

Etching of GaAs substrates to create As-rich surface

A CHANDA, S VERMA[†] and C JACOB*

Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302, India

[†]Institute of Physics, Bhubaneswar 751 005, India

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Abstract. Several different cleaning procedures for GaAs (100) substrates are compared using X-ray photoelectron spectroscopy and optical microscopy. This work emphasizes the effect of the last etching step: using either HCl, HF–ethanol (5%) or static deionized water after HCl cleaning. All the procedures except HCl solution (1 : 1) produce an As-rich surface. Also, none of the etchants except HF–ethanol solution produce Ga or As-rich (oxide free) surfaces. Optical microscopic study shows different etch pits produced due to etching in different solutions.

Keywords. Etching; semi-insulating; XPS spectrum.

1. Introduction

In the last few decades, several XPS studies have been published on the effects of different etching procedures of GaAs (Chang *et al* 1977; Bertrand 1981; Vasquez *et al* 1983a, b). The most common etching method used for GaAs substrates is chemical etching based on an H₂SO₄/H₂O₂/H₂O–HCl etching, followed by an ultimate rinse in deionized water which is supposed to produce a thin passivating oxide film. This oxide layer is less reactive towards carbonaceous species than the naked GaAs surfaces and thus preserves the etched surface from contamination during the manipulations of the substrate after the chemical etching process. This procedure, previously described by Cho and coworkers (Cho and Tracy 1976; Cho *et al* 1980; Cho 1983) is presently used by most groups. The present work has been done with the intention of creating an As-rich GaAs surface on which Mn could be deposited and annealed so as to produce a MnAs layer on a GaAs surface. MnAs is a room temperature ferromagnet (T_C , 318 K) and the integration of ferromagnetic material with a semiconductor has wide use in spintronics devices. Also, MnAs which shares common atoms with GaAs is thermodynamically and morphologically stable on GaAs. Although a lot of work has been done on the etching of GaAs surface, this study was undertaken in order to confirm which procedure is suitable to produce an As-rich surface. The present study deals with the characterization of GaAs (100) surfaces by X-ray photoelectron spectroscopy (XPS) processed with different solutions.

2. Experimental

Semi-insulating undoped GaAs (100) substrates with resistivity, 1×10^7 ohm-cm, were used. The surfaces were originally covered with native oxides. Four different cleaning procedures were used. Two samples were rinsed in acetone, methanol and deionized water and then etched in H₂SO₄:H₂O₂:H₂O::5:1:1 for 10 min. Then, one sample was dipped in concentrated HCl for 5 min while the other sample was dipped in HF at a concentration of 5% in ethyl alcohol for 2 min and then both were rinsed in deionized water. Another sample was prepared by treating GaAs wafer in HCl solution for 10 min. The last sample was treated with HCl solution (1 : 1) for 10 min, then in deionized water for 10 s. After treating with different solutions, these substrates were dried in a stream of dry nitrogen. XPS analysis was carried out in a VG Microtech-ESCA2000 Multilab instrument. When recording spectra, the pressure in the chamber was around $2-5 \times 10^{-9}$ Torr. The polar emission angle, defined as the take-off angle of emission of photoelectrons from a surface, was 90°. All the spectra were recorded using MgK_α radiation (1253.6 eV). The binding energies were calibrated from the C1s level taken at 284.6 eV. The spectra are analysed with a curve fitting program for WIN95/98 XPSPEAK Version 4.1 [Kwok] using Gaussian and Lorentzian functions and the background was calculated according to Shirley's method (Shirley 1972; Sherwood 1984). An optical microscope (Leica DMLM) was used to study the surface morphology at different magnifications.

3. Results and discussion

Figures 1–3 show the spectra obtained for Ga, As and O using the four techniques described in table 1 and for an

*Author for correspondence (cxj14_holiday@yahoo.com)

untreated GaAs surface. Inset in figures 1–3 shows the peak fit of Ga, As and O spectra of untreated GaAs. The numbers 1–4 in figures 1–3 indicate the techniques used. Table 2 shows the peak positions, area and corresponding FWHM of different peaks taken for curve fitting of Ga and As peaks.

3.1 Untreated GaAs

Ga 3d, As 3d, C1s, O1s XPS peaks were measured for the as received GaAs wafer before chemical etching. O1s signal corresponds to a mixture of Ga₂O₃ and As₂O₃. The Ga 3d peak at a binding energy of 21.4 eV was assigned to the oxide and that at 20.04 eV to the bulk GaAs. The ratio of oxidized Ga over total Ga atoms calculated from deconvoluted peak area is 0.30. The ratio of the inte-

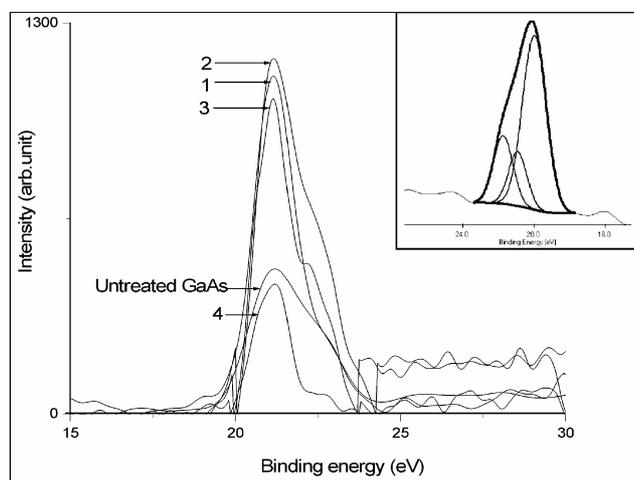


Figure 1. XPS spectra of Ga obtained using procedures 1–4 as described in table 1.

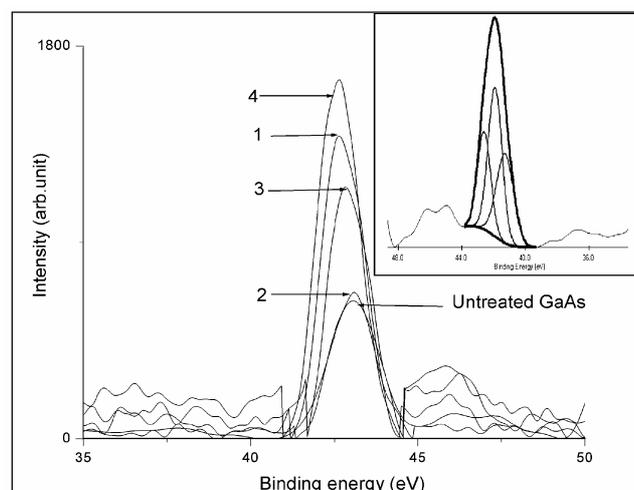


Figure 2. XPS spectra of As obtained using procedures 1–4 as described in table 1.

grated areas of 3d As and 3d Ga peaks, calculated considering both substrate and oxidized phase atoms, is 0.99 which is very near to 1 which means untreated GaAs is neither Ga-rich nor As-rich. Both Ga and As atoms are equally distributed.

3.2 GaAs treated in H₂SO₄/H₂O₂/H₂O :: 5 : 1 : 1 and then in conc. HCl for 5 min and then in deionized water

Using this procedure, the chemical shifts measured on Ga and As levels are close to 2 eV for 3d levels. An important contribution from the surface oxygen bound atoms is observed. This contribution is more clearly detected on Ga atoms. No trace of oxidation is observed on the As 3d level, which is most sensitive to superficial chemical reactions. The ratio of oxidized Ga atoms to total Ga atoms is 0.36 which indicates that the surface gets oxidized after etching. Also, as the samples are not immediately put inside the XPS analysis chamber, a comparatively thick oxide surface results. The ratio of 3d As and 3d Ga atoms obtained by taking the integrated area into calculation is 0.96 which gives an As-deficient oxidized phase. However, Massies and Contour (1985) have shown that if instead of static deionized water, running deionized water is used after HCl dip, an As-rich deoxidized surface will be produced.

3.3 GaAs treated in HF at a concentration of 5% in ethyl alcohol

This procedure leads to a deoxidized GaAs surface i.e. the Ga and As atoms are not in the oxidized form. The 531.85 eV oxide peak is due to atmospheric oxygen during substrate manipulation. The ratio of As and Ga atoms

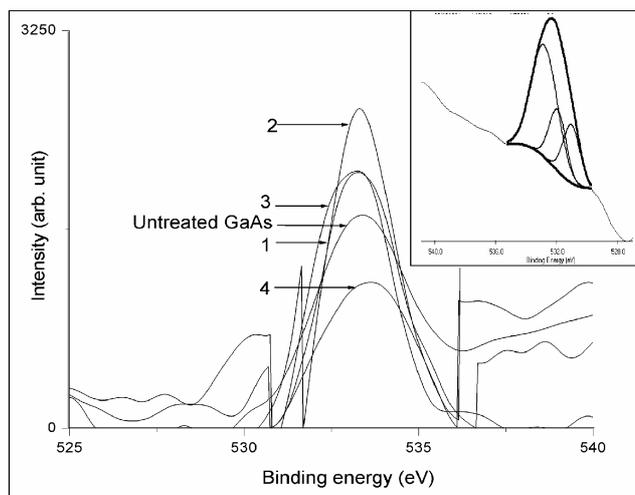


Figure 3. XPS spectra of O obtained using procedures 1–4 as described in table 1.

Table 1. Treatment procedures used.

Techniques	Treatment			
	1st stage	2nd stage	3rd stage	4th stage
1	Treated with acetone, methanol, DI-water	H ₂ SO ₄ : H ₂ O ₂ : H ₂ O :: 5 : 1 : 1 for 10 min	HCl (5 min)	Rinsed in DI-water
2	Same as 1	Same as 1	HF at a conc. of 5% in C ₂ H ₅ OH (2 min)	Rinsed in DI-water
3	HCl solution (10 min)			
4	Same as 3	DI-water for 10 s		

Table 2. Peak positions, area, FWHM of different peaks taken to fit the Ga and As peaks using XPS peak fit 4.1 software.

Techniques	Gallium				Arsenic			
	Peak	Position	Area	FWHM	Peak	Position	Area	FWHM
1	0	20-775 eV	1549-215	1-363 eV	0	42-527 eV	1461-752	1-101 eV
	1	22-230 eV	228-550	1-191 eV	1	43-323 eV	685-964	0-970 eV
2	0	20-749 eV	1374-157	1-903 eV	0	42-469 eV	389-221	0-990 eV
	1	19-352 eV	657-616	0-845 eV	1	41-319 eV	1544-260	1-077 eV
	2	19-905 eV	524-819	0-899 eV	2	41-933 eV	644-547	0-812 eV
3	0	22-320 eV	660-014	1-355 eV	0	43-254 eV	1116-260	1-224 eV
	1	20-523 eV	139-744	0-504 eV	1	42-542 eV	724-684	0-935 eV
	2	21-126 eV	1023-412	0-982 eV				
4	0	21-294 eV	370-717	0-891 eV	0	44-344 eV	41-933	0-522 eV
	1	20-625 eV	198-220	0-812 eV	1	42-557 eV	404-762	1-048 eV
	2	22-528 eV	113-325	1-026 eV	2	43-316 eV	658-203	1-144 eV

obtained from the total peak areas is 1.07 which gives a slightly As-rich surface.

3.4 GaAs treated with HCl

From As 3d and Ga 3d peaks, the ratio of their area is 1.7 which gives an As-rich surface. No oxides of As are present on the surface. The repeated chemical species on the GaAs surface etched with HCl solution were a mixture of gallium oxides and chlorides (Song *et al* 1994). But in this case, only oxidized Ga is obtained and the ratio of this with the total Ga atoms from the deconvoluted peaks is 0.17.

3.5 GaAs treated with HCl and water

The ratio of As and Ga signal obtained from the ratio of the total area is 1.21 which indicates an As-rich surface. Also the ratio of gallium oxide to the total gallium from the deconvoluted spectra is 0.13. Song *et al* (1994) have shown that almost all oxides and chlorides were removed from the surface by the short rinse with water after HCl etching. But in this study, the surface is not completely free of oxides. Although, there is no arsenic oxide (as

these are soluble in water), there are still some oxides due to gallium (as gallium oxide is not soluble in water).

When the GaAs with some native oxide is immersed in HCl solution, the thick overlayer of oxides reacts with HCl and most of the oxides dissolve into the solution leaving a mixture of gallium chlorides and oxychlorides on the surface. When the GaAs substrate is subsequently dipped in water for several seconds, the surface species (gallium chlorides and oxychlorides) dissolve leaving an As-rich surface. However, in this case some oxide species due to gallium are still present which may be due to the time of dipping in water being insufficient to dissolve gallium oxychlorides.

3.6 Surface morphology study

Figures 4–7 show the (Nomarski) optical microscopic images of GaAs surfaces after etching in different solutions. Figure 4 shows the optical image of a GaAs surface taken after etching in H₂SO₄/H₂O₂/H₂O :: 5 : 1 : 1 and then in conc. HCl for 5 min and then in deionized water. Conical etch pits are seen which are due to dislocations nearly normal to the {100} plane (Abrahams and Buiochhi 1965). Figure 5 shows tails associated with each etch pit,

which are obtained after etching in HF at a concentration of 5% in ethyl alcohol. This kind of behaviour is typical

of that expected from a dislocation inclined to the surface. Figure 6 shows the image taken after etching in HCl



Figure 4. Optical microscopic image of GaAs treated with procedure 1 as described in table 1.

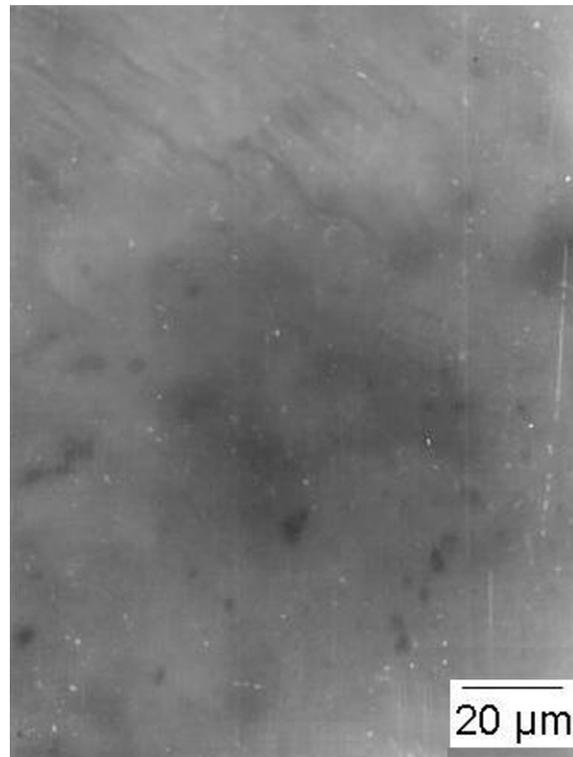


Figure 6. Optical microscopic image of GaAs treated with procedure 3 as described in table 1.



Figure 5. Optical microscopic image of GaAs treated with procedure 2 as described in table 1.

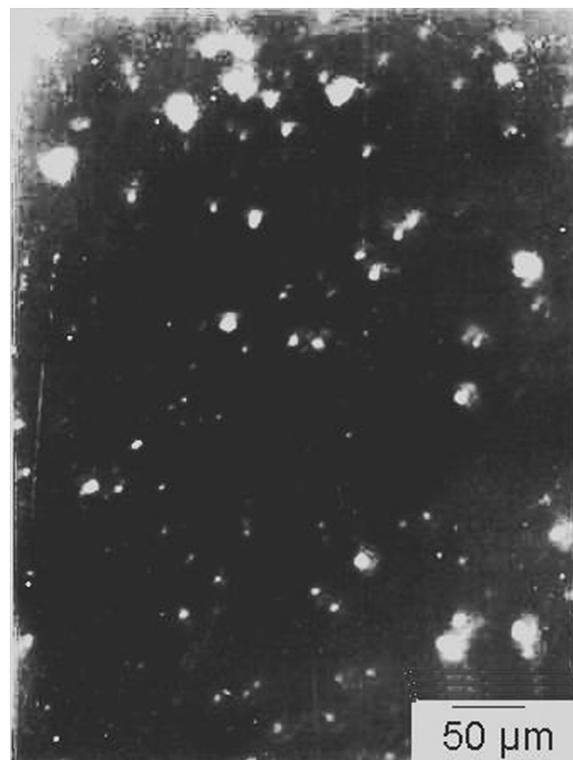


Figure 7. Optical microscopic image of GaAs treated with procedure 4 as described in table 1.

solution for 10 min and then in deionized water for 10 s. This figure reveals relatively long dislocation segments lying in the {100} plane. Figure 7 is the image taken from the GaAs surface after etching in only HCl solution for 10 min. Conical etch pits along with some foreign particles (dust) are seen on this surface.

4. Conclusions

From the above study it is seen that, except for the first procedure (generally used), all the other three processes used for etching GaAs produce an As-rich surface. Also, it is seen that the second method which uses HF–ethanol mixture produces oxide free (no Ga or As oxide) As-rich surfaces and in other procedures no arsenic oxide is observed. From the optical microscopic study, it is seen that different types of etch pits are produced due to different solutions and from which dislocations (normal, inclined and parallel to the plane of observation) are revealed.

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