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CHEMICAL COMPOSITION OF GaAs OXIDE LAYERS BY AUGER IN-DEPTH PROFILES AND X-RAY PHOTOELECTRON SPECTROSCOPY EXPERIMENTS

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Abstract

GaAs oxide layers resulting from an oxygen plasma etching have been studied by Auger in-depth profiles and angle-resolved XPS experiments. From the Auger profiles, using the sequential layer sputtering (SLS) treatment, a quantitative determination of thickness and composition of the oxide layers has been performed. A model with several layers has been deduced. From the angle-resolved X-ray photoelectron spectroscopy (XPS) experiments, another model with several layers of different chemical compounds has also been deduced. The oxide layer is non-uniform in thickness and composition. Two or three different oxide layers are formed depending on the probed area. The interface layer is made of a mixture of Ga_2O_3 and elemental arsenic. The intermediate layer consists of an equal mixture of Ga_2O_3 and As_2O_3 with a small amount of As_2O_5. From the Auger experiments, an upper layer of Ga_2O_3 is found in the central part of the wafer, corresponding to a more important loss of arsenic due to a thermal effect.

Key Words: Auger electron spectroscopy, X-ray photoelectron spectroscopy (XPS), depth profiling, angle dependence, gallium arsenide, oxide, sputtering, chemical composition.

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Introduction

Etching procedures are required for III-V compound device technology. A knowledge of the chemical composition of the etched layers is important for the technological steps such as epitaxial regrowth or ohmic contact deposition which require very clean and stoichiometric surfaces.

GaAs oxide layers formed after chemical etching [1, 4, 10, 17, 20], ion etching [11, 14, 22], or ultraviolet (UV) chemical etching [6, 25] have been studied by Auger and X-ray photoelectron spectroscopy (XPS) experiments.

The Auger intensity profiles, corrected for the elemental sensitivity factors, reflect the layer composition convoluted by a resolution function which includes the Auger electron escape depth, the depth broadening due to the ion milling, and the effect of preferential sputtering. These three effects may be deconvoluted using the sequential layer sputtering (SLS) treatment [16]. This treatment has previously been applied to determine the composition and the thickness of GaAs oxide layers formed after chemical and ion etching [2].

Angle-resolved XPS experiments may provide, utilizing the knowledge of the photoelectron escape depth, chemical composition and thickness of these layers in a non-destructive manner [5].

Both experiments have been performed for oxide layers resulting from an oxygen plasma etching of GaAs. The results have been compared from the point of view of composition and thickness of the layers.

Materials and Methods

The sample is a GaAs substrate, (100) oriented, n-type silicon doped (doping level 10^{17} cm^{-3}). The wafer has been deoxidized using 30% diluted HCl. The sample is placed in a reactive ion etching chamber with a planar structure (Nextral NE 110, Alcatel Nextral, St. Imier, France) with a residual vacuum of 5 x 10^{-7} Torr. Pure oxygen is used for the plasma with a pressure of 5 mTorr, a radio frequency (RF) power of 50 watt and an

ion energy of 300 eV. The cover of the cathode plate is in SiC. The time of exposure is 5 minutes.

The Auger measurements were performed with a JEOL JAMP 10S (JEOL, Tokyo, Japan) scanning Auger microscope, using a 10 keV primary electron beam energy, an electron beam current of 0.5 μA and a beam spot size of 100 μm. The Ar^+ ion beam was generated by a VG EX05 (Fisons, Beverly, MA) differential pumping sputtering gun at 1 keV ion energy, 100 nA ion current. The ion beam was focused at 200 μm and rastered 1 mm by 1 mm, giving an ion current density of around 10 $\mu A/cm^2$. The ion incidence angle is 55°. The residual pressure in the analysis chamber was 1.0 x 10^{-9} Torr and the Ar^+ partial pressure 5.0 x 10^{-8} Torr. The sample was attached with metal strips.

The Auger peak-to-peak height was monitored as a function of the time in a cyclic mode with the ion sputtering of the sample. The Auger signals of C (272 eV), O (510 eV), Ga LMM (1070 eV), and As LMM (1228 eV) were recorded. The spectra were acquired and processed using a Kevex/JEOL (JEOL, Peabody, MA) made software on a Digital PDP11/23 computer (Digital Computers, Maynard, MA). The Auger intensities were corrected by taking into account the elemental sensitivity factors. The values for C and O are those of the JEOL Handbook [8]. For Ga and As, the values are slightly modified in order to obtain a 50/50 composition in the substrate. The chemical effect may modify the Auger line shape and has an influence on the peak-to-peak height, so the results cannot be quantified with an accuracy better than 30%.

For the depth calibration, we have used the sputtering rate determined with a native oxide formed on the GaAs substrate exposed to air for about 2 weeks. As previously reported, its composition is a mixture of Ga_2O_3, As_2O_3 and other suboxides. Its thickness has been evaluated by XPS experiments to be 8-12 Å [7, 12]. Choosing a mean value of 9.6 Å, we get a sputtering rate of 4.8 Å/min, i.e., 2 ML/min (1 ML = 0.24 nm, where ML = monolayer).

The angle-resolved XPS experiments have been performed with the CNRS-University of Nantes Leybold apparatus (Leybold, Köln, Germany). The analyzed area is 10 mm x 15 mm. The sample is maintained on the grounded sample rod by two gold coated stainless steel screws. The X-ray excitation is obtained with a Mg anode ($h\nu$ = 1253.6 eV), using a pass energy of 50 eV; the overall energy resolution is 1.0 eV. As an example, the Au 4f 7/2 core level has a full-width-half-maximum (FWHM) of 1.1 eV under these experimental conditions. The calibration of the XPS spectrometer is achieved using 2p 3/2 (932.67 eV) and Au 4f 7/2 (84.00 eV) core level lines. XPS spectra are acquired with a 18 channel electron detector and stored for different take-off angles in order to vary the effective escape depth. The take-off angle can be varied from 0° to 74°.

Auger In-Depth Profiles and Data Treatment

The sequential layer sputtering (SLS) treatment was introduced to predict the broadening associated with the statistical nature of the sputtering process [16]. This treatment is based on simple statistical arguments. It is assumed that the solid is constituted of monolayers and that the sputtering proceeds only in that part of the surface which has become exposed to the ion beam. It leads to good results for thin layers with one or two constituents when collisional mixing and surface diffusion do not occur during the ion sputtering.

The general formula giving the intensity variation as a function of the depth is [16]:

$$I(z) = I_0 \sum_{m=0}^{M} \sum_{n=1}^{N} X^0_{n+m} \frac{z^{n-1}}{(n-1)!} \exp(-z) \exp(-\frac{m}{\lambda}) \tag{1}$$

where: I(z), total Auger intensity as function of depth; I_0, normalized intensity taking into account the sensitivity factor; m, layer number from where the Auger electron escaped; n, layer number for which the statistical nature of the sputtering is applied; M and N, practical limits for the summation over m and n; N, is greater than the layer thickness, M, usually taken as 4 λ to integrate the Auger emission; λ, Auger electron escape depth; X^0_{n+m}, molar fraction of a given element in the n+m layer.

To take into account the preferential sputtering effects, the molar fraction in the n layer, is given by [16]:

$$X_n = (X^0_n - X^\infty_n) \exp(-z/z_1) + X^\infty_n \tag{2}$$

where X^∞_n is the steady-state value of the concentration which would be attained after a transition depth characterized by z_1. Equation (2) can be incorporated in eq. (1) substituting X^0_n to take into account the compositional change due to the preferential sputtering.

For the calculations, the monolayer thickness has been considered equal to the thickness of a GaAs monolayer (0.283 nm) [23]. The escape depth has been calculated using the formula given for elements [19]:

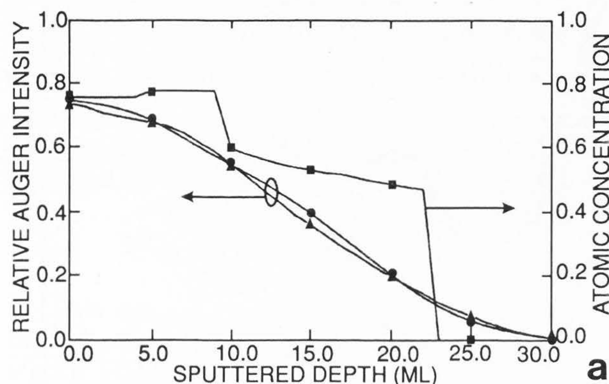
$$\lambda\ (ML) = (538/E^2) + 0.41\ (\alpha E)^{1/2} \tag{3}$$

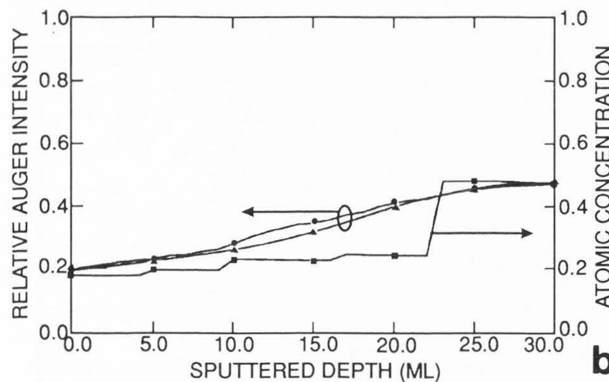
where: a is monolayer thickness (nm); and E is Auger electron energy (eV).

The escape depth was corrected by the sine value of

Table 1. Layer thickness, atomic concentration of O, Ga, As and total atomic concentration deduced from Auger experiments.

Layer	Thickness (nm)	X^0_O	X^0_{Ga}	X^0_{As}	X_{total}
Upper 1	1.13	0.76	0.18	0.0	0.94
Upper 2	1.42	0.78	0.20	0.0	0.98
Intermediate	1.98	0.60	0.24	0.10	0.94
Interface	1.70	0.52	0.26	0.13	0.91





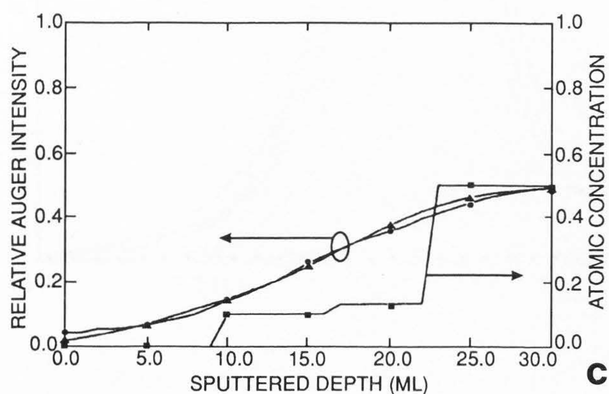


Figure 1 (at left). AES in-depth profiles for **(a)** oxygen, **(b)** gallium, and **(c)** arsenic. For each element, the experimental curve of the relative Auger intensity profile (circles, corrected with the sensitivity factors), the atomic concentration (squares), and the calculated curve (triangles) using the SLS treatment are shown.

the take-off angle (42° 10'). The respective value of the escape depth are: for O, 3.31 ML; for C, 2.46 ML; for Ga LMM, 4.79 ML; and for As LMM, 5.13 ML.

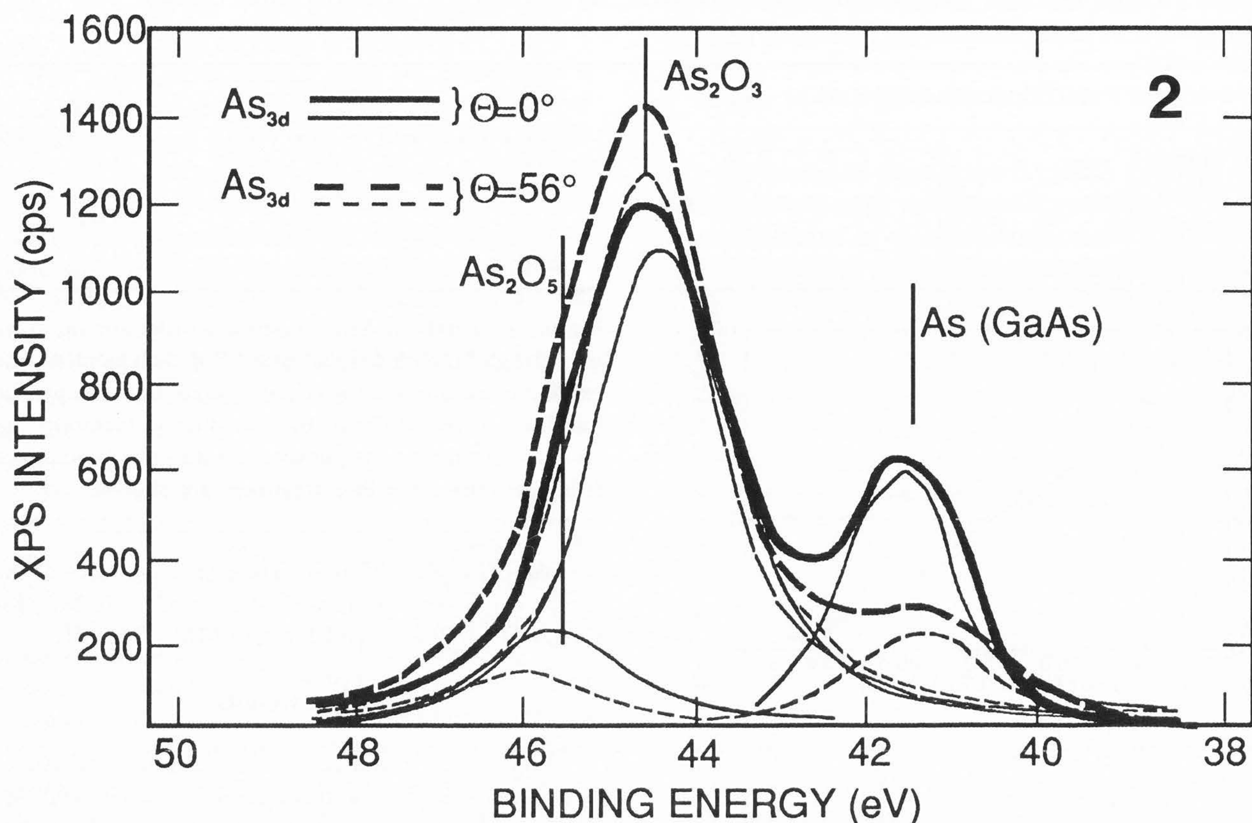
Auger Results

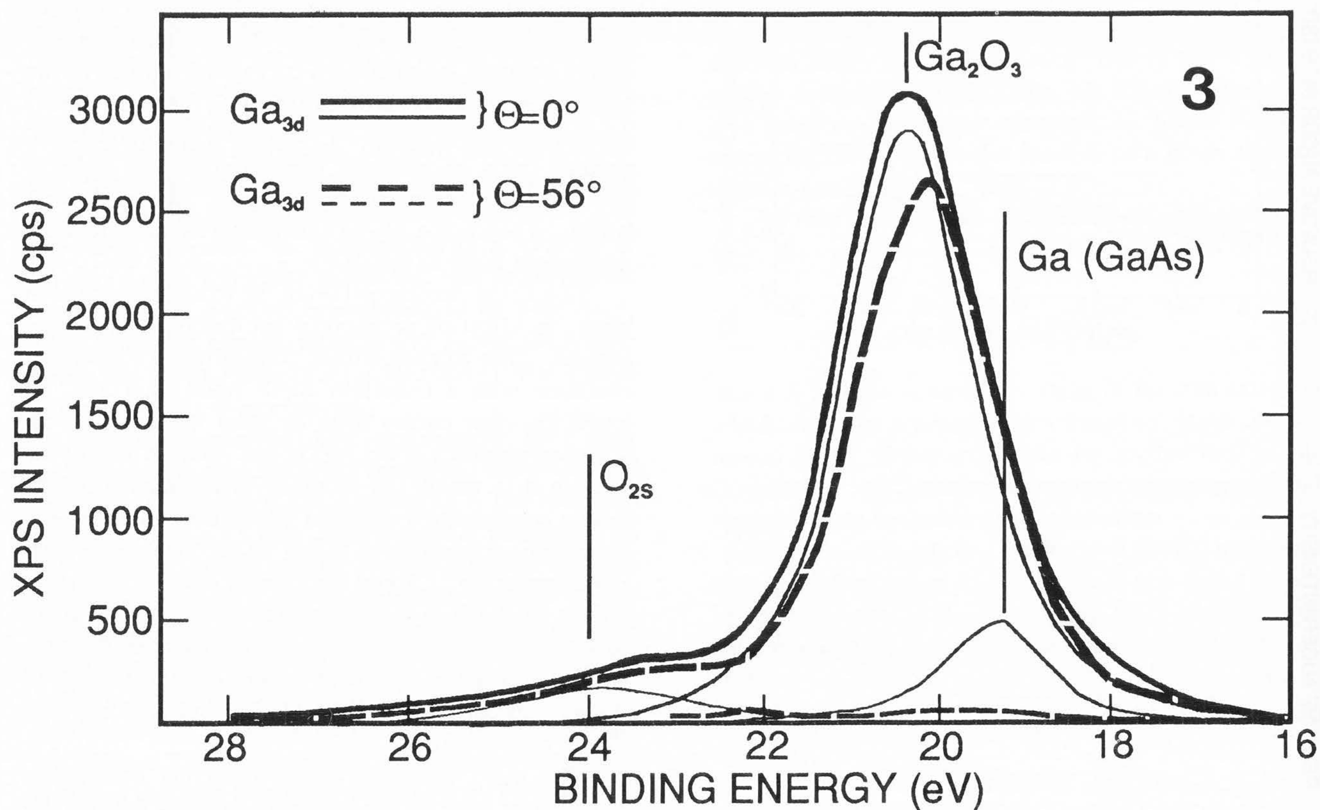
Figures 1a, 1b and 1c show the experimental Auger in-depth profiles for the three elements O, Ga, and As, (corrected by the sensitivity factors), the atomic concentration used for the simulation (including the effect of the preferential sputtering) and the calculated curve. The fit between the calculated curve {convolution of the atomic concentration according to eq. (1)} and the experimental curve is obtained by successive approximations, starting from an assumed concentration and a layer thickness (expressed in ML) for one, two or several layers. The choice of the number of layers and their thicknesses leads to the fit.

Due to the decomposition of the oxide under the ion beam, an effect of preferential sputtering is taken into account. The oxygen atomic concentration follows an evolution with a transition depth equal to 6 ML, as found for other oxides with the same ion energy [15]. The corresponding effect for Ga and As does not appear because it is within the accuracy of the method. The atomic concentration reported on Figures 1a-1c is surface atomic concentration taking into account the preferential sputtering. Carbon (not shown in these results) is present in the first monolayer for an amount of 10 to 40% (atomic concentration) but is not detected in depth.

Table 1 gives, for each layer, the thickness, the atomic concentration, X^0 of O, Ga, As and the total atomic concentration.

The more plausible formulae of the compounds which agree with the atomic concentrations are: for the two upper layers, Ga_2O_3; for the intermediate layer, a





Figures 2 and 3. XPS spectra for the As_{3d} (**Fig. 2**) and Ga_{3d} (**Fig. 3**) region at take-off angles of 0° and 56°.

Table 2. Layer thickness and composition deduced from Auger experiments.

Layer	Thickness (nm)	Composition
Upper	2.55	Ga_2O_3
Intermediate	1.98	$(Ga_2O_3)_{0.7} + (As_2O_3)_{0.3}$
Interface	1.70	$(Ga_2O_3)_{0.5} + As_{0.5}$

mixture of Ga_2O_3 and As_2O_3; and for the interface layer, a mixture of Ga_2O_3 and elemental As. For each layer, Table 2 gives the thickness and the composition assuming the presence of certain compounds. The two upper layers, which have nearly the same composition, are joined in one layer.

XPS Results and Data Treatment

Data were acquired and analyzed with the Leybold DS 100 software. The data manipulation consists of: Mg Kα satellite substraction, background substraction using the Shirley's method [21], and spectra decomposition with Gaussian-Lorentzian analytical curves. The XPS spectra were recorded for different take-off angles. The spectra taken with the largest take-off angle represent the surface more.

Figures 2 and 3 show two portions of spectra taken at a take-off angle of 0° and 56°. The distribution of As_{3d} (Fig. 2) may be split in three components: As(GaAs) at 41.3 eV, $As(As_2O_3)$ at 44.2 eV, and $As(As_2O_5)$ at 45.5 eV. The Ga_{3d} distribution (Fig. 3) may be split in two components: Ga(GaAs) at 19.5 eV, and $Ga(Ga_2O_3)$ at 20.6 eV. The peak located at 24.0 eV does not belong to the Ga_{3d} distribution, but corresponds to the O_{2s} distribution which overlaps with that of Ga_{3d}.

The relative variations of each component as a function of the take-off angle give an idea of the importance of that component as a function of the depth. The results are explained by a three layers model as presented in Figure 4. The model assumes that each layer is of constant thickness and composition and sharply separated from the next layer. It is then possible to estimate the thickness of the various layers by using classical relations for the expression of intensity of each contribution [18].

The total thickness of the overlayer, z, is estimated from the relation:

$$I_{substrate} \propto \exp(-z/\lambda\cos\theta) \qquad (4)$$

λ is considered as the same for each layer and the substrate. For Ga_{3d} and As_{3d}, the Seah and Dench relation [19] gives: $\lambda = 2.35$ nm.

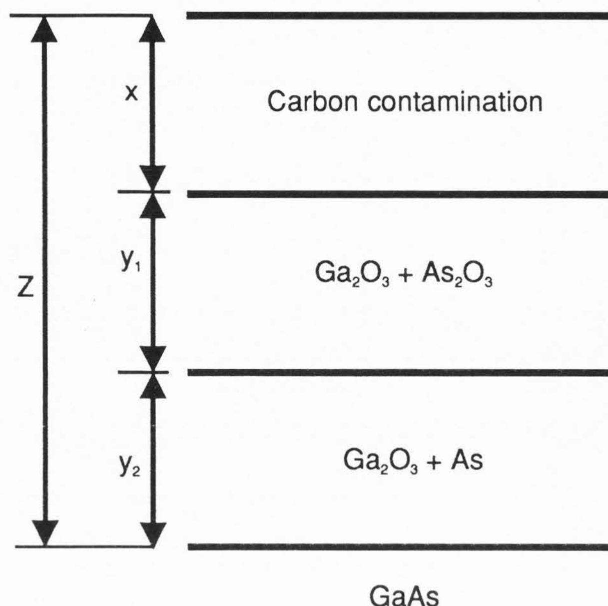


Figure 4. Model deduced from XPS experiments (z, total thickness of the overlayer; x, carbon layer; and y_1 and y_2, oxide layers thicknesses).

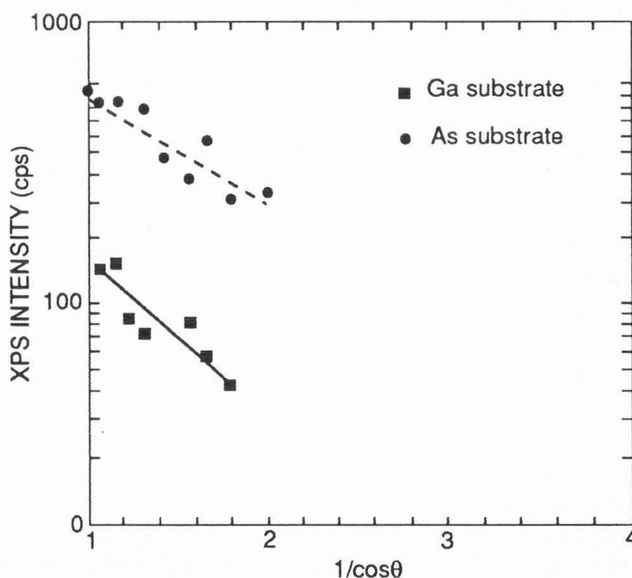


Figure 5. Ga(GaAs) and As(GaAs) XPS intensity as function of the take-off angle.

Figure 5 shows the experimental variations of the substrate intensity for Ga_{3d} and As_{3d} as a function of the take-off angle. The experimental points fit an exponential variation law. The value of z_{Ga} (3.53 nm) obtained with the variation of Ga(GaAs) is more important than

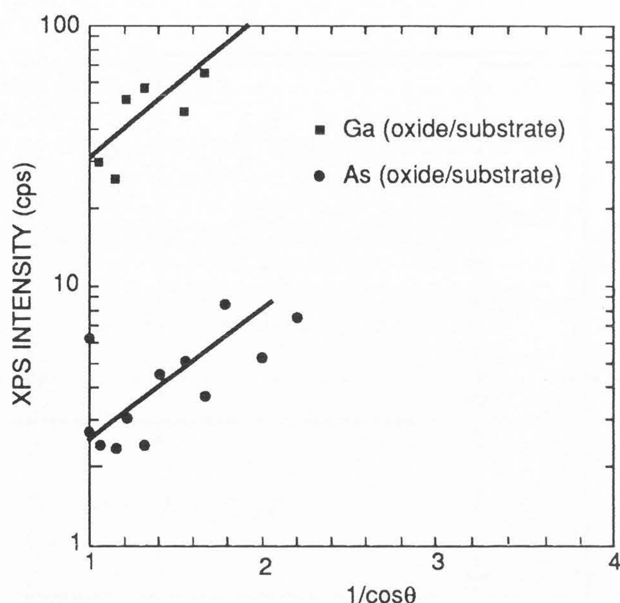


Figure 6. Ga_2O_3 and As_2O_3 XPS intensity as function of the take-off angle.

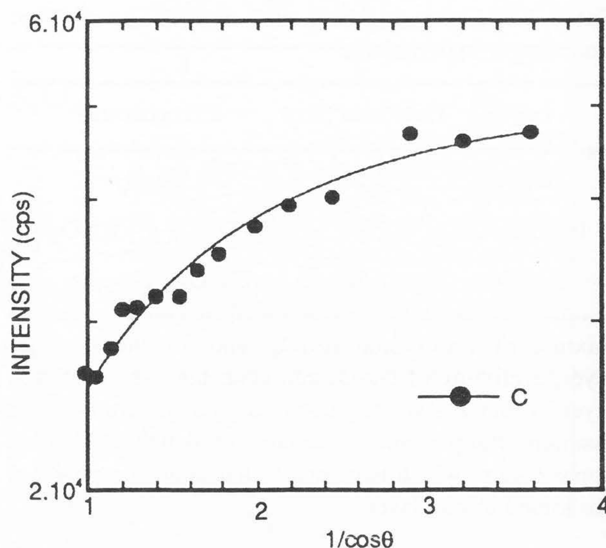


Figure 7. C_{1s} XPS intensity as function of the take-off angle.

the value obtained with As(GaAs) (2.74 nm). As z is the total thickness of the overlayer above the substrate, z_{Ga} and z_{As} should be equal; the discrepancy indicates that some arsenic species belonging to the overlayer are included in the substrate contribution. Elemental arsenic is known to exist in the native oxide on GaAs [24] and is located in the first layer above the GaAs substrate [3]; its contribution to the As_{3d} distribution is located at +0.8 eV from that of As(GaAs) and may be separated from the As(GaAs) line using monochromatized XPS. An alternative to elemental arsenic exists in As atoms in a chemical environment, such as Ga_3-As-O, the contribution of which to the As_{3d} spectrum is expected around 42.1 eV, assuming a chemical shift with respect to elemental As of -0.2 eV per As-Ga bond and +0.8 eV per As-O bond [9]. These species, elemental As, or As in Ga_3-As-O groups, belong to the oxide layer, but their contribution to the As_{3d} spectrum cannot be separated from that of As(GaAs) in our experimental conditions.

The oxide thickness, y, is given by the relation:

$$\{I_{oxide} / I_{substrate}\} \propto [\{1-\exp(-y/\lambda\cos\theta)\} / \{\exp(-y/\lambda\cos\theta)\}] \quad (5)$$

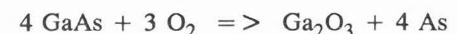
Figure 6 represents the experimental variations of the Ga_2O_3 and As_2O_3 intensity as function of the take-off angle. The experimental points fit an exponential variation law. The ratio for the Ga contribution gives $y_{Ga} = y_1 + y_2 = 2.12$ nm, and the ratio for As gives $y_{As} = y_1 = 1.35$ nm. The difference between y_{Ga} and y_{As} is thus the same as that between z_{Ga} and z_{As} which confirms the interpretation (see Fig. 4). The thickness of the carbon overlayer is estimated either indirectly by substraction of y_{Ga} to z_{Ga}, or y_{As} to z_{As}, or directly from the variation of the intensity of the C_{1s} spectrum with the take-off angle (Fig. 7). The origin of this carbon contamination is the exposure of the samples to the atmosphere during their transfer from the plasma equipment to the XPS apparatus. Table 3 gives the thickness and the formula of the compounds present in each layer and an estimation of their relative proportion deduced from the XPS experiments. The presence of As_2O_5 is detected for all take-off angles, and the ratio of the intensities $I(As_2O_5)/I(As_2O_3)$ is nearly constant and equal to 0.1. Therefore, As_2O_5 is present in the intermediate layer. For $\theta \geq 60°$, the intensity ratio $I(As_2O_3)/I(Ga_2O_3)$ is constant and equal to 0.65. The probed depth corresponds to the two upper layers. Using the

Table 3. Layer thickness and composition deduced from XPS experiments.

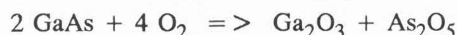
Layer	Thickness (nm)	Composition
Upper	1.39	Carbon contamination
Intermediate	1.35	$(Ga_2O_3)_{0.67} + (As_2O_3)_{0.30} + (As_2O_5)_{0.03}$
Interface	0.79	Ga_2O_3 + As

same sensitivity factors for Ga_2O_3 and for As_2O_3 as for Ga and As, the concentration ratio $C(As_2O_3)/C(Ga_2O_3)$ is equal to 0.45. The composition of the intermediate layer is deduced from the concentration ratios $C(As_2O_3)/C(Ga_2O_3)$ and $C(As_2O_5)/C(As_2O_3)$.

The presence of elemental As and As_2O_5 could be explained by the two chemical reactions [13]:



$$4\ GaAs + 3\ O_2 \Rightarrow Ga_2O_3 + 4\ As$$



$$2\ GaAs + 4\ O_2 \Rightarrow Ga_2O_3 + As_2O_5$$

The presence of Ga_2O_3 in the upper layer may be explained by the out-diffusion of As. During the etching, the mean increase of temperature due to the plasma heating is estimated to be 80°C; the temperature increase at the center can be much higher.

Discussion

From the Auger experiments, it is possible to determine the layer thickness and the amount of each compound in the layers. The accuracy of the layer thickness is mainly determined by the accuracy of the sputtering rate. The atomic concentration is evaluated from the Auger intensity using elemental sensitivity factors. The relative proportion of the compounds can be deduced from the atomic concentration, assuming the presence of certain species. XPS experiments give the layer thickness and the presence of compounds in each layer. The layer thickness is mainly given by the knowledge of the escape depth of each component, assuming the same escape depth in the layer as in the substrate. An estimation of the composition can be made, for well separated species, using the elemental sensitivity factors. Differences are observed in composition and thickness of the layers determined by the two techniques. This may be explained by the followings: the Auger profiles are obtained with a probed area of 100 μm in diameter near the central part of the wafer; the angle-resolved XPS experiments are probing an area of 10 mm x 15 mm in a quarter of the wafer. From the plasma etching process, it is known that in the central part of the wafer, there exists a more important etching rate which explains the thicker oxide layer and there is also a more important increase in temperature which explains the loss of arsenic and the formation of a Ga_2O_3 layer.

The presence of a carbon overlayer is due to the long storage in air of the samples before the XPS experiments.

Conclusions

Despite the non-uniformity of the oxide layers formed after plasma etching on a GaAs wafer, Auger in-depth profiles taken with a low ion energy and a low sputtering rate and the angle-resolved XPS experiments give complementary results for the thickness and the composition of the layers. XPS identifies the presence of a chemical compound and allows an estimation of the thickness. The atomic concentration of each element is given by the Auger experiments, and the thickness can be estimated with an accuracy down to 0.3 nm.

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Discussion with Reviewers

L.K. Magel: Is there any evidence from the angle-resolved data that the oxide is actually a layered structure or is this merely a simplifying assumption?

Authors: The angle-resolved XPS results agree well to an assumed layered structure. As a matter of fact, the thicknesses of the interface layer, y_2, determined either by the difference between y_{Ga} and y_{As} (0.77 nm) or by the difference between z_{Ga} and z_{As} are very close (0.79 nm). In addition, the thicknesses of the carbon contamination, x, determined either by the difference between z_{Ga} and y_{Ga} (1.41 nm) or by the variation of the C_{1s} intensity as a function of the take-off angle (1.39 nm) are also very close.

L.K. Magel: What has been done to explore the effect of altering the oxygen plasma conditions?

Authors: All the parameters governing the plasma conditions have been explored: oxygen pressure, RF power, carrier gas flow, nature of the cover of the cathode plate. The oxygen pressure and the RF power have a strong influence on the etching rate. For example, for a photoresist (AZ 4400), at a pressure of 5 mTorr and a RF power of 50 watt, the etching rate is around 12 nm/min. At a pressure of 50 mTorr and a RF power of 100 watt, the etching rate is around 240 nm/min. For a power greater than 120 watt, the etching is purely anisotropic due to the role of the energetic ions. Different metals and materials have been used for the cover of the cathode. Metals have been detected in the surface oxide layer and in residues. The best results have been obtained with a SiC cover plate.

L.K. Magel: What is the relative contribution of suboxides compared to As_2O_3, As_2O_5?

Authors: From the deconvolution of the As region spectrum (Fig. 2), the relative contribution of suboxides is very small as compared to As_2O_3 and As_2O_5.