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Investigation of Residual Oxide Layers on GaAs Surfaces

GaAs(100) and (111) oriented samples, treated by means of different chemical procedures, are studied by X-ray photoelectron spectroscopy (XPS). The thickness and composition of the residual oxide layers are estimated using the intensity ratio of Ga 3d and As 3d core levels from the substrate and the oxide overlayers, respectively. Residual oxides containing As_2O_3 and Ga_2O_3 on GaAs surface are observed. The thickness of the oxide layers is found to range from 3 Å to 15 Å. Optimal conditions for pre-epitaxial surface preparation of GaAs substrates are suggested.

Образцы из арсенида галия с ориентацией (100) и (111) подвергнутые различным химическим процедурам исследованны рентгеновской фотоэлектронной спектроскопией. Толщина и состав остаточных оксидных слоев оценены при использовании отношения интенсивностей линий Ga3d и As3d связянных с электронами эмитированными подложкой и верхным слоем. Наблюдаются остаточные оксиды, содержащие As_2O_3 и Ga_2O_3. Толщина оксидных своев находится в диапазоне 3 Å – 15 Å. Предлагаются оптимальние условия для пре-эпитаксиальной подготовки поверхности.

1. Introduction

Gallium arsenide is of increasing importance for the electronics industry because of its high electron mobility and energy band structure which give undoubted advantages for creating microwave and optoelectronic devices. The technology of their production is sensitive to properties of the semiconductor surface.

During the growth of GaAs epitaxial layers the status of the substrate surface (chemical composition and oxide film thickness) is very important for the initial stages of growth and the defect formation in the layers. The substrate surface preparation is of a particular interest in case of metalorganic vapor phase epitaxy (MOVPE) where no "in-situ" gas etching is normally used. The procedure mainly involves cleaning in organic solvents and chemical etching in $H_2SO_2:H_2O_2:H_2O$ mixture followed by rinse in de-ionized water (Yakimova et al; Deep, Gandhi). The last step might be essential in order to produce a thin oxide film protecting the surface against contamination during subsequent manipulations of the sample. Such a passivating layer is particularly attractive since it can be easily removed after loading the sample into the epitaxial reactor by thermal desorption.

During the last years the GaAs surface have been intensively studied. For instance (Ingrey et al.) have shown phase distribution with depth by using angle resolved XPS analysis, (Lucovski) presents a chemical bonding model for the local order in the native oxide phases associated with the III–V compound semiconductors.

In this study the efforts have been concentrated on an estimation of thickness and composition of residual oxide layers formed on GaAs wafers after different chemical treatments. An attempt is made to suggest a suitable procedure for cleaning of GaAs surfaces which are intended to be used as substrates in MOVPE.

2. Experimental

The investigations were carried out with an Escalab II (VG Scientific Ltd) electron spectrometer at a residual gas pressure of 1×10^{-8} Pa. The XPS measurements were made using Al Kα exitation source ($h\nu = 1486.6$ eV), the total instrumental resolution being 1 eV as measured with the FWHM of the Ag $3d_{5/2}$ photoelectron peak. It is known that the ion bombardment could lead to changes in surface stoichiometry of the compounds as well as to changes in the chemical state of the elements in the surface layer (RANKE, JACOBI). However, in order to obtain at least semiquantitive depth profile of elements an Ar^+ bombardment with beam energy 1 keV, current 1.4 $\mu A\ cm^{-2}$ and ion beam diameter ca 5 mm was applied. The crater effect during ion sputtering was avoided using unfocused beam.

The samples studied were n-type Te-doped GaAs and semiinsulating GaAs (both Cr-doped and undoped) monocrystalline substrates obtained from commercial vendors. The wafers had been cut from (100) and (111) oriented ingots and were purchased after final chemo-mechanical polishing. Before measurements the samples were cleaned and chemically etched using procedures commonly applied to preparation of GaAs substrates for MOVPE. In order to record changes of characteristics of the residual oxide overlayers on the GaAs surface, the samples were studied using XPS at different steps of surface preparation. The sequence of treatments is listed below:

I degreasing in hot isopropanol.
S chemical etching in 3:1:1 mixture ($H_2SO_4:H_2O_2:H_2O$) for 1 min at 60 °C which produced mirror-like surface and removed 15—20 μm of material from the substrate surface.
W rinsing in deionized (DI) water following removal from the etch. The procedure was done immediately after the etch in order to prevent an intensive surface oxidation.
I, W final rinse in isopropanol (room temperature) or hot DI water, respectively.
F immersing in 48% HF acid for 30 s. The procedure aimed removal of eventual oxides and was applied at different steps of the surface treatment.

It is important to notice here that for the XPS analysis special care was taken against sample exposure at the air before they were loaded into vacuum system of the electron spectrometer.

3. Results and discussion

In this work we make an atempt to estimate the thickness of the oxide layer using the method described by BERNSTEIN and GREPSTAD. This method is based on deriving the ratio of intensities of photoelectron peaks of two core levels of atoms of the GaAs substrates which peaks differ significantly in their binding energies.

The relation for the estimation of the oxide layer thickness used by BERNSTEIN and GREPSTAD is:

$$\frac{I_{\text{sub}}^{\text{l}}}{I_{\text{sub}}^{\text{k}}} = \frac{\sigma_{\text{l}}}{\sigma_{\text{k}}} \left(\frac{E_{\text{l}}}{E_{\text{k}}}\right)^{m-1/2} \exp\left\{-\frac{d_{\text{ox}}}{\lambda_{\text{ox}}}\left[1 - \left(\frac{E_{\text{l}}}{E_{\text{k}}}\right)^{m}\right]\right\},$$

where $I_{\text{sub}}^{\text{l}}$ and $I_{\text{sub}}^{\text{k}}$ are intensities of peaks from two levels l and k; σ_{l} and σ_{k} are the two photo-ionization cross sections; E_{l} and E_{k} are the kinetic energies of electrons emitted from respective levels; d_{ox} is the thickness of oxide layer; λ_{ox} is the electron mean free path in the oxide layer and $\lambda_{\text{ox}} = 7.6$ Å according to GANT and MÖNCH); the value of m ranges from 0.35 to 0.8 according to WAGNER et al. In our calculations we used $m = 0.5$ according to BERNSTEIN and GREPSTAD.

The estimation of the oxide layer thickness of 16 samples of GaAs prepared by using different surface procedures are given in Table 1. The estimated error is about 1 Å as follows from BERNSTEIN and GREPSTAD. The initial thickness of the oxide layers of the samples was approximately 10 Å.

Table 1
Data on the GaAs samples, surface treatment and thickness of the oxide overlayers

Sample no	procedure, dopant and orientation of the samples			oxide thickness Å
1	ISWW	GaAs	(100)	6
2	ISWI	GaAs	(100)	5
3	ISWW	GaAs:Cr	(100)	7
4	ISWI	GaAs:Cr	(100)	6
5	ISWW	GaAs:Cr	(111)	4
6	ISWI	GaAs:Cr	(111)	3
7	ISWW	GaAs:Te	(100)	5
8	ISWI	GaAs:Te	(100)	5
9	IWI	GaAs. Cr	(100)	15
10	IWI	GaAs:Cr	(111)	11
11	IWI	GaAs:Te	(100)	14
12	IWI	GaAs	(100)	14
13	ISWF	GaAs:Cr	(100)	8
14	ISFWI	GaAs:Cr	(100)	11
15	ISWF	GaAs:Cr	(111)	8
16	IFSWI	GaAs:Cr	(111)	10

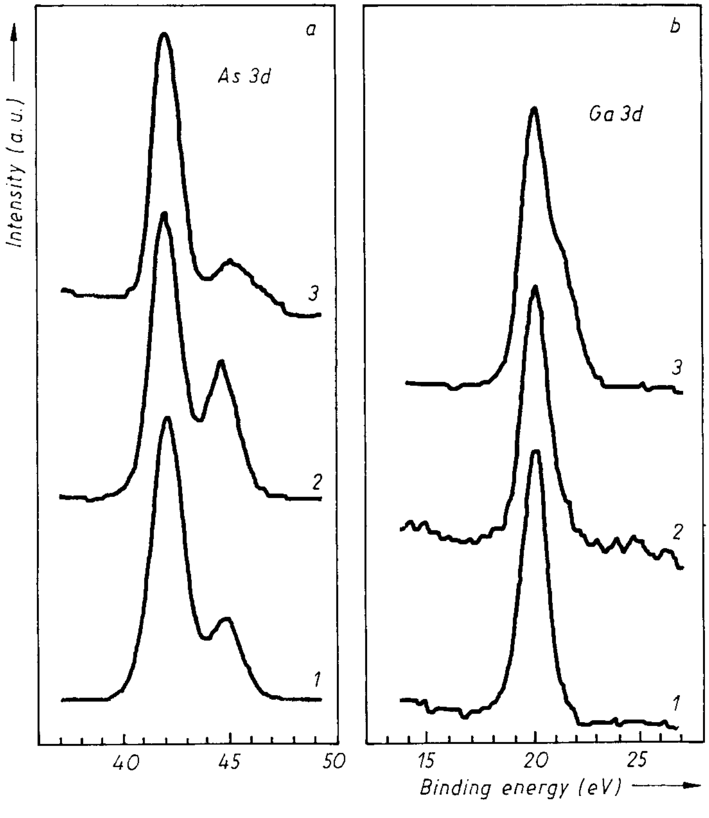

Fig. 1. As 3d peaks (Fig. 1a) and Ga 3d peaks (Fig. 1b) in the XPS spectra (curve 1 – sample 5, curve 2 – sample 8, curve 3 – sample 11)

As can be seen from Table 1, samples 5 and 6 have the smallest thicknesses of oxide layers, regardless of the fact that the last treatment is different in the two cases (with DI water of isopropanol). Samples 1 to 4 which have (100) orientation show thicker oxide layers compared to samples 5 and 6 which have a (111) orientation. The thicknesses of oxide layers on samples treated with IWI (9 – 12) are biggest regardless of the orientation and doping. Comparison of samles 1 – 8 treated by sulfuric acid, hydrogen peroxide and water, with samples 9 and 12 which are not etched, shows that the oxides on samples 1 – 8 are twice thinner. When HF is used (13 – 16) for cleaning the surface, a thinner oxide layer is found after application of HF in the last stage of treatment (samples 13, 15), but it appears that this procedure reduces the effect of ($H_2SO_4:H_2O_2:H_2O$) etch.

According to our observations the thicker oxide layers on the sample, the higher charging during the XPS analysis. Sample 9 which has a charge correction of 1.3 eV according to peak C(ls) at 285 eV, exibits an oxide overlayer with thickness of 15 Å, whereas sample 6 shows 0 eV charge correction and has oxide overlayer thickness of 3 Å. The observed relation could be explained by the effect of capacitor charging to a voltage inversely proportional to its capacity which in turn is inversely proportional to the dielectric thickness (Luves).

Figure 1a and 1b show the 3d peaks of As and Ga for samples 5, 8 and 11, while Figures 2a and 2b present the $2p_{3/2}$ peaks of As and Ga for the same samples. The chemical shift of 3d peak is more pronounced in the case of As. It is ca (3.0 ± 0.2) eV

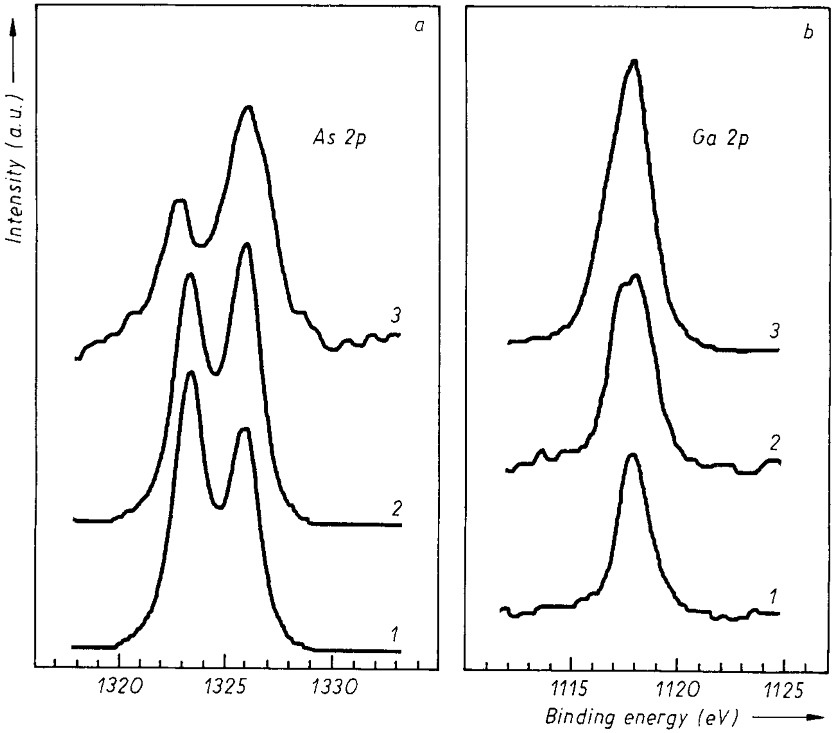

Fig. 2. As $2p_{3/2}$ peaks (Fig. 2a) and Ga $2p_{3/2}$ peaks (Fig. 2b) in the XPS spectra (curve 1 – sample 5, curve 2 – sample 8, curve 3 – sample 11)

which is typical of As_2O_3 on the surface of GaAs (McGuire et al.). The estimated error on the chemical shifts of Ga core levels as well as the intensities of Ga 3d and Ga $2p_{3/2}$ peaks from the substrate and the oxide is larger than in the case of As. For this reason we use peaks of As for assessing the thickness of the oxide layer. For samples 9–12 which have thicker oxide layers, the chemical shift of Ga 3d peaks is ca. (1.4 ± 0.2) eV, which corresponds to Ga_2O_3 (Leonhardt) (see for example Fig. 1b, curve 3 – sample 11).

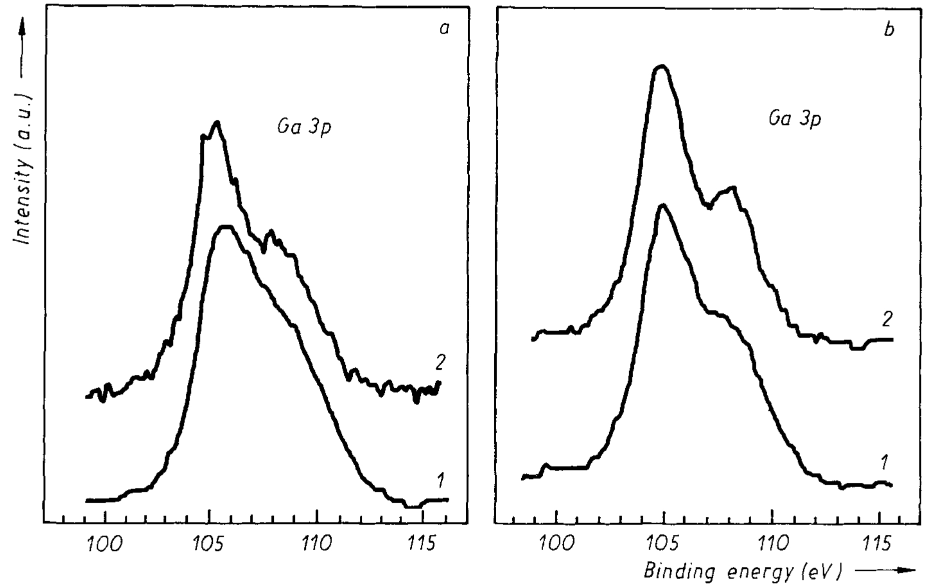

Fig. 3. Ga 3p peaks in the XPS spectra; Fig. 3a – samples 9 and 13; Fig. 3b – samples 10 and 15 (curves 1 – treated with IWI) and (curves 2 – treated with ISWF)

In Figure 3a, b 3p Ga peaks of samples 9, 10 (oriented 100) and (111), respectively) which are cleaned using IWI (curves 1) and of samples 13, 15 (oriented (100) and (111), resp.) treated by ISWF (curves 2) are shown. From the comparison of curves 1 with curves 2 it is seen that the samples treated with HF etch have better resolved $3p_{1/2}$ doublet with energy of 108 eV. The observed difference in shape of the $3p_{1/2}$ is probably connected with the existence of small amount of GaF_3 (McGuire et al.), in which compound the $3p_{3/2}$ peak of Ga shifts ca. 3 eV to higher binding energies and coincides with the doublet $3p_{1/2}$ line of GaAs. The Ga 3p peak differs in shape in the samples treated by HF from the samples cleaned with other chemicals which suggests the formation, of GaF_3 on the surface, although in a small amount.

Figure 4 shows depth profile of As and Ga taken using different times of sputtering for sample 11. The well resolved 3d peak in As_2O_3 (Fig. 4a, curves 1) and well defined bend (asymmetry) of the Ga 3d peak (Fig. 4 b, curve 1) disappear after 90 s etching and only As and Ga peaks of GaAs are observed (Fig. 4a, curves 6).

Conclusion

The thickness and composition of the residual oxide layers of GaAs surfaces are studied using XPS after different chemical procedures.

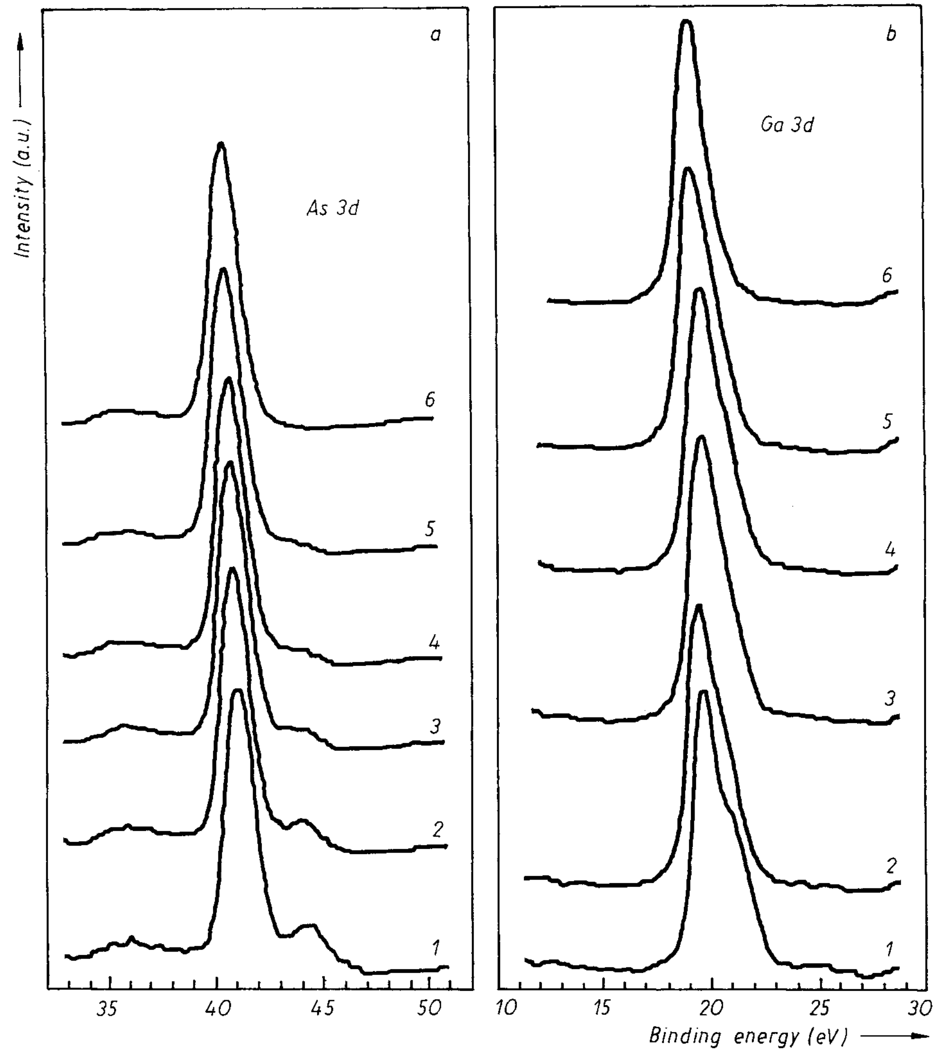

Fig. 4. XPS spectra of Ar^+ ion bombarded (1 keV; 1.4 μA cm^{-2} sample 11 depending on the time of bombardment; Fig. 4a – As 3d; Fig. 4b – Ga 3d (curves 1 – surface; 2 – after 15 s; 3–30 s; 4–45 s; 5–60 s; 6–90 s)

Oxides containing As_2O_3 and Ga_2O_3 are observed on (100) and (111) oriented GaAs substrates. The thickness of the oxide layers ranges from 3 Å to 15 Å. The oxide overlayers on (111) oriented surface are thinner than those formed on (100) surface at all other conditions being the same. The oxide layers found after using 3 : 1 : 1 polishing etch are thinner compared to those obtained as a result of the other procedures applied to the GaAs substrates. No difference of the oxide layer thickness is observed when the procedure is performed either with DI water or with isopropanol. From XPS analysis it appears that doping of the samples have no detectable effect on the residual oxide thickness. The use of 48% HF in the surface processing of GaAs wafers does not result in a drastic decrease of the oxide layer thickness which is probably related to some passivating effect. In the case when HF etch is applied as a final procedure a small amount of GaF_3 can be observed on GaAs surfaces.

From the results obtained the following suggestions could be made concerning preepitaxial preparation of GaAs substrates (for axample in the case of MOVPE):

- since only native oxides are detected in GaAs surface after using standard cleaning procedures of the substrates their heating in the epitaxial reactor is necessary in order to decompose the oxides before the growth.
- the use of concentrated HF favours the process of surface passivation.

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