d) and Ga (3d) spectra)

The evolution of the native oxides on n-GaAs(100) and p-GaAs(100) can be observed in parallel from as received sample, chemical etched for 5 and 10 seconds and thermal treated at 350°C in high vacuum (10^{-8} torr). Initial oxidation of GaAs wafers appears at the arsenic sites [10] and this is a very rapid surface reaction, in few days As_2O_3 reaches 1-2 nm. From the overall XPS spectrum it is extracted the evolution of Carbon C1s and Oxygen O1s signal in the sense of the decreasing as a result of GaAs cleaning also for chemical etching and thermal treatment. It is worth to observe that that the oxygen signal is still present after etching due to the oxides presence and after thermal treatment we have a line at 532 eV for O adsorption on GaAs surface. In Fig.8(a,b) we present the evolution for Ga 3d and As 3d in n-GaAs at TOA=60°. As can be seen (Fig.8a) after chemical etching the signal for As oxides (blue line) in its most part vanishes as a result for oxide removal (it remains only few percent of oxide-green line) and after thermal treatment there exists only the signal from As in GaAs without the GaAsO phase (red line). In Fig.8(b) is presented the Ga signal, in this part after chemical etching there is no Ga oxide or GaAsO phase.



(a)



(b)

Fig.8 Evolution of oxides on n-GaAs after chemical etching and thermal treatment (a-As oxides; b-Ga oxides)

In p-GaAs the evolution of As and Ga oxides follows the same trend as in n-GaAs as can be observed in Fig.9 (a,b).

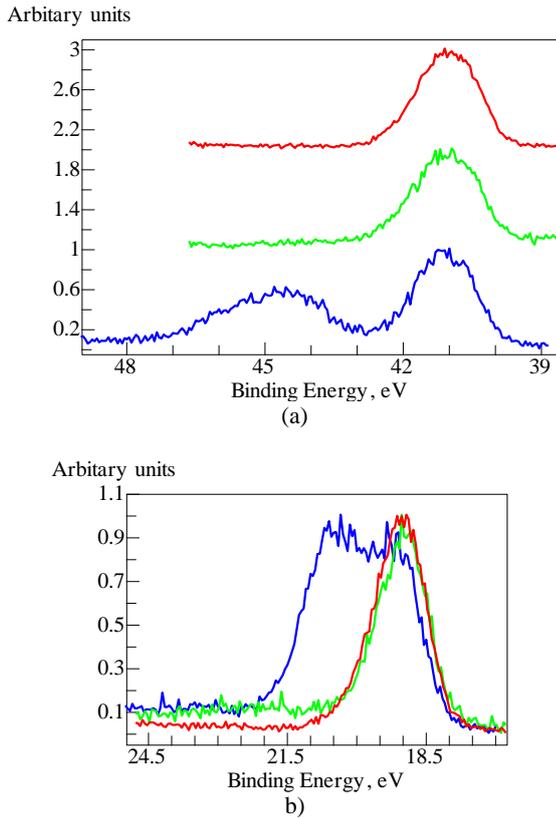


Fig.9 Evolution of oxides on p-GaAs after chemical etching and thermal treatment (a-As oxides; b-Ga oxides)

The As oxides after chemical etching are completely removed due to the increased reactivity of a polar etchant on positive charged surface. Thermal treatment does not change the curve aspect and as a general remark the GaAsO disappeared. As regards the Ga oxides after chemical etching and thermal treatment the Ga_2O_3 and GaAsO phase are removed from the surface.

As it was observed there were no defects on the GaAs surface related to high temperature annealing and also it was put into evidence the effects on decomposition of oxide films.

Extending the experiment for low temperature annealing and long treatment time as can be observed in Fig. 9 (a,b) and Fig. 10 (a, b), the As 2p line (As in oxide and As in GaAs) is sensitive to the surface composition. In this view over $400^\circ C$ the As oxide vanishes and $450^\circ C$ the gallium oxide starts its decomposition. After few hours (i.e. $t=3$ h) the Ga oxide disappeared. This experimental procedure represents a technological line for obtaining a clear surface ready for preparing ohmic or Schottky contacts.

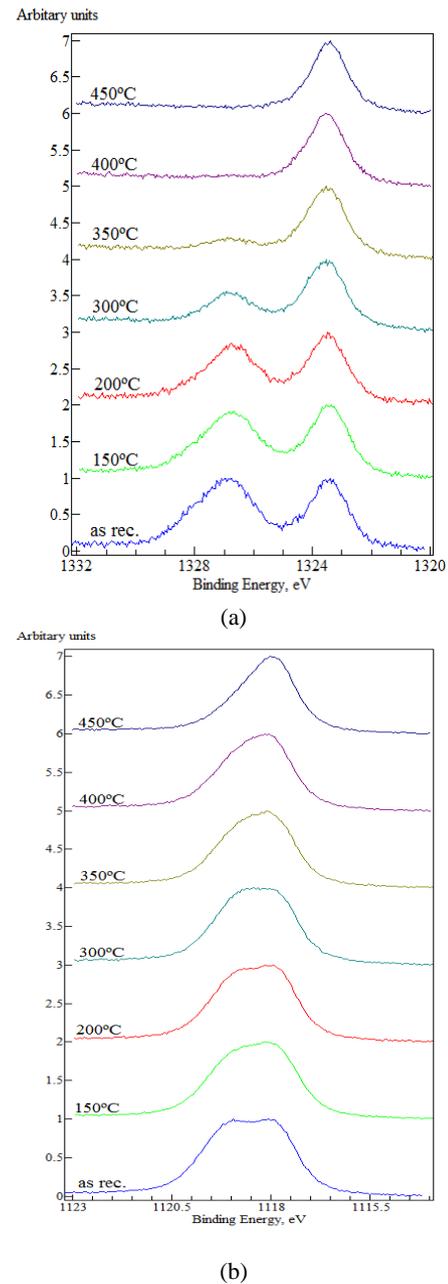


Fig.10- Evolution of oxides on GaAs for As $2p_{3/2}$ (a) and Ga $2p_{3/2}$ (b) for low temperature annealing and long treatment time

4. Conclusions

This work put into evidence the presence of a Ga-As-O oxide precursor in the deconvolution of As 3d and Ga 3d XPS spectra. The measurements at different TOA indicated that the most sensitive TOA as 15° , angle at which it was measured the concentration of As and Ga in native oxide. The surface sensitivity for As oxide and Ga oxide was put into evidence by an ARXPS measurement. The evolution from RT to $700^\circ C$ put into evidence the disappearance of As oxide at $400^\circ C$ and Ga oxide at $700^\circ C$ (TOA= 30°). At $700^\circ C$ the surface is enriched in Ga and it is observed from the evolution of $C_{As\ oxide}/C_{Ga\ oxide}$ a

continuum decrease in As oxide and at 600⁰C the As oxide is evaporated. The spectral data in ARXPS analysis indicated the same evolution for As and Ga oxides. In this paper is presented a protocol of experiments for oxide removing of GaAs using chemical etching in HCl:DIW (1:1) and thermal treatment up to 350⁰C in high vacuum. Is to be remarked that this experimental procedure conduced to a clean GaAs surface, prepared for different deposition as epitaxial or ohmic and Schottky contacts.

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