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An X-ray photoelectron spectroscopy study of the oxides of GaAs

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Abstract

In this paper, by the use of X-ray photoelectron spectroscopy, we unequivocally identify the oxides present on GaAs surfaces and accurately measure the binding energies associated with the $2p_{3/2}$, 3d, and Auger lines in the X-ray photoemission spectra. These measurements intended to provide reliable reference data for further work. We conducted an extensive analysis of the oxidation states of Ga metal and oxide powder reference samples, air exposed GaAs wafers, and wafers subjected to various surface treatments (argon plasma treatments and boiling). Based on this experimental evidence, an assignment of the photoelectron peaks to various chemical states is proposed. © 2001 Published by Elsevier Science B.V.

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1. Introduction

Knowing the oxidation states of the GaAs oxides and the typical conditions for their formation has many benefits for semiconductor and opto-electronic applications. The oxide films have important roles in passivation of semiconductor surfaces, in mask diffusion and in preparation of wafers for epitaxy. Following the success of the thermal oxide as a passivating dielectric layer on silicon, a similar technique was employed for GaAs but without success. Because limited success was achieved with native oxides of GaAs, other dielectrics grown on GaAs substrates are

under investigation for improved electrical properties. Nevertheless, a better understanding of GaAs oxides would probably lead to a new era of GaAs-based electronic devices.

In the current literature the characterization of surface oxides of GaAs is still an open issue. In this work we have employed X-ray photoelectron spectroscopy (XPS) to study and characterize the oxides of GaAs through identification of photoelectron peaks associated with different oxidation states on the surface. Accurate energy assignment of these peaks is essential for identification of the various components produced under different conditions.

There is much disagreement in the current literature concerning the correct assignment of the photoelectron energies and identification of the oxidation states to which these energies belong. In addition, not all oxidation states are normally identified, e.g. the only

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Ga oxide which is covered by NIST XPS standard reference database is Ga₂O₃ [1]. Also, a large number of workers do not give the energy position of the photoelectron lines belonging to various oxidation states, but only give the energy-separation values between the photoelectron line of the bulk and that of the oxides [2–6].

The majority of workers have concentrated on the Ga and As 3d lines, but both the 2p_{3/2} and the LMM Auger lines are required if the surface is to be properly characterized. Accurate identification of 2p_{3/2} peaks is as important, since these peaks represent smaller sampling depths and hence are more sensitive to surface modification than 3d peaks. This has not been generally recognized as can be seen from the NIST XPS database where there are few entries for 2p_{3/2} lines of GaAs as opposed to the large number for the 3d lines. In addition, the identification and quantification of the components using the 2p_{3/2} line could be more accurate than using the 3d region due firstly to the simple line shape of the 2p_{3/2} peak, which is only a single photoelectron line, not an unresolved spin-orbit doublet. Secondly, the Ga 2p_{3/2} and As 2p_{3/2} peaks have the highest intensities in XPS spectra of GaAs, which statistically give more accurate identification of the peaks in a shorter collection time.

In the XPS spectra, the As oxide components may be more easily identified and with greater accuracy than those of Ga, since chemical shifts of oxidized As are considerably greater than those of oxidized Ga. This together with the fact that the predominant oxides are those usually of Ga, is why a considerable amount of work is currently employed to determine different chemical states of Ga.

Although much work has been conducted in this area, in many references the peaks are wrongly assigned [7,8]. Some of the erroneous assignments are due to inaccurate practices in the measurements. As an example, in studying chemical states using XPS some have not synthesized the oxide peaks, but wrongly assign the whole peak envelope as a single oxide. Some other examples are discussed in detail in later sections.

One of the peaks that has been detected and not consistently identified is the peak having a binding energy (BE) of around 23.2 eV. When this peak was detected it has been assigned to a chemical state of Ga [9], an “intrinsic photoemission processes” [10] or to O 2s [11].

Further, there is some uncertainty on the assignment of the peak around 21.6 eV in the literature. The main chemical state proposed for this peak is the hydroxide Ga(OH)₃ [3,5]. The other possible compound is GaAsO₄ but with this there is a corresponding peak at 45.2 eV in the As 3d region [5,9,10,12]. There is general agreement about the assignment of the peak with a BE of around 20.6 eV, where most authors agree that it originates from Ga₂O₃ [13–15].

Out of the various oxidation states of Ga, there is more uncertainty about formation of Ga₂O than the others. Obtaining Ga₂O by hydrogen treatment of Ga₂O₃ with C 1s as internal reference at 284.6 eV, Carli and Bianchi [16] reported incorrectly a BE of 19.0 eV for Ga₂O. A chemical shift of 0.4 eV between Ga₂O and Ga₂O₃ was also noted by Aydil et al. [13]. Ballutand et al. [7] reports that a photoelectron peak at a shift of 1 eV from Ga in the GaAs spectrum is due to formation of GaO, while they claim that a shift of 0.5 eV is due to Ga₂O. Others attribute a shift of about 1 eV from the bulk to Ga₂O₃, while in fact it corresponds to Ga₂O [17–19]. Cuberes and Sacedon [20] suggested a new Ga oxide (GaO_x) from comparison of the Auger spectra of different thermally treated GaAs samples. The mechanism of GaO_x formation is not explained in this paper, but the fact that its structure was different from that of Ga₂O₃ has been outlined by another interesting experiment made by the same authors. Nevertheless, the shift value 0.9 eV relative to the BE for bulk emission corresponds to Ga₂O rather than Ga₂O₃. A number of authors [21,22] suggest that the GaAs surface contains a single-phase oxide instead of having separated well-defined oxidation states. For example, using thermal oxidation of n-type (1 0 0)GaAs, Hollinger et al. [21] showed that the presence of As³⁺, As⁵⁺ and Ga³⁺ peaks is correlated to a single-phase oxide made up of a mixture of different molecular units (such as AsO₃, AsO₆, GaO₄, GaO₆).

In the identification of photoelectron lines (2p_{3/2} and 3d) of bulk Ga(-As), a large number of workers do not report BEs. Instead, they use the line as a reference for energy assignment of peaks for other chemical compounds, and quote the energy difference between them for identification of these compounds.

Using an appropriate reference peak for calibration of the BE scale is essential for obtaining reliable values of peak positions. The standard procedure of

using the C 1s line as calibrant for this system gives erroneous results [23,24]. This problem has been identified by many workers in the field who chose to use a different reference material. Deng et al. [25] and Debiemme et al. [26] used Au 4f_{7/2} as a calibrant. Iwami et al. [27] reported that the BE of the Ga 3d Ga(-As) peak as 19.2 ± 0.2 eV from the energy difference between the Ga 3d peak and the top of the valence band.

The BE ranges for the GaAs components found from our literature survey and the NIST XPS data base are 23–24 eV for O 2s, 20.2–21.6 eV for Ga(OH)₃ or GaAsO₄, 19.7–20.9 eV assigned to Ga₂O₃, 19.6–20.1 eV for Ga₂O, 18.5–19.8 eV for Ga(-As) and 18.2–18.9 eV for elemental Ga. There are few measurements of the Ga 2p_{3/2} line, but the corresponding ranges are 1116.4–1118.1 eV for elemental Ga, 1116.4–1117 eV for Ga(-As) and 1116.9–1118.9 eV for Ga₂O₃. The overlap in these ranges leads to obvious problems in accurate identification. No Ga 2p_{3/2} data appear to have been reported for Ga₂O.

There is less dispute in the case of the As oxides. In the As 3d region, the following BEs have been reported: 40.7–41.2 eV for As(-Ga), 41.6–42 eV for As metal, 44–44.9 eV for As₂O₃ and 45.2–46 eV for As₂O₅. The As 2p_{3/2} BEs are 1322.7–1323 eV for As(-Ga), 1323.2–1323.8 eV for As-metal, 1325.8–1327.3 eV for As₂O₃ and 1327.7–1328 eV for As₂O₅.

In this paper we have designed experiments to accurately measure the BEs associated with the Ga 3d, Ga 2p_{3/2} and LMM peaks using XPS analysis and give proper identification in terms of the oxides of Ga and As.

2. Materials and sample preparation

The samples studied were Ga₂O₃ powder, metallic Ga and GaAs wafers subjected to different treatments.

The Ga₂O₃ powder used in this work was supplied by PI-KEM. For XPS analysis, the powder was mounted by pressing it gently onto double-sided tape.

Two samples of metallic Ga were also analysed. One of the metallic Ga samples was in the form of lumps and was supplied by BDH Labs., and the other was prepared in a separate vacuum system by thermal evaporation through a fine mesh and deposited on a gold substrate. The first sample was analysed after

prolonged exposure to air and the other one was analysed soon after fabrication (but also after air exposure).

The polished wafers used were supplied by GEC Marconi. Prior to any treatment, the samples were cleaned in acetone for 15 min, rinsed in isopropanol using an ultrasonic bath and then dried with compressed air.

A series of experiments were conducted on the wafers after treatment in Oxford Instruments PLAS-MALAB 100 RF capacitively coupled plasma cell using an argon plasma at 150 W, 10 mT and 30 sccm. The exposure time was always 30 min. Chemical changes with exposure time to air of plasma-treated GaAs wafers were also conducted. Samples of GaAs wafers that had been chemically etched in a solution of (3H₂SO₄:H₂O₂:H₂O) were also included. To test for the presence of hydroxides, a number of GaAs wafers boiled in deionized water for 4 h were also analysed.

3. XPS analysis

The XPS investigation was carried out in a VG ESCALAB 200D multi-technique spectrometer at a base pressure of better than 1×10^{-9} mb with a twin anode X-ray source. The sample surface was kept normal to the axis of the analyser input lens. Al K α unmonochromatized radiation was employed for the analysis, with the source operated at an emission current of 20 mA and an anode voltage of 15 kV. The analyser pass energy was 20 eV, the energy step size was 0.05 eV. Under these conditions, the measured full width at half maximum (FWHM) of the Ag 3d_{5/2} line is 0.8 eV and this is a measure of the energy resolution of the instrument for these measurements. Photoelectron peaks were recorded and resolved by spectrum synthesis in which the spectral line shapes were simulated by 30% Gaussian and 70% Lorentzian combinations of line shapes. Relative atomic concentrations were calculated from the intensities of the major photoelectron spectral lines (integrated peak areas) after subtracting a Shirley background. The spectra were reduced in this way with Eclipse software incorporated in the instrument data system using Scofield and self-generated sensitivity factors [28] taking into account the transmission function of the analyser. Depth profiles were obtained by Ar⁺

sputtering at 53° to the sample surface. The analysed area of the samples was normally $2\text{ mm} \times 3\text{ mm}$.

Corrections of the charging shift for the wafers were accomplished with reference to the As(-Ga) peak at 41.1 eV. This value was chosen from extensive previous work within the group on GaAs [29,30] and agrees with many entries in the NIST database. These investigations showed that the C 1s line cannot be used as a reliable reference in this system as confirmed by other workers [10,31]. A large number of workers have used a reference other than C 1s [5,7,32]. Another point is that some workers do not attempt to do charge correction but just give the raw data [33].

Narrow-scan spectra were collected for Ga $2p_{3/2}$ and 3d peaks, Ga LMM Auger lines, O 1s and C 1s peaks with all samples. For the GaAs samples, as lines were also measured curve synthesis was employed to determine the BEs and relative concentrations. A considerable amount of data was collected in order to properly determine the positions of all peak components and FWHM values. These BE and FWHM values were kept constant to $\pm 0.1\text{ eV}$ in all fitting. This procedure ensured complete consistency when analysing spectra from different samples. Accurate assignment of Auger lines was different than for photoelectron lines since the Auger lines cannot be synthesized due to broadening, in mixed oxides. Therefore, samples with a single oxide had to be used for Auger line identification.

For the wet-etched GaAs sample, the major oxide detected was Ga_2O_3 and this was used for identification of the LMM line in this compound. The Ga_2O_3 powder sample in which the powder grains are fully enclosed by Ga_2O oxide was used for identification of the LMM line in the latter oxide.

Not only the compositions of the various oxides are of interest, but also their thicknesses. The calculation of oxide thickness was based on the model described by Briggs and Seah [34]. For As 3d and Ga 3d photoelectrons, a mean free path value of 26 \AA was used from the work of Lu et al. [17].

The $2p_{3/2}$ and 3d regions give complementary information on the composition (versus depth) of the surface. The $2p_{3/2}$ region of the spectrum is the result of detection of photoelectrons from the outermost layer of the surface. This is because the BE is high and the photoelectrons from deeper layers do not have enough kinetic energy to reach the surface. Thus

the information given by this region roughly refers to the first few atomic layers (approx. 10 \AA). Similarly, the information given by the 3d region refers to deeper layers (approx. 80 \AA).

4. Experimental results

4.1. XPS analysis of reference compounds: Ga_2O_3 powder and metallic Ga

Spectrum calibration is very difficult when analysing samples which do not contain reference peaks (e.g. As (41.1 eV) as in the case of GaAs). Synthesizing the Ga 3d peak of the Ga_2O_3 powder, two peaks were found with an energy separation of 0.6 eV and an FWHM of 1.6 eV. The FWHM value was deduced by iteration over a large number of samples, as explained earlier. One of the peaks must be Ga_2O_3 . We have assigned the BE for this peak as $20.7 \pm 0.1\text{ eV}$ for this compound. This was done on the basis of extensive cross-referencing of oxide peaks formed on GaAs samples where the As(-Ga) peak can be used as a calibrant. We also relied strongly on using Auger parameters for this identification as have [35,36]. Auger parameters found in this work are shown in Table 3. This assignment also agrees with other measurements [11,37,38]. The peak at lower energy has been observed by many authors [8,16,19,20], but its assignment is in some doubt. According to Sheka et al. [39], the lowest oxidation state of Ga that is stable long enough to be detected is Ga_2O . GaO is not stable and would not be detected. Hence the peak at 0.6 eV below the Ga 3d peak of the Ga_2O_3 (at 20.1 eV) must be assigned to Ga_2O . This is in agreement with [3,13].

The Ga $2p_{3/2}$ lines for these powder samples show peaks at 1118.8 and 1118 eV corresponding to Ga_2O_3 and Ga_2O , respectively. These results are used in the later analysis.

The Ga LMM spectrum provides useful additional information in the determination of the components present on the surface. Auger parameters for the compounds found on a cleaned GaAs wafer (determined using the Ga $L_3M_{45}M_{45}$ peak with respect to the BE value of As(GaAs) 3d at 41.1 eV) were used for complete identification of samples where no standard was available (e.g. Ga_2O_3 powder, Ga metallic). For example, we will show later from our measurements

Table 1
Surface composition of the reference compounds

Sample/region	Ga metal		Ga ₂ O		Ga ₂ O ₃	
	3d	2p _{3/2}	3d	2p _{3/2}	3d	2p _{3/2}
As-received Ga (%)	31.7	13.5	14.2	24	54.1	62.5
Ga ₂ O ₃ powder (%)	–	–	89	100	11	–
Thermally evaporated metallic Ga	35.9	15	45.6	65.4	18.5	19.6

that the Auger parameter of Ga₂O₃ at 405.0 eV is distinctly different from that of Ga₂O at 403.8 eV. Fig. 1(a) with 3d peaks of Ga₂O₃ powder shows that the majority of the oxide (89%) is Ga₂O. Calculations using the 2p_{3/2} peaks (which give more surface-specific information) indicates almost 100% Ga₂O. This is somewhat surprising since the powder is specified as Ga₂O₃ (determined from XRD characterization); therefore, this result must be due to the fact that the Ga₂O₃ grains are covered with a thick layer of Ga₂O. The calculated relative concentrations are given in Table 1. Thus, as was mentioned earlier, this material is an ideal sample for confident identification of the position of the Ga₂O LMM line at 424 eV.

Analysis of the thermally evaporated metallic Ga sample revealed the existence of three peaks in the Ga 3d region of the spectrum. In addition to the two oxide peaks at 20.7 and 20.1 eV, there is a peak at 18.3 eV corresponding to metallic Ga. The corresponding peaks in the 2p_{3/2} spectrum were 1118.8, 1118 and 1116.4 eV. Peak positions are shown in Table 2. The Ga LMM spectrum also contained an extra doublet at 418.4 eV and 414 eV attributed to metallic Ga. The calculated oxide layer thickness was 26 Å and it is clear from Fig. 1(b) that the majority oxide is Ga₂O at a concentration of about 45.6%, whereas the concentration of Ga₂O₃ was only 18.5%. The relative concentrations of Ga₂O and Ga₂O₃ calculated from the 2p_{3/2} peaks were about 65.4% and 19.6%, respectively.

Table 2
BEs and FWHM intensity in the 3d and 2p_{3/2} region (in eV)

	Chemical compound					
	Ga metal		Ga ₂ O		Ga ₂ O ₃	
Region	3d	2p _{3/2}	3d	2p _{3/2}	3d	2p _{3/2}
BE (eV)	18.3	1116.4	20.1	1118	20.7	1118.8
FWHM (eV)	1.5	1.7	1.6	1.8	1.6	1.8

As a further reference, an “as-received” solid metallic Ga sample was also examined. This was exposed much longer to the ambient air than the deposited sample. The 3d and 2p_{3/2} photoelectron and Auger LMM lines are shown in Fig. 1(c). In this sample very similar peak positions were observed as those found for the evaporated Ga sample, but the relative concentrations of the oxides was much different. In the case of the sample exposed longer to air, the total oxide film thickness was 30 Å. The majority oxide was Ga₂O₃ with the Ga₂O concentration (derived from the 3d peaks) here representing only 14.2% while the relative Ga₂O concentration calculated from the 2p_{3/2} peaks was about 24%. We attribute the difference in the oxide composition and thickness of the two samples to the extended exposure to air. It was found in one of our earlier experiments on a wafer cleaved inside the vacuum chamber that only Ga₂O forms inside the chamber. On taking the sample out of the chamber, a mixed oxide grows with Ga₂O₃ growing at a greater rate than Ga₂O. Samples exposed for a short time to the atmosphere will therefore contain a lower proportion of Ga₂O₃ than those exposed for longer periods.

In this sample, the 2p_{3/2} peak positions were identical to those found for the previously deposited sample. Comparison of 2p_{3/2} with the 3d peaks (Table 1) indicates that the outer layer of the oxide is rich in Ga₂O₃.

4.2. XPS analysis of GaAs wafers

GaAs wafers subjected to different surface treatments were used for the further characterization of surface oxides.

4.2.1. Cleaned GaAs wafer

The Ga 3d spectra of a cleaned GaAs wafer (shown in Fig. 2) contained three major components with

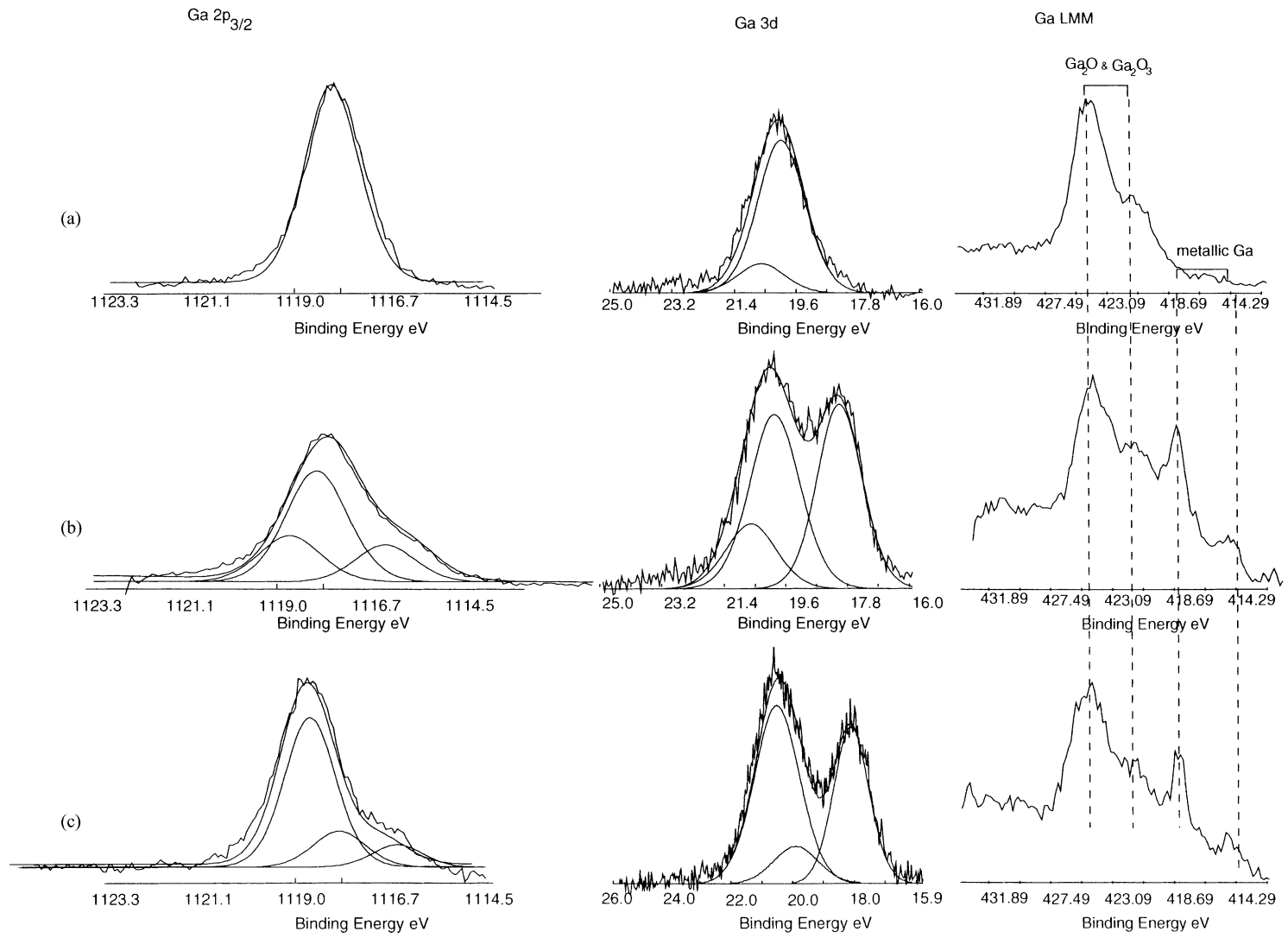


Fig. 1. Ga 2p_{3/2}, Ga 3d and Ga LMM spectra of: (a) Ga₂O₃ powder; (b) thermally evaporated metallic Ga; (c) as-received metallic Ga.

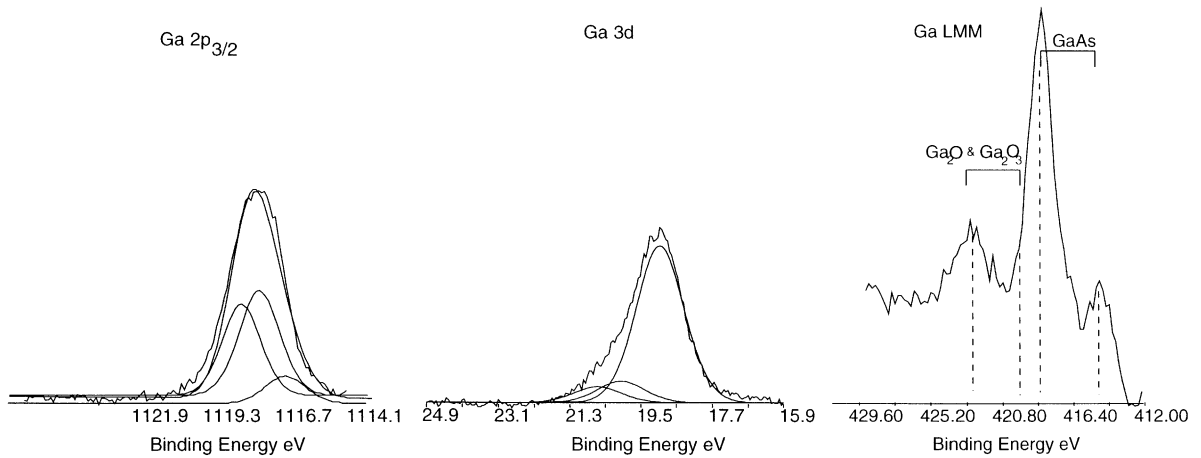


Fig. 2. Ga 2p_{3/2}, Ga 3d and Ga LMM spectra of a cleaned GaAs wafer.

BEs of 19.1, 20.1, 20.7 eV corresponding to Ga(-As), Ga₂O and Ga₂O₃. The corresponding BEs of the 2p_{3/2} lines were 1117.0, 1118.0 and 1118.8 eV. A very small concentration of a compound with associated BE of Ga 3d at 21.6 eV was also observed with a corresponding 2p_{3/2} peak at 1119.8 eV. A further peak was detected in the 3d spectra at 23.2 eV in some samples. The As 3d spectrum consisted of three components at 41.1 (used as a calibrant), 44.2 and 45.2 eV, corresponding to As(-Ga), As₂O₃ and As₂O₅, respectively, and the corresponding As 2p_{3/2} peaks were found at energies of 1322.9, 1325.9 and 1327.0 eV. The positions of the Ga LMM line are similar to those found in previous experiments with some variation in the positions of the Ga₂O₃/Ga₂O LMM lines due to broadening effects for mixed oxides. The LMM lines of As(-Ga) is at 261.6 eV

Table 3

BE of the 3d peaks of Ga and As, the Ga and As Auger parameters (APs) and the FWHM intensity for the indicated materials

Element	BE (eV)	AP (eV)	FWHM (eV)
Metallic Ga	18.48	400.2	1.6 ± 0.1
Ga(GaAs)	19.1	401.2	1.55 ± 0.1
As(GaAs)	41.1	220.6	1.8 ± 0.1
Ga(OH) ₃	21.6	–	1.7 ± 0.1
Ga ₂ O ₃	20.7	405	1.7 ± 0.1
Ga ₂ O	20.1	403.8	1.7 ± 0.1
As ₂ O ₃	44.3	223.4	1.9 ± 0.1
As ₂ O ₅	45.3	–	1.9 ± 0.1

on the BE scale while the position for As₂O₃ is 267.4 eV. Table 3 shows the BEs, Auger parameters and the FWHM of the important peaks. The calculated oxide thickness for these samples was 8 Å;

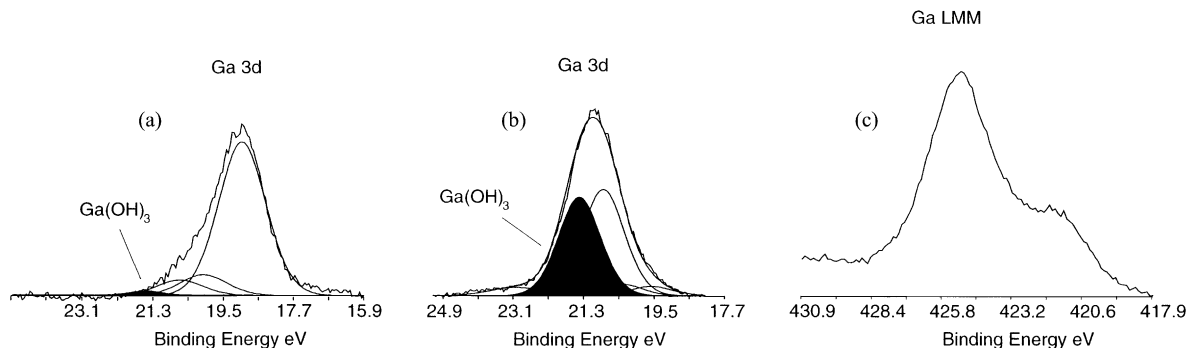


Fig. 3. 3d fit of GaAs wafer: (a) clean; (b) boiled; (c) Ga LMM of boiled wafer. The shaded peaks in (a) and (b) indicate the increase in the Ga(OH)₃ component as a result of boiling the sample.

similar values have been reported by other authors [11,40].

Spectrum processing of the $2p_{3/2}$ and 3d regions has given us a better view of the first few layers of the surface. In the case of as-received metallic Ga sample, e.g. we found that in the 3d region the ratio of Ga_2O to Ga_2O_3 is 1:1.4, while in the $2p_{3/2}$ region this ratio became 1:0.34. This fact suggests that Ga_2O_3 is the

major component of the surface since the concentration is higher in the outermost layers. It is interesting to note that for all the samples studied we found that Ga_2O is formed in the outermost layer.

4.2.2. Cleaned wafer boiled in deionized water

Doubt exists concerning the assignment of the 21.6 eV peak. The O 1s is a very complex peak,

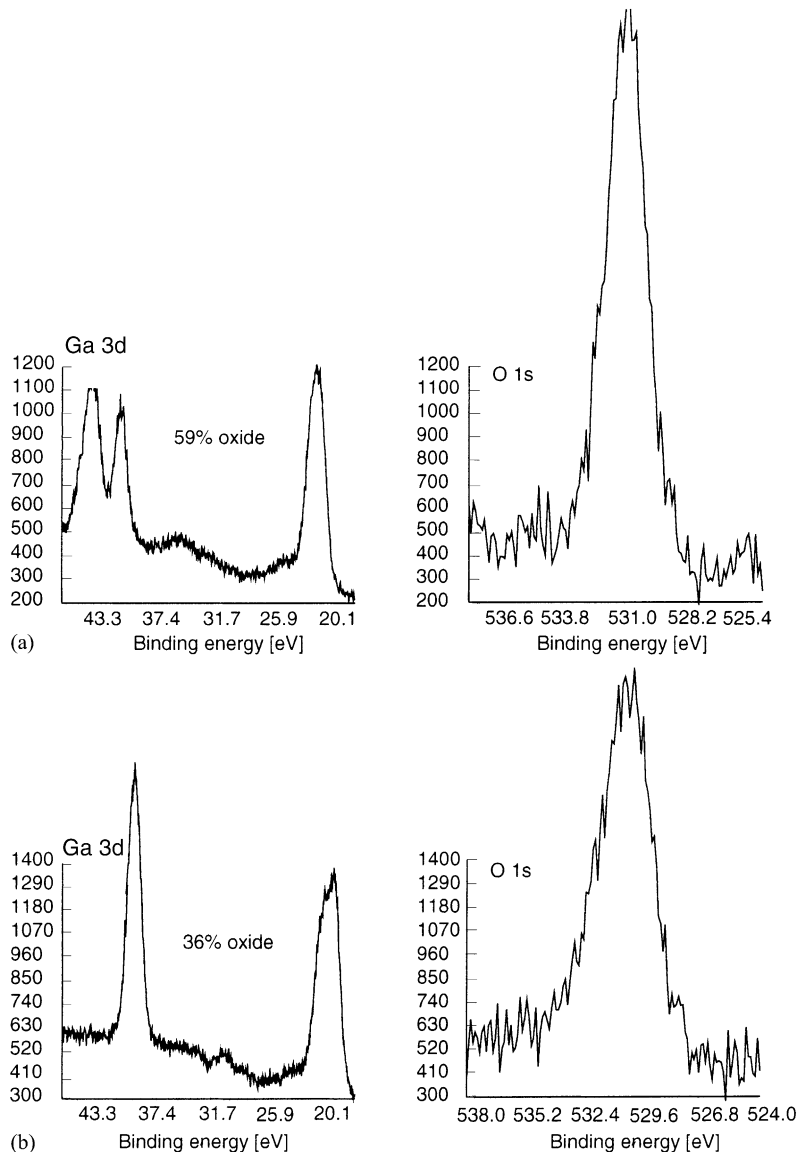


Fig. 4. Normalized spectra of Ga 3d and O 1s for: (a) GaAs wafer etched in Ar plasma 5 W, 90 mT; (b) GaAs wafer etched in Ar plasma 200 W, 90 mT; (c) clean GaAs wafer; (d) GaAs wafer etched in Ar plasma 150 W, 10 mT.

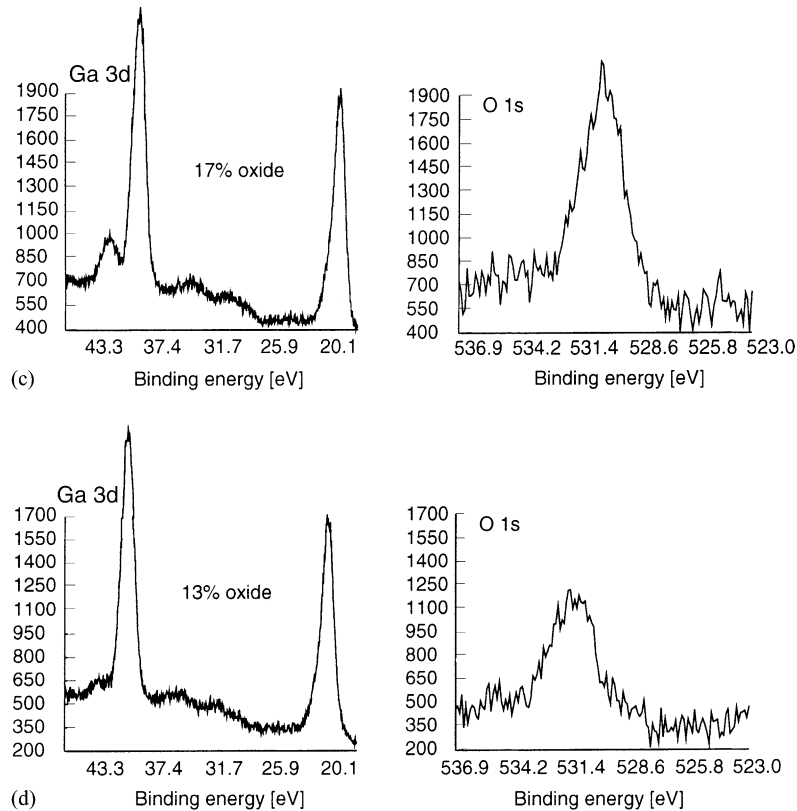


Fig. 4. (Continued)

and peak synthesis is not reliable for the identification of Ga and As oxides. Therefore, it was decided to deliberately promote formation of the hydroxide by boiling a sample of GaAs in water. The XPS analysis showed a big increase in the amount of the component having a BE of 21.6 eV, from 3% on the surface of the virgin sample to 27% on the boiled sample, as shown in Fig. 3(a) and (b). These results suggest that the 21.6 eV is due to the hydroxide $\text{Ga}(\text{OH})_3$. This conclusion is also confirmed by the fact that no peak corresponding to GaAsO_4 (at 45.2 eV) was observed in the As 3d spectrum. In the Ga LMM spectrum (Fig. 3(c)), movement of the larger peak of the doublet to higher BE suggests also the appearance of this new compound (see Fig. 1 for comparison).

4.2.3. Plasma-treated wafer

In the current literature, a peak appearing in the spectrum of certain samples with a BE of 23.2 ± 0.4 eV

is given different assignments, but no explanation of its origin is given [11,17].

Ga and O 1s spectra for argon-plasma-etched samples, normalized to As(-Ga) at 41.1 eV, are given in Fig. 4. A correlation between the O 1s peak height and the appearance of the peak at 23.2 eV is easily observable. As the O 1s peak becomes smaller, the 23.2 eV peak intensity decreases until it disappears. We believe that this peak is the 2s peak of oxygen. This peak can be observed for surfaces containing more than approx. 20% oxide (the percentages are shown in Fig. 4). This approach was verified for many samples studied. This result agrees with the findings of Lu et al. [17] who suggested that the broad peak at 23 eV was due to O 2s. It is interesting that the O 2s peak has often been missed in previous work probably due to the fact that a narrow energy range was used for the Ga 3d core levels.

Air-exposed argon-plasma-treated GaAs surfaces (150 W, 10 mT) showed an increase of Ga_2O concentration within 1 month of exposure (see Fig. 5). The

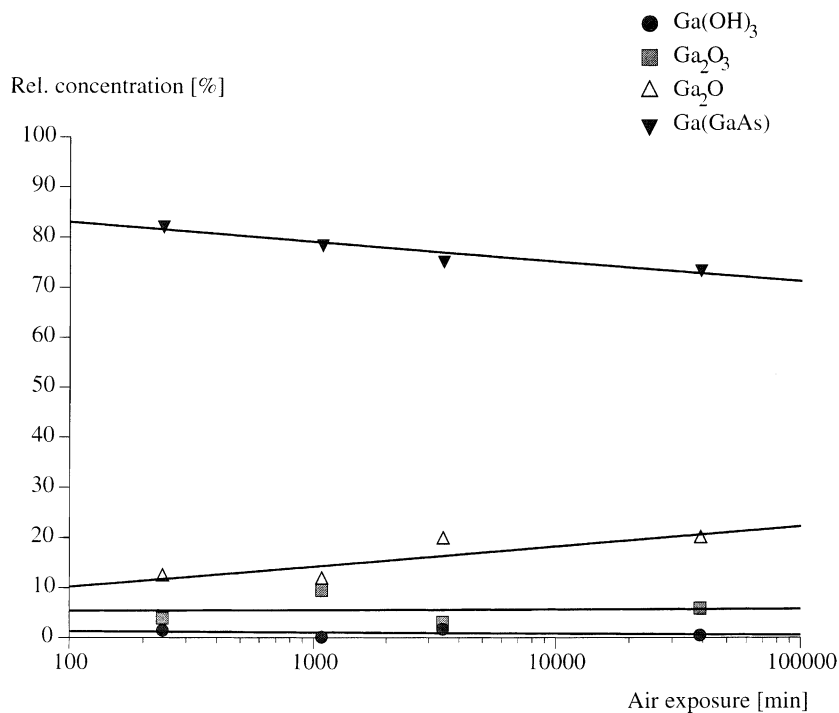


Fig. 5. Variation of surface chemical composition of argon-plasma-treated GaAs with exposure time to air.

thickness of the air-grown oxide increased by about one monolayer during this time. This result confirms again the model of the layered structure of the surface showing that the formation of the lower oxidation states takes place at the outermost layer.

5. Conclusions

There is lack of a precise knowledge of the oxides formed on GaAs and the assignment of associated peaks in the XPS spectrum. In this paper, we unequivocally identify the oxides present on GaAs surfaces and accurately measure the BEs associated with the 2p, 3d, and Auger lines in the X-ray photoemission spectra. An attempt has been made to explain their formation based on experimental evidence, and a model of the layered structure of the surface is also given.

Our analysis showed that some surface-compositional changes occur when the surface is exposed to air. These changes are related only to the lower oxidation states of the components of the substrate.

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