loreover, the interest in MOS structures with non-leal insulators increases at present.

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A study of the compositional changes in chemically etched, Ar ion bombarded and reactive ion etched GaAs(100) surfaces by means of ARXPS and LEISS

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Abstract

The effects of chemical etching, noble gas ion bombardment and reactive ion etching on GaAs(100) surfaces was investigated by angle resolved X-ray photoelectron spectroscopy (ARXPS) and low energy ion scattering spectroscopy (LEISS). The results show that at the "as received" GaAs surface, Ga oxide is the major component, resulting in a Ga concentration slightly higher than As. Chemical cleaning by hydrochloric acid (at a HCl(conc.) to H_2O ratio of 1:1) followed by solvent washing efficiently removed the oxide layer, however, ARXPS showed that strong As enrichment occurs at the cleaned GaAs surface. Ion bombardment was carried out using 3 keV Ar ions with a beam current density of 1 μA cm^{-2} for a period of 50 min. XPS results show that at steady state the ion bombarded GaAs surface is depleted in As (As/Ga $\approx$ 0.8), but ARXPS indicates an As increase at the very surface. This is further confirmed by Ne^+ LEISS analysis, which shows in the top layer the As concentration is increased by 50% after ion bombardment. The results indicate that bombardment induced compositional changes in this surface are due to Gibssian segregation. The results of reactive ion etching in a 200 W Freon 12 plasma for a period of 5 min at 60 mTorr, showed that this apparently low damage process also produces significant compositional changes in the surface. The report illustrates the benefits of using complementary surface analytical techniques in such studies.

1. Introduction

Ion bombardment, reactive ion etching and wet chemical processes are all widely used in the fabrication of III–V semiconductor devices. Dry processing gives increased control and precision and enhanced yields, particularly in integrated circuit technology, but can cause harmful effects in the final device characteristics [1,2]. As a consequence wet etching is still extensively used in industrial processes despite the difficulty of compositional changes [3], controlling the process over large area wafers and the problems of reducing yields. The demands on the etching processes are greatest in more advanced devices such as HFETs and HBTs, particularly in small feature size self-aligned structures designed to operate at very high frequencies. Because of the small dimensions of these devices very accurate control is needed and this can only be provided in an industrial process by the use of dry etching techniques. It is thus essential that these processes are

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understood so that damage may be minimised and yield increased.

As stated above, dry etching of III–V semiconductors often leads to degradation of electrical performance as a result of "damage", particularly in devices that are surface sensitive. This damage adversely affects several critical device parameters and leads, among other things to, increased surface depletion, high reverse leakage currents, short minority carrier lifetime and low breakdown voltages. All of these factors affect overall performance and device yield.

Bombardment damage falls into four broad categories: (i) surface and sub-surface contamination caused by deep penetration of light molecules (particularly hydrogen) or surface residues, (ii) stoichiometric changes due to preferential chemical action at the surface and the effects of bombardment induced preferential removal of one or more of the components, (iii) structural changes due to bond breaking and atomic rearrangement in an altered layer in the near-surface region and (iv) the introduction of deep and shallow defects into the material being etched. Contamination may be reduced by avoiding certain gases, by good process control and by post-treating residues. Compositional or stoichiometric changes are dependent to a large extent on the surface matrix and are most pronounced in materials, such as InP, containing volatile components. This effect may be reduced, but it cannot be eliminated since the kinetic effects of energetic particle bombardment are still present. Structural changes are similarly produced by energetic ion and radical bombardment of the surfaces which can lead to bond breaking, preferential sputtering and chemically driven relaxation. The latter two effects undoubtedly influence the introduction of defects in the materials, however, the depth of penetration and the exact nature of these defects is not understood. The defects appear at a far greater depth than the projected range of either the primary species or the substrate recoils and models employing thermal or complex diffusion mechanisms, quasi-channeling or "lucky atoms" do not adequately explain these effects.

There is an obvious requirement to understand and elucidate the mechanisms responsible for these structural and compositional changes in III–V semiconductors. Although this class of semiconductor, and in particular GaAs surfaces [4,5], have been extensively studied, difficulties in interpretation of analytical data still exist. One of the major problems is that a single surface analytical technique cannot provide comprehensive experimental evidence on compositional distribution in a compound surface and hence the mechanisms responsible for these effects are still not understood. In this work, chemical etched, noble ion beam bombarded and reactive etched GaAs(100) surfaces have been analysed with a combination of angle resolved X-ray photoelectron spectroscopy (ARXPS) and low energy ion scattering spectroscopy (LEISS) techniques.

2. Experimental

The samples used in the study were GaAs(100) crystalline surfaces doped with low dose Si. Pure Ga and As samples were also prepared for accurate quantification. Ga thin films were made by evaporating gallium on to a highly polished pure titanium substrate in high vacuum. The thickness of the gallium film was of the order of a few microns. Pure arsenic surfaces were prepared by sequentially polishing a lump of arsenic on a series of different grade abrasive papers until a mirror-like surface was achieved. Both samples were cleaned in UHV by prolonged ion beam etching and examined by means of XPS and LEISS under the same experimental conditions.

Chemical etching was carried out using a similar cleaning procedure to that described by Epp et al. [3]. The sample was cleaned in 1 : 1 HCl(conc.)/H_2O at room temperature for about 10 min, rinsed in de-ionized water, ultrasonically cleaned in methanol and then rinsed again in de-ionized water. The chemically etched GaAs sample was quickly transferred in air to the analysis chamber.

Monoenergetic ion bombardment was performed with a VG EX05 electron impact source, employing a rastered Ar ion beam, with beam current density and energy of 1 μA cm^{-2} and 3 keV, respectively. The rastered area was about 8×6 mm^2. The base pressure within the analysis chamber was always better than 5×10^{-10} mbar.

RIE was performed in a Plasmatech 80 plasma cell where the GaAs surfaces were subject to a 5 min radio frequency (13.56 MHz) plasma etch in dichlorodifluoromethane, Freon 12, under standard conditions of 200 W at a pressure of 60 mTorr. Under these conditions etch rates of about 200 Å/min are produced, giving a total removal of material to a depth of about 0.1 μm for these

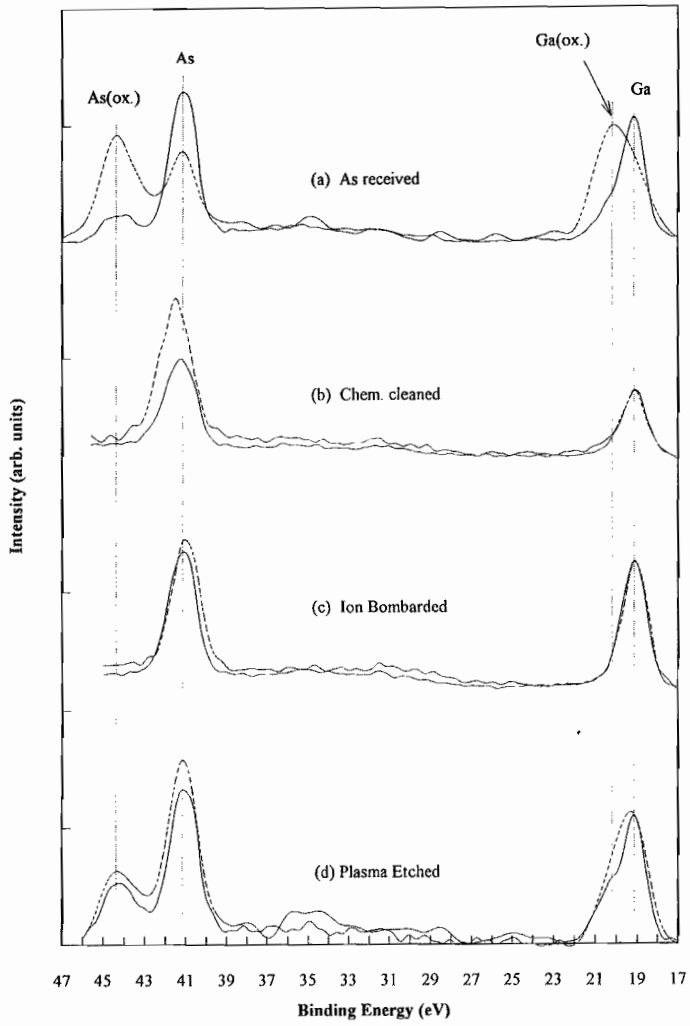


Fig. 1. XPS spectra showing Ga 3d and As 3d peaks from GaAs surfaces at 80° take-off angle (dotted line) and 0° take-off angle (full line) for: (a) "as received" sample, (b) wet chemically cleaned sample, (c) sample after 50 min Ar ion bombardment at 3 keV and 1 μA and (d) RIE sample etched in Freon 12 for a period of 5 min.

experiments. This is more than enough to remove any native oxides present on the surface prior to etching.

XPS and LEISS analyses were carried out in a VG ESCALAB 200D spectrometer. The HSA analyzer polarities were reversed to allow positive and negative charged particle energies to be measured.

In XPS, Al Kα (1486.6 eV) radiation was used for the analyses. For ARXPS, the small area analysis facility of the ESCALAB 200D was employed at a 1000 μm diameter analysis area and with the iris at the nose of the input lens set to restrict the acceptance angle to less than 8°, that is, below the 10° acceptance angle required for the collection of meaningful ARXPS data. The electron take-off angles (TOA) were varied from 0° to 80° (to the surface normal) in 10° steps. During ion bombardment, XPS spectra were collected at 0° TOA at 1 min intervals to a total of 50 min. Quantitative analysis in XPS was achieved using measured peak intensities and self-generated relative sensitivity factors employing codes incorporated in the VG VGS5250 instrumental data system. Curve synthesis was employed throughout to assess the relative concentrations of the components of the elements found in the surfaces and to accurately determine their associated binding energies. This was accomplished after Shirley background subtraction using the procedures within the VG VGS5250 data system. Binding energy measurements were referenced initially to the C 1s line at 284.6 eV and then after bombardment to Ga and As 3d peaks as secondary standards.

In LEISS analysis, a defocused Ne ion beam of current 10 nA and energy 1 keV generated by the same electron impact source that was used for Ar ion bombardment was incident on the sample surface at 51° to the surface normal (at 0° TOA). The scattering angle in the system is 129°. All parameters were selected to minimise primary beam damage. Quantitative analysis of LEISS results for a compound surface is difficult as the intensity of the scattering ions is strongly dependent on such factors as, the ion survival probability, neutralisation and shadowing effects, all of which are matrix dependent and difficult to estimate. These difficulties may be avoided by using standard samples. For a system, AB, the measured intensity of ions scattering at surface atom A may be expressed by:

$$\frac{x_A}{x_B} = \frac{I_A/I_A^0}{I_B/I_A^0}\,\frac{N_A^0}{N_B^0}.$$

Here I_i and I_i^0 (i = A or B) are the intensities of ion scattering at i atoms measured from the surface AB and from the pure elemental standard A or B; N_i^0 is the number density of standard surface, which is assumed proportional to $(d_i/M_i)^{2/3}$. Here d_i and M_i represent the density and atomic mass of element i.

3. Results

3.1. XPS analysis

X-ray photoelectron spectra showing the Ga 3d and As 3d peaks from the various GaAs surfaces examined are shown in Fig. 1. Spectra for 0° and 80° take-off angles are shown in this figure. These two

Table 1
The binding energies (in eV) and the FWHM of Ga and As 3d electrons in the different states (referenced to C 1s at 284.6 eV)

		Elemental	As received		Chem. etch GaAs	Ar bomb. GaAs	RIE GaAs
			GaAs	Oxide			
Ga	BE (eV)	18.8 (18.4–18.9)	19.1 (19.0–19.6)	20.4 (19.6–21.0)	19.0	19.1	19.1
	FWHM	1.35	1.38	1.60	1.58	1.50	1.56
As	BE (eV)	41.8 (41.5–42.0)	41.1 (40.8–41.6)	44.7 (43.9–46.3)	41.2	41.2	41.2
	FWHM	1.59	1.56	1.99	1.77	1.63	1.70

The values in brackets are taken from the NIST XPS database [7].

extreme angles chosen for the ARXPS study represent integrated XPS analysis depths of about 60 and 10 Å, respectively. The spectra have been normalised to the Ga 3d signal. The raw spectra (after charge compensation) are shown in this figure in order to illustrate the immediate and apparent differences observed in the various surfaces. The individual peaks for both Ga and As were subject to Shirley background removal and then synthesized using the procedures inherent in the instrument data system. The results of the energy measurements gained from these analyses are shown below, however, in the interest of brevity the synthesized peaks are not shown.

3.1.1. "As received" GaAs(100)

Ga 3d and As 3d together with C 1s and O 1s spectra were collected in the XPS analysis of this sample. The atomic ratios of As to Ga in the GaAs matrix under the different conditions were calculated using measured sensitivity factors self generated from standard materials. The matrix factor for the GaAs system was taken as 0.95 based on Seah's [6] model. All binding energies were corrected to the C 1s line at 284.6 eV. The binding energies of 3d core electrons of Ga and As taken from the "as received" GaAs(100) surfaces are listed in Table 1, where they are compared with data from the reference samples and published results. The reference data, shown in brackets, illustrate the range of all measurements for this system published in the NIST database [7]. Compared with the reference samples, the binding energy shifts of the Ga and As 3d lines from the GaAs surface showed that electron transfer occurred in the formation of the compound. This may be predicted from the electronegativities of Ga [ε_{Ga} = 1.6 (eV)$^{1/2}$] and As [ε_{As} = 2.0 (eV)$^{1/2}$] as defined by Pauling [8].

Measurements from the synthesized Ga 3d and As 3d spectra from the "as received" GaAs surface taken at 0° and 80° take-off angles show that the concentration of Ga oxide is greater than that of As oxide. This is also apparent from Fig. 1a. This is due to the relatively greater affinity of oxygen (ε_O = 3.5) to gallium than to arsenic and results in Ga enrichment in the air exposed GaAs surface. The distributions of Ga oxide and As oxide in the overlayer revealed by ARXPS (shown in Fig. 2) are very

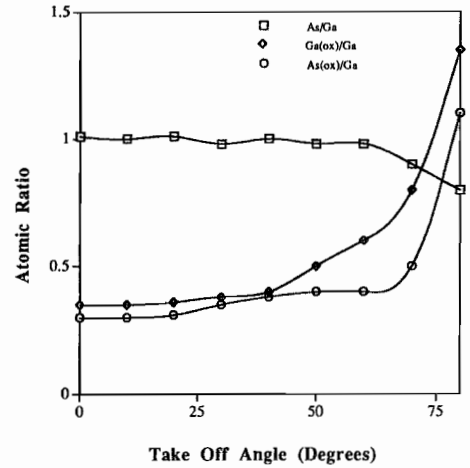


Fig. 2. Atomic ratios of As, As oxide and Ga oxide to Ga for the untreated "as received" sample.

similar. The As/Ga ratio in the bulk of the "as received" GaAs sample is close to the stoichiometric value, but at the interface between GaAs substrate and oxide layer, the ratio decreased to about 0.82. Lu et al. found an As/Ga ratio of 0.86 for a similar system of an atmospheric room temperature oxide [9]. This Ga enrichment is probably due to the fact that Ga is more easily oxidised [10,11] and hence moves more rapidly than As towards the surface [11] under the chemical driving force of oxidation at the air/solid interface.

3.1.2. Chemically etched GaAs

The spectra in Fig. 1b shows that chemical cleaning, using the procedure detailed in the experimental section, effectively removes the oxide overlayer from the GaAs(100) surface. A small amount of carbon and oxygen remain due mainly to physical adsorption from the air during sample transfer or possibly due to residues from the methanol solvent. This wet etching process, however, causes significant damage to the crystal structure in GaAs surface. This is shown by (1) the broadening of Ga and As peaks, possibly due to an increase in defect density in the GaAs surface produced during the etching process resulting from formation of both Ga–Ga and As–As

bonds; and (2) by the change in surface concentration from the stoichiometric value, that is depletion of Ga in the surface. The As to Ga atomic ratio for the sample surface is plotted in Fig. 3 as a function of take-off angle. The figure clearly shows a substantial increase in As concentration in the near-surface region, but suggests that stoichiometry has been maintained in the immediate subsurface region.

The reasons for As enrichment are not clear. Simplistically, it may be though that since the oxide overlayer of "as received" GaAs is Ga-rich, the immediate subsurface will be depleted in Ga and consequently, the surface which remains after the overlayer has been removed must be As-rich [12]. This explanation will not, however, explain the results. The erosion rate of an acidic etchant is generally very high, of the order of 0.1 μm/min. The oxide overlayer and As-rich regions are only a few tens of ångströms thick, hence, both these original regions will be completely removed during the wet etching process. We must therefore assume that the As-enrichment in the surface after the wet etching is a purely chemical effect and is due to the greater reactivity of gallium towards chlorine anions (ε_{Cl} = 3.0 eV) in the dilute acid. This leads to more Ga chloride formation, which is soluble in water and consequently washed away by rinsing. Lu et al. [9] found similar results for HCl etchants, but found Ga enrichment for H_3PO_4/NH_4OH and H_2SO_4/NH_4OH etchants where there was favourable dissolution of the As° in the NH_4OH.

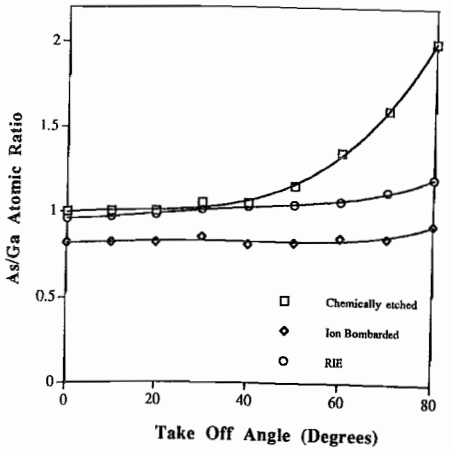


Fig. 3. As/Ga atomic ratios for wet chemically etched sample, 50 min Ar ion bombarded sample and RIE sample.

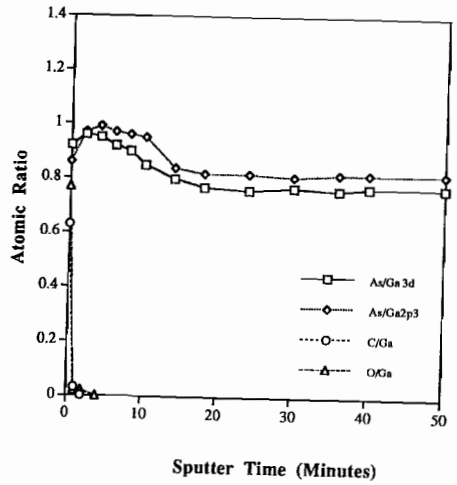


Fig. 4. As/Ga(3d), As/Ga(2p3), C/Ga and O/Ga atomic ratios as a function of bombardment time for the Ar sputtered (3 keV, 1 μA) GaAs sample surface.

3.1.3. Ar ion bombarded GaAs

An "as received" sample was subject to 3 keV argon ion beam bombardment for periods up to 50 min. Fig. 4 shows the surface compositional changes against bombardment time observed with XPS at 0° take-off angle. Both the 3d and $2p_{3/2}$ core level electrons were monitored in XPS and the results of both are shown in the figure. The benefit of using multiple core level electrons in XPS analysis is that since the sampling depths depend on the kinetic energies of the different core level electrons, variations in XPS results using the different core level signals may indicate changes in compositional distributions [13]. For example, the ratio of As 3d to Ga 3d peaks prior to bombardment is greater than that of As $2p_{3/2}$ to Ga $2p_{3/2}$. This indicates a Ga-rich initial surface layer confirming the previous ARXPS analysis. The figure shows that the contaminant overlayer was removed after about 1–2 min, both 3d and 2p ratios of Ga and As decrease starting from about

2 min sputtering until after 15 min, the 3d ratio reached a steady value of 0.77; and the 2p ratio reached 0.82. The sampling depths ($\sim 3\lambda$) are ~ 45 Å for the p-orbitals and ~ 55 Å for the d-orbitals at 0° take-off angle and ~ 8 and ~ 9.5 Å respectively at 80° take-off angle.

These measured changes in both core level signals of Ga and As clearly illustrate that ion bombardment causes As depletion in GaAs surface layers sampled by this technique. The difference in the atomic ratios measured from 3d and 2p signals, however, indicates that the As concentration at the outermost surface may be higher than that in the immediate subsurface region. The results of ARXPS analysis repeated on the 50 min bombarded surface supports this proposition. The spectra shown in Fig. 1c and the As/Ga atomic concentrations calculated from synthesized spectra and plotted in Fig. 3 both indicate greater As concentrations in the outermost layers of the surface. Thus for this surface the results show As depletion, but a gradation of As concentration increasing towards the surface.

3.1.4. Reactive ion etched GaAs

Fig. 1d shows a comparison of spectra taken at 0° and 80° take-off angles for the RIE surface. This together with the results of As to Ga atomic ratios plotted in Fig. 3 for this surface, show that plasma etching in Freon 12, produces considerably changes, leading to significant As enrichment (Ga depletion) in the outer layers. This enrichment is certain to have an effect on deeper levels. The result shown in Fig. 3 of As/Ga atomic ratios as a function of take-off angle (effectively related to the reciprocal of the integrated analysis depth) for this sample are similar in nature to those of the wet chemically etched surface. The figure shows a somewhat lesser increase in As concentration in the near-surface region than for the wet chemically etched sample, but as for that sample suggests that stoichiometry has been maintained in the immediate subsurface region. This suggests that the As-enrichment in the surface is, like the wet etching process, largely a chemical effect due to the greater reactivity of gallium to the chlorine and fluorine species in the Freon 12 plasma.

Table 2 shows the atomic ratios of As, As(oxide), Ga(oxide), C, Cl and F to Ga. From this data, in addition to the observed plasma induced As enrichment, a number of other interesting results emerge. It may, for example, be seen that the Freon 12 etched surface has suffered heavy oxidation. Since the sample was exposed to the atmosphere between the etching process and the surface analysis, it is probable that this is the result of ambient oxidation, but a possibility exists that oxidation occurred during the etching process [14]. The preferential oxide at the surface is the Ga oxide. The growth of these oxides themselves can lead to stoichiometrical and chemical changes in the immediate surface region, but as may be seen for the results for the "as received" sample the effects of ambient oxidation on composition would be expected to be opposite to those observed here.

As may be seen from the table both F and Cl are found in the surface. F is concentrated more at the outer surface, but the Cl signal does not vary with depth, indicating some incorporation of this element in the substrate to a depth of at least 60 Å. Levels of C are unusually high and again there appears to be some incorporation of C possibly at a level intermediate between substrate and outer oxide layer. This has almost certainly occurred during reactive ion etching. Similar effects have been observed by Wronski et al. [14].

Table 2
The atomic ratios of As, O, C, Cl, F and native oxides to Ga at various take off angles

Take off angle (deg)	As/Ga	As(ox)/Ga	Ga(ox)/Ga	O/Ga	C/Ga	Cl/Ga	F/Ga
0	0.96	0.44	0.51	5.26	11.3	0.86	0.58
40	1.03	0.48	0.79	5.64	19.5	0.9	0.55
80	1.13	0.67	1.05	9.96	3.08	0.87	0.65

3.2. LEISS analysis

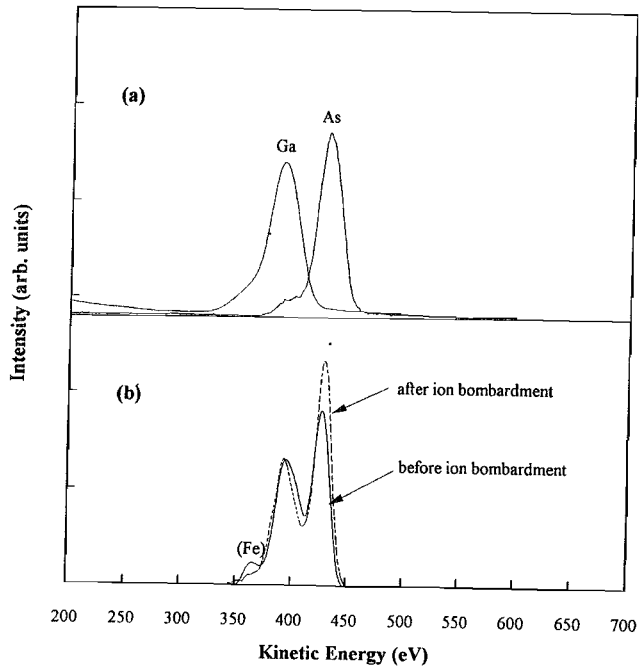
3.2.1. LEISS spectra of pure Ga and As samples

1 keV Ne LEISS spectra taken from Ga and As tandard samples are shown in Fig. 5a. Ga and As cattering peaks appear at kinetic energies of 389 nd 429 eV, respectively. The shoulder found on the ower kinetic energy side in both spectra is due to ie Ne^{22} isotope. The abundance of this Ne isotope ; about 10%. The Ga scattering peak was situated n a sloping background; this may be due to a larger mount of sputtered gallium atoms since the melting oint of Ga is about 30°C. The pure Ga film during ie experiment (at room temperature) was nearly in quid phase, the Ga atoms at the surface were more asily sputtered away.

The peak areas of Ga and As from the standard mples are about 73.0 and 70.2 kC eV/s, respecvely. For these Ga and As standard samples, the value $N_{As^0}/N_{Ga^0} = 0.97$. These values may then be used with measured As and Ga peak intensities from the GaAs samples to determine the As/Ga atomic ratios for the outermost layer of the material.

3.2.2. Ar ion bombarded GaAs

LEISS spectra of GaAs surfaces before and after ion bombardment are shown in Fig. 5b. Since an oxide layer was present on the "as received" sample surface, LEISS analysis for GaAs surface prior to ion bombardment was carried out after heating the sample at 180°C for about 10 h. An additional small Fe peak was found in the initial surface which may be due to contamination from the sample holder. Peak intensities were determined by peak fitting and quantification was then performed by the method detailed above. Results showed that the As/Ga ratio in the outermost layer of the GaAs surface before ion bombardment, but after heat treatment, was about



. 5. LEISS spectra for: (a) pure Ga and As standard materials and (b) GaAs surfaces before and after 50 min of Ar ion bombardment (3 /, 1 μA).

1.0; after 50 min of bombardment the ratio reached a value of 1.51. It is clear that ion bombardment causes significant As enrichment at the outermost layer.

3.2.3. Reactive ion etched GaAs

Because of the relatively heavy oxidation in the Freon 12 RIE GaAs surfaces and the extreme surface sensitivity of the LEISS technique, it was not possible to gain meaningful LEISS data for these samples. Sample heating to remove surface oxides, as was performed for the "as received" samples, was not attempted in this case as it was thought that due to the more complex nature of the RIE surface the results might not be representative of the original etched condition.

4. Theoretical models and discussion

4.1. Sigmund linear collision cascade theory

Sigmund linear collision cascade theory [15] based on Boltzmann's linear transport equation and classic binary collision approximation is an established method for the description of energetic particle behaviour in solids. (The binary collision approximation will not apply when the time of collision is of the same order as the period of vibration of the atoms in the solid surface. Hence one would not expect this model to hold for the vast majority of low energy species bombarding the surface from within the RF plasma.) According to this theory, the ratios of the partial sputtering yields for a compound system are not necessarily identical to the atomic ratios of the material [16], that is, the sputtering will not be compositionally stoichiometric. In the case where the mass difference of the elements is not significant, the ratio may be expressed by Sigmund as:

$$\frac{Y_A}{Y_B} = \frac{x_A}{x_B}\left(\frac{M_B}{M_A}\right)^{2m}\left(\frac{U_B}{U_A}\right)^{1-2m},$$

where x_i, M_i and U_i $(i = A, B)$ represent the concentrations, mass and surface binding energies of element A and B in a compound AB. Malherbe et al. [17], ignored mass difference restrictions and determined the parameter m to be 0.165 in the low keV regime for a large number of compounds (mainly metallic oxides). They then expressed the above equation as:

$$\frac{(x_A/x_B)^s}{(x_A/x_B)^b} = \left(\frac{M_B}{M_A}\right)^{2m}\left(\frac{U_B}{U_A}\right)^{1-2m}.$$

Here superscript s and b stand for surface and bulk, respectively. For a covalent compound A_xB_y, Malherbe et al. [17] have proposed a model for estimation of surface binding energy by modifying Pauling's formalism. The model was initially established for oxides, and later applied to the InP [18] system. For cation A and anion B, the binding energies may be calculated from:

$$U_A = H_s + \frac{1}{2}(\varepsilon_A - \varepsilon_B)^2,$$

$$U_B = \frac{y}{x+y}D(\text{B–B}) + \frac{x}{x+y}D(\text{A–B}) + \frac{1}{2}(\varepsilon_A - \varepsilon_B)^2,$$

where H_s is the heat of sublimation for cation A; ε_i is the electronegativity; D(A–B) and D(B–B) represent the strengths of A–B and B–B bonds in the A_xB_y system.

For GaAs, the bond energies of As–As and Ga–As bonds are 3.96 and 2.17 eV; the heat of sublimation of Ga is 2.87 eV [19], the surface binding energies of As and Ga atoms in GaAs matrix calculated from the above equations are 3.09 and 2.89 eV, so the As/Ga ratio in an ion bombarded GaAs surfaces predicted from the model based on Sigmund linear collision cascade is about 1.35.

The result for the As/Ga atomic ratio using this model is in fair agreement with our LEISS measurement for the Ar ion bombarded sample. It may be thought that this is a reasonable prediction considering the fact that the origin of sputtered species is from within a few Å of the surface, a distance comparable with the sampling depth of LEISS. The conflict between our XPS and LEISS results, however, may not be explained by Sigmund's theory. According to this model, the partial sputtering yield for Ga is greater than As and this means that in the equilibrium state a net movement of Ga from the

immediate subsurface to the top layers must exist. Hence, within the detection range of XPS, Ga depletion would be expected. This assertion is not supported by our XPS observations and other published results which show As depletion (Ga enrichment) within the surface volume sampled by the XPS technique. The theory should also, of course, not hold for reactive ion etching where the ion energies are low and no proper linear cascade should be established.

3.2.2. *Bombardment induced segregation and enhanced diffusion*

Compositional changes in a compound surface due to bombardment have been explained by models based on theories of surface segregation and diffusion. From a thermodynamic point of view a trend always exists to drive one of the components from the bulk to the outer surface of a multicomponent system to maintain minimum surface free energy. This effect is negligibly small at room temperature for a system in equilibrium, since few atoms can overcome the constraint of the crystal field in the lattice. The effect can, however, be substantially enhanced by energetic ion bombardment since large numbers of mobile atoms and vacancies will be generated in the region of the collisional cascade; the resulting mobility thus allowing effects such as Gibbsian segregation to take place.

The surface composition of a binary system altered by surface segregation is generally expressed by the Langmuir–Mclean equation:

$$\frac{x_A/x_B)^s}{x_A/x_B)^b} = e^{-Q/kT}.$$

where the heat of segregation, Q, may be expressed as the difference in surface energy between a single atom A and an atom B, that is:

$$= \gamma_A a_A - \gamma_B a_B,$$

where γ_i and a_i (i = A or B) are the surface tension and the area of a bulk atom (A or B), respectively. In the case of GaAs, the size of the As atom is similar to that of the Ga atom, but the surface energy As (~ 0.2 J/m^2) [19] is much less than that of Ga (0.784 J/m^2). Hence it may be predicted that, under the influence of energetic ion bombardment, As will preferentially move to the GaAs surface due to surface energy driven segregation. This results in As enrichment in the outer layer as observed in our LEISS experiments on Ar bombarded GaAs. Since the As atoms segregate to the top layer of the GaAs surface during ion bombardment, the partial sputtering yield for As will increase. In order to maintain minimum surface free energy, there must be a net flux of As from the immediate subsurface region, which causes As depletion in the subsurface, the volume sampled by XPS. This is the result which we have obtained. It is therefore likely, from our results, that bombardment enhanced Gibbsian segregation is responsible for the induced compositional changes wrought in the GaAs sample subject to energetic Ar ion bombardment. This qualitative interpretation for the compositional changes in the GaAs surface, however, requires, a better description of the physical properties of Ga and As atoms in the surface matrix at room temperature.

The results for the reactive ion etched and wet chemically etched samples are in many ways similar in that in both cases the measurement of As/Ga atomic ratios show As enrichment in the outer layers of the surface, but indicate that the immediate subsurface region remains as stoichiometric GaAs. This result suggests that RIE is a chemical process taking place in the outer layers of the surface of the compound semiconductor similar in nature to the wet etching process with none of the characteristics of energetic ion bombardment apparent. This is clearly not wholly the case since it is known that the RIE process produces deep defects far beyond the range of the surface chemical reaction which are responsible for poor performance in many device structures [20–22]. Models of energy distribution of species in such RIE plasmas [23,24], indicate that the depth of these defects is also beyond the range of plasma ion implantation or recoil atoms due to the plasma bombardment.

5. Conclusions

Chemically cleaned, energetic ion beam bombarded and Freon 12 reactive ion etched GaAs(100) surfaces have been investigated by means of angle resolved XPS and LEISS.

Results show that the chemical cleaning with dilute HCl acid can remove the oxide overlayer on GaAs surface effectively, but causes As enrichment in the surface. This is mainly due to the greater affinity of chlorine in HCl to Ga, which results in the formation of soluble Ga chloride which is then more easily removed. Results for the Freon 12 RIE surface suggest that a similar chemical process is responsible for the observed As enrichment in this surface, with the Cl and F species in the plasma reacting more readily with the Ga in the GaAs surface. This does not, however, explain the deep defects formed when such surfaces are subject to plasma processing.

The ARXPS and LEISS examinations of the GaAs(100) surface after 50 min of 1 μA, 3 keV Ar ion beam bombardment show that unlike chemical and plasma etching, energetic ion bombardment leads to As depletion within the sampling depth of XPS. This depletion is probably due to Gibssian surface segregation which drives As atoms to the outmost layers of GaAs (as observed with LEISS), leading to preferential sputtering of As from the GaAs surface. The combination of XPS with a sampling depth of about 60 Å and LEISS which samples only the outermost atomic layer provides more information on the true compositional changes with depth into the surface and gives a greater opportunity of gaining a knowledge of these surface effects.

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