X-RAY PHOTOELECTRON SPECTROSCOPY STUDY ON n-TYPE GaAs

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A surface characterization has been performed on *n*-type GaAs (Si: GaAs) samples by using x-ray photoelectron spectroscopy (XPS) technique in order to get information on the degree of surface contamination during the device processing steps. The GaAs samples were etched by "in situ" ion sputtering (Ar plasma) before and after carrying out the measurements. According to XPS measurements the native oxide layer on as-received surface contains As2O3, As_2O_5 and Ga_2O_3. Large amounts of C and O are also present at surface before plasma cleaning of surface: C-C bonds, chemisorbed oxygen atoms. The XPS spectra recorded on the surface sample sputtered with 5 keV Ar^+ ions were analyzed using SDP subroutines program facilities. After the first sputtering step it was observed different shifts of the principal peaks of GaAs bonding and compounds together with a modification of the relative peak intensities. The C1s and O1s peak size decreased but remained still significant. The following sputtering steps lead to a drastically decrease of C and O peaks down to the noise level.

1. Introduction

GaAs is used as a basic material for high-speed electronic and optoelectronic devices. The performances of these devices are strongly dependent on substrate surface quality. In the case of GaAs, the major problem is the presence of the native oxide layer and oxygen and carbon contamination [1,2]. In order to improve device performances, passivation of GaAs surface defects is one of the most important issues to be solved [3-5]. Therefore, the present work is concerned to obtain detailed informations on compositional and chemical-state as regards the surfaces and any treatment-induced. The surface compositions of polished, air-exposed, solvent cleaned, and sputtered, Si: GaAs, samples have been examined using x-ray photoelectron spectroscopy. This it is an important technique for the study of material surfaces, and interfaces. The surface sensitivity of XPS, which is typically of 40-100 Å, makes the technique ideal for putting in evidence the oxidation states and oxide layer thickness in III-V and other semiconductor materials [6]. The oxide characterization needs the acquisition of high-energy resolution spectra of C1s, O1s, Ga3d and As3d photoelectron peaks and the application of mathematical curve deconvolution routines. The relative percentages of the different chemical species can be determined. The obtained data indicate that the native oxide layer is complex, containing a significant amount of carbon and oxygen. Ion sputtering treatment resulting in significant changes at the surface, has been examined in this study. The results confirm the presence of a complex oxide structure with Ga_2O_3 just above the interface [7].

2. Experimental

Samples were prepared from (100) oriented n-type GaAs crystals doped with silicon to donor levels of about $1 \times 10^{18} cm^{-3}$. The test samples was chemically polished to remove surface damage and then subsequently ultrasonically solvent cleaned in acetone. XPS spectra were obtained with a VG

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ESCA 3 MK II spectrometer using monochromatized Al-K$_\alpha$ radiation (1486.6 eV). The analysis chamber was maintained at ultra high vacuum (p>>10^{-9} torr) and the sample position was oriented at $\theta = 45$ $^\circ$ in respect to the analyser. The XPS spectra were recorded with energy 20 eV window, 50 eV resolution, and 256 channels recordance. Data collection was accomplished using a computer-interfaced digital pulse counting system. The XPS spectra were processed using Spectral Data Processor v 2.3 (SDP) software which allow smoothing and deconvolution of the curve The-GaAs substrate was exposed to plasma etching in a preparation chamber at the argon pressure of about 5×10^{-6} torr, 5 kV accelerated voltage for argon ions and 4 kV focus voltage. As the standard practice in XPS studies the C$_{1s}$ line (285 eV) corresponding to the C-C bond has been used as BE reference.

3. Results and discussion

To determine the chemical species on the Si: GaAs surface, XPS spectra were recorded in the range of C$_{1s}$, O$_{1s}$, As$_{3d}$ and Ga$_{3d}$ core-level photo-emission lines. The de-convoluted spectra of C$_{1s}$, O$_{1s}$, As$_{3d}$ and Ga$_{3d}$ lines obtained from an as-received, solvent-cleaned GaAs substrate are shown in Figs. 1a,b, c, and d, respectively.
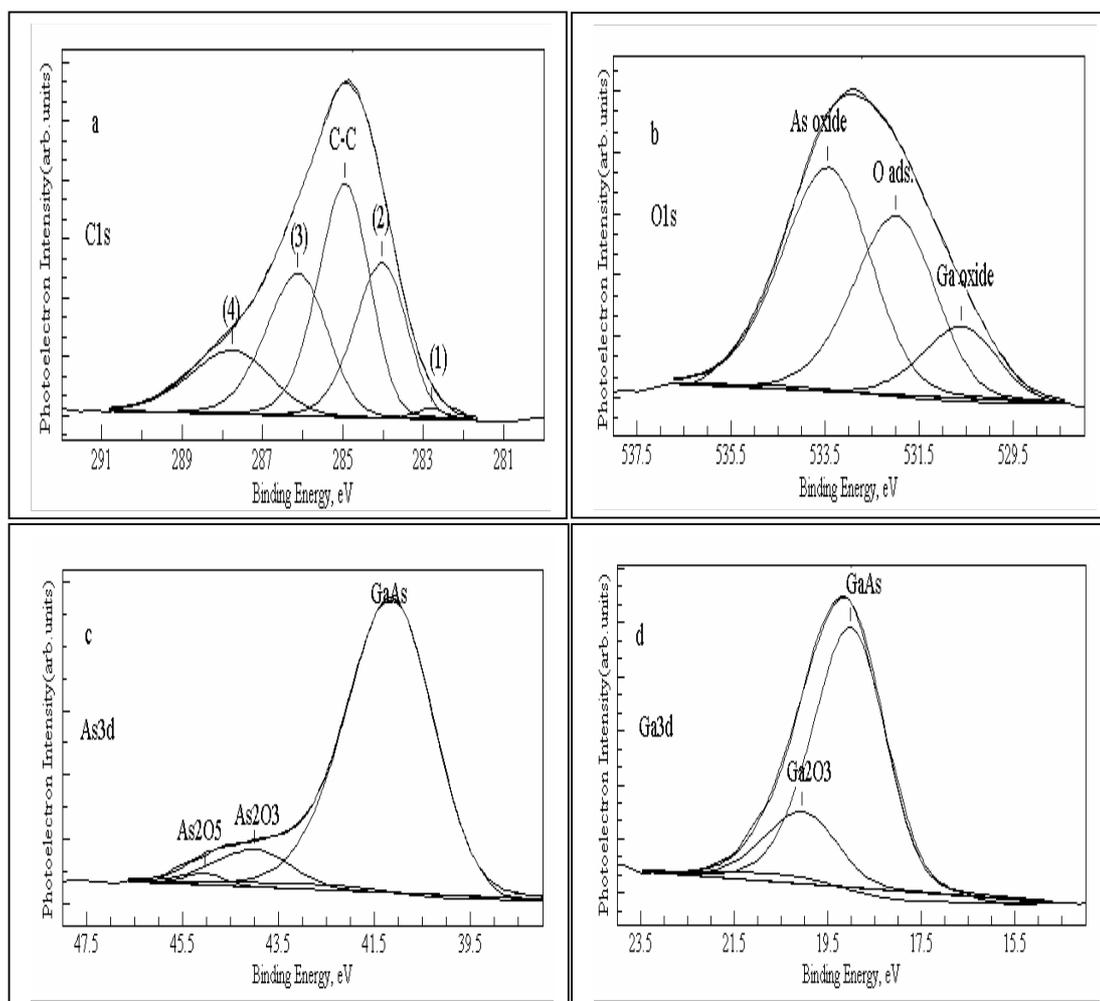
Fig. 1. The deconvoluted spectra of C$_{1s}$, O$_{1s}$, As$_{3d}$ and Ga$_{3d}$ obtained from a solvent cleaned GaAs sample.

The C$_{1s}$ peak shapes (Fig. 1a) are complex, peaks and shoulders due to several different carbon species being located at 283.0 284.1, 285.0 286.1, and 287.84 eV. The predominant peak at 285 eV, used for BE calibration, is due to the presence of C-C bonds on surface [8]. A shoulder is present at a BE of 287.8 eV, possibly due to adsorbed species such as M2CO, and a shoulder is present at 286.1 eV due to the presence of adsorbed alcohol. The low energy peaks at 283.0 eV and 284.1eV is attributed to Ga carbide and to hydrocarbons, respectively [7,9].

The O$_{1s}$ spectrum, (Fig1b), is broad and consists of contributions from chemisorbed oxygen (532 eV), As oxides (high BE) and Ga oxide (low BE).

From the As$_{3d}$ spectrum presented in Fig.1c, we found the following contribution: the 41.16 eV peak attributed to GaAs and two high BE peaks corresponding to As$_2$O$_3$ (44.02 eV) and As$_2$O$_5$ (45.3eV), respectively.

The spectrum presented in Fig. 1 (d), are related to the Ga signal from Ga$_{3d}$ line with the following deconvolution: the 19.02 eV line (Ga from GaAs,) and the 20.06 eV line (Ga from Ga$_2$O$_3$).

From the spectra recorded on the sputtered GaAs surface (5 keV Ar$^+$ ions, three steps each of 15 min.) significant variations in the peak shapes and positions are observed, indicating that the nature of the chemical species present at surface is strongly modified. Using published sensitivity factors [10] the spectra of C$_{1s}$, O$_{1s}$, A$_{3d}$ and G$_{3d}$ lines were processed and the surface composition was calculated. The corresponding results are resumed in Table I. Fig. 2 illustrates the composition evolution at sample surface as a result of successive sputterings.

Table 1. The composition at GaAs surface before and after successive plasma sputterings.

	Surface composition(%)			
	GaAs as-receved	15 min.PS	30 min. PS	45 min PS
C	60.77	17.51	2.14	0.60
O	24.81	13.19	6.85	0.91
As	7.25	27.46	35.57	37.75
Ga	7.17	41.83	55.44	60.41
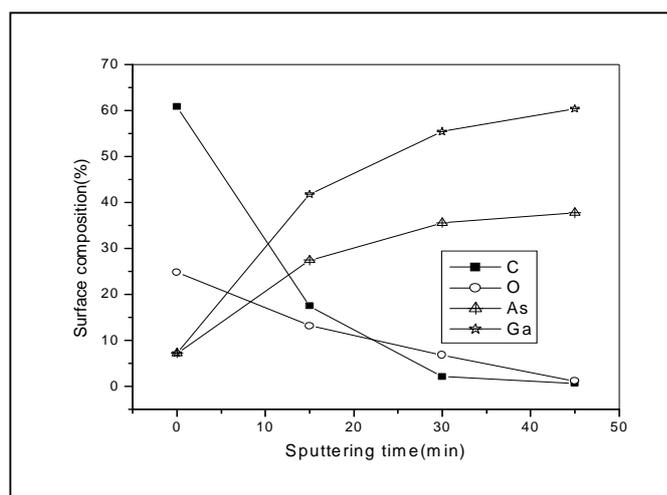
Fig. 2. The evolution of surface composition as result of the successive sputterings.

From the C1s spectrum is observed a decrease of carbon concentration from 61.65% (as received sample) to 0.61% (after 45min. sputtered). The decrease of the intensity for carbon signal corresponds to a de-contamination of the surface for the main bond C-C.

The analysis O1s spectrum indicates a decrease in concentration from 24.81% to 0.91%. and,

as a direct result, the surface is clean, without oxides.

The surface concentrations of As and Ga increased from 7.25% and 7.17% to 37.75% and 60.41%, respectively.

It is remarkable that after plasma etching the concentration ratio Ga/As indicates a modification of the surface stoechiometry in GaAs compound, the Ga/As concentration ratio varies from >> 1(as received) to 1.6 (after 45 min. sputtering).

In the Fig. 3 a, b, c and d, are presented the superimposed XPS spectra of C_{1s}, O_{1s}, A_{3d} and G_{3d} obtained before (curve denoted 1) and after plasma etching (curves denoted 2, 3, 4 corresponding to 15, 30, 45 min. sputtering time, respectively).
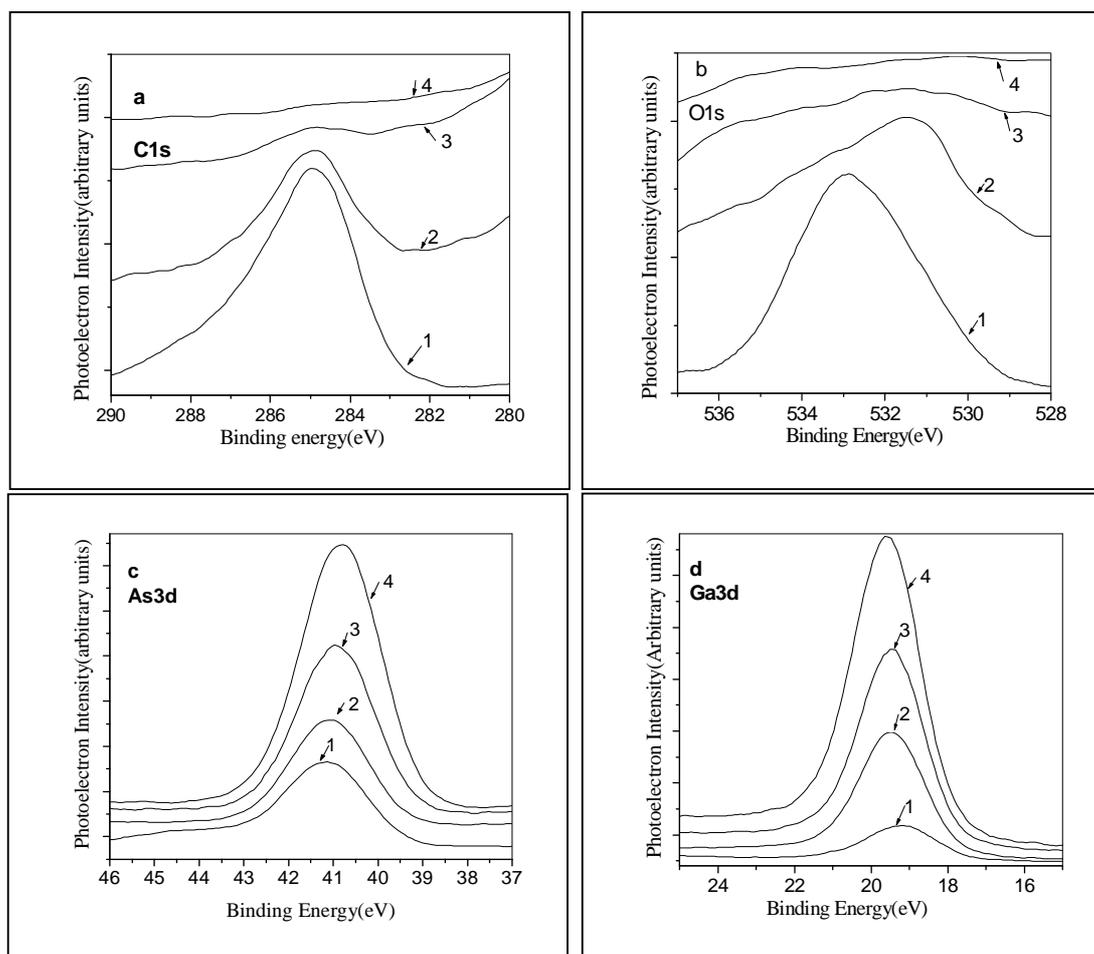
Fig. 3. The C_{1s}, O_{1s}, A_{3d} and G_{3d} spectra obtained before and after plasma sputtering (PS); as received GaAs, **1**; after 15 min. **2**, 30 min. **3** and 45 min. **4,** plasma sputtering

From Fig. 3a and b it is observed that the sputtering treatments change the shape and the size of C_{1s} and O_{1s} spectra. After the first sputtering step, the predominant form of C is still C-C bonds together with carbide, hydrocarbons and alcohol. The next two steps determine drastically decrease of the carbon signal just the noise level (Fig. 3a).

After the first sputtering step, the O_{1s} peak is shifted to low binding energy corresponding to Ga line from Ga_2O_3 (Fig. 3b). This fact suggests the presence of gallium oxide just above of GaAs substrate. The following sputtering steps lead to a drastically decrease of O peaks and this indicates a clean surface, without oxides or chemisorbed oxygen.

From As3d spectra (Fig.3c) it is observed that after the sputtering treatments the signal

corresponding to arsenic from GaAs increase and the signal due to As oxides disappears just after the first sputtering step.

The Ga_{3d} spectrum recorded after 15 min. plasma sputtering confirms the result got from O_{1s} XPS curve. This curve may be decomposed in two peaks: a main peak at 19 eV corresponding of Ga from GaAs and a small peak at high BE (>>20 eV) which indicate that Ga_2O_3 is still present on GaAs surface. The signal due to Ga oxides disappears after the third-sputtering step (Fig. 3d).

4. Conclusions

X-ray photoelectron spectroscopy has been used to examine the surface regions (cleaned in solvent) of *n*-type GaAs substrates before and after cleaning by ion sputtering treatments. It was shown that the XPS analysis provides important information on oxidized GaAs surface. The data on bonding character provided by XPS are essential for the determination of the chemical state of the interface. According to the XPS data, the native oxide layer on the chemical cleaned GaAs substrate contains large amounts of carbon, oxygen, As and Ga oxides(As_2O_3, As_2O_5, and Ga_2O_3). The sputtering etching treatment results in significant changes in the surface composition. After 45 min. sputtering time the GaAs surface is practically clean, without carbon, chemisorbed oxygen or As and Ga oxide contaminants.

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