Elevated temperature low energy ion cleaning of GaAs

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We have studied various cleaning procedures for obtaining atomically clean, well-ordered surfaces of GaAs(100) and (110). We have evaluated the resulting surfaces by angle resolved ultraviolet photoelectron spectroscopy (ARUPS), x-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED). We report results for thermally cleaned, ion bombarded and annealed, and ion bombardment at elevated temperature cleaning procedures. The most reproducible results, giving the best, lowest background LEED patterns and the sharpest ARUPS results, were obtained from the elevated temperature ion bombardment cleaned samples. Our thermally cleaned samples, while showing low impurity concentrations to XPS studies, had a relatively high background LEED pattern. The ARUPS results were not indicative of a high degree of surface order; the normal emission spectra more resemble angle integrated UPS results. The room temperature ion bombarded samples, followed by anneals of 30 min at temperatures up to 520 °C, yielded a high quality 1×1 pattern on a GaAs(100) surface, but no higher order reconstruction could be obtained. The ion bombardment typically used in this work was 200 eV Ar ions. Substrate temperature during bombardment were varied from 300 to 800 K. Post anneals were also examined. Temperatures of 300 °C were quite adequate to obtain a high quality 1×1 LEED pattern on both (100) and (110) surfaces. Post anneals at 520 °C yielded a low background (8×2) Ga surface.

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I. INTRODUCTION

A reproducible surface is a basic requirement for any class of surface studies. A clean, well-ordered surface is required for surface studies, and something approaching this ideal is required for the molecular beam epitaxial growth of semiconductors.[1,2] The primary techniques used in surface studies have been annealing and ion bombardment followed by annealing the surface.[3] For compound semiconductors such as GaAs, the dominant technique for clean surface work has been cleavage, which is only applicable for generating (110) surfaces. MBE growth, on the other hand, has emphasized (100) surfaces, primarily since these surfaces are the ones used for device fabrication, but also due to difficulties in MBE growth on (110) oriented substrates.

In this paper, we have studied cleaning techniques for (100) surfaces. We have compared the surfaces generated by the thermal annealing typical for preparing a substrate for MBE growth to the surface after various combinations of ion-bombardment and anneal cycles, as well as **simultaneous** ion bombardment and annealing. We find that the latter cleaning procedure provides a highly reproducible surface that exhibits high-quality LEED patterns, no observable contaminants, and angle resolved photoelectron spectra that are very similar to those of MBE grown materials. We have found that applying this procedure to (110) oriented substrates leads to similar results, with an angle resolved ultraviolet photoelectron spectrum very similar to that reported for *in situ* cleaved surfaces, except for the surface potential being pinned at the position normal for "pinned" surfaces rather than at the valence band where the bulk Fermi level is located.

II. EXPERIMENTAL

Ion bombardment, annealing, or the combination of *simultaneous* ion/heat treatment (IHT) of GaAs substrates have been performed *in situ* in a UHV preparation chamber connected with a UPS/XPS/LEED analyzing chamber. The samples received a relatively standard MBE cleaning (involving a detergent rinse, water rinses, ethanol, acetone, and ethanol rinses, water rinse, 7:1:1-H_2SO_4:H_2O_2:H_2O etch, water rinse, spin dry) prior to mounting with indium on a high purity molybdenum heater plate. Before doing any measurements of cleaning procedures, the entire system was baked (≈ 150 °C) and was typically operating at a base pressure of 1.4×10^{-8} Pa. The sample temperature was measured by means of an optical pyrometer (Ircon #300HC) using a graphite spot (Aquadag from Acheson Colloids Company, Port Huron, Michigan) with a calibrated emissivity. The Ar-ion etching has been performed by means of a Physical Electronics model 04-161 ion gun, with an angle of $\approx 55°$ to the sample normal. Ion currents of the order of 1–2 μA on the sample surface (1/2 in. $\times$ 1/2 in.) were typically used. After the IHT, the GaAs samples were transferred to the analyzing chamber. The UPS and XPS measurements were performed with an angle resolved photoelectron spectrometer (ADES 400, Vacuum Generators) either by using the resonance lamp ($h\nu = 16.8$, 21.2, and 40.8 eV) or the x-ray source ($h\nu = 1253.6$ eV). The photoelectron spectra were recorded in the constant resolution mode, with typical system energy resolutions of ≈ 0.15 eV ($h\nu = 16.8$ and 21.2 eV), ≈ 0.25 ($h\nu = 40.8$ eV), and ≈ 1.2 eV ($h\nu = 1253.6$ eV). Normal emission and 45° angle of incidence were typically used for the UV photons, whereas in XPS the emission angle was

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14.5° (with respect to the sample normal) and the angle of incidence was 45°. The surface structure of the samples was analyzed by means byLEED (Varian #981-0127).

The Ga 3*d*, As 3*d*, O 1*s*, and C 1*s* core levels were analyzed with XPS. Typical spectra of Ga and As 3*d* core levels of a GaAs(110) substrate after baking the preparation chamber containing the sample (but without further surface treatment) are shown in Fig. 1. The As 3*d* core level shows the main line (the intensity I was obtained after subtracting a linear background) and the surface oxide (As_2O_3) related line,[4] shifted by about 3.2 eV to higher binding energy with respect to the main line (intensity I'). In contrast to the As 3*d* core level, the Ga 3*d* main line and the oxide related line are not resolved in our measurements. The deconvolution of the Ga 3*d* line into two lines [the shape of the main line was obtained from a spectrum of a clean GaAs(110) surface] shows an oxide related line shifted by about 1.5 eV to higher binding energy, most probably related to Ga_2O_3.[4] The oxide related line gives rise to an asymmetry of the Ga 3*d* and the ratio a/b can be used as a measure of the amount of Ga oxide at the sample surface. The oxygen and carbon content was determined from XPS measurements of the O 1*s* and C 1*s* core lines. In addition, the substrate surfaces have been characterized by UPS and LEED measurements. The work function Φ and the surface Fermi level position have been determined from the ultraviolet photoelectron spectra, whereas the surface structure has been studied by examining the LEED pattern.

III. RESULTS

A. Thermal cleaning

Heat treatments in the temperature range $550 < T < 611$ °C are the usual surface cleaning procedures for GaAs substrates.[5] A typical cleaning cycle of a *n*-type GaAs(100) is shown in Figs. 2 and 3. The oxygen content of the surface is shown in Fig. 2(a). No significant change in the O 1*s* intensity has been observed after annealing at temperatures below 560 °C. However, in the range between 560 and 580 °C the oxygen content drops essentially to a vanishing amount. In our XPS measurements, the limit of detection for

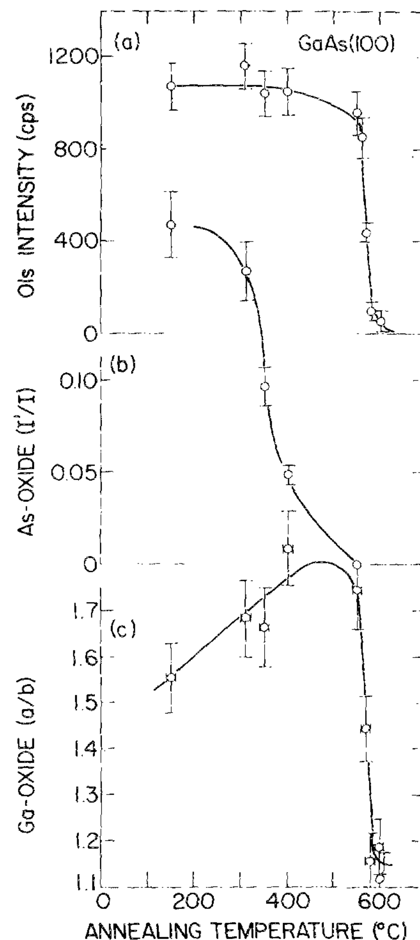

FIG. 2. Surface oxide content vs annealing of a GaAs(100) substrate as studied by XPS. (a) Overall oxygen content of surface. (b) Relative amount of As oxide I'/I (see Fig. 1). Note the distinct decrease of As oxide at low annealing temperatures ($T < 350$ °C). (c) Relative amount of Ga oxide as determined by the ratio a/b (see Fig. 1). A similar sharp drop as in (a) can be observed for temperatures $550 < T < 580$ °C.

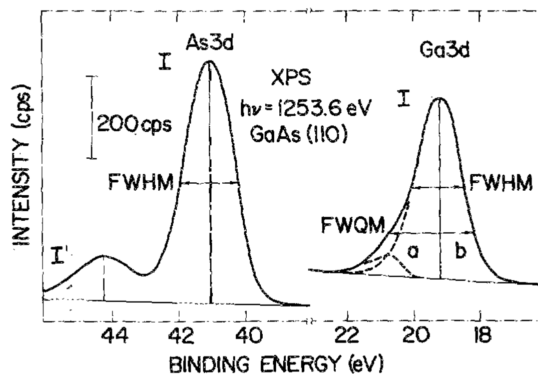

FIG. 1. XPS As 3*d* core lines of a *p*-type GaAs(110) substrate as introduced into the UHV system and baked with the preparation chamber of 150 °C. The As oxide can be characterized by the well-resolved peak with intensity I', whereas the presence of Ga oxide causes an asymmetry of the Ga 3*d* core line. The ratio a/b is used to characterize the amount of Ga oxide.

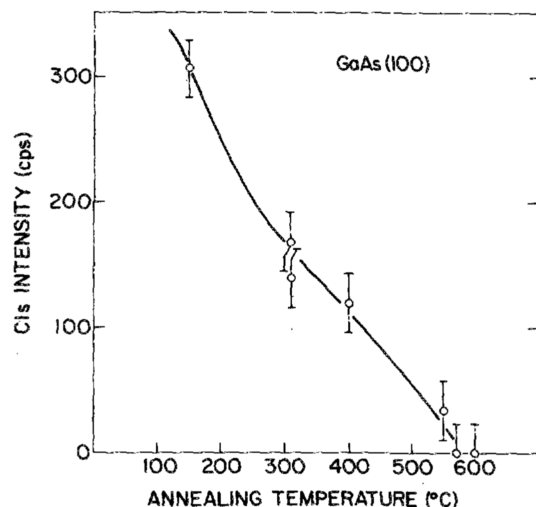

FIG. 3. Annealing behavior of the surface carbon content as determined by XPS C 1*s* intensity.

oxygen is of the order of 1.5 at. % in the surface layer where the photoelectrons come from. Figure 2(b) shows the annealing behavior of the As oxide. The relative amount of As oxide is decreasing continuously at temperatures between 300 and 500 °C. The Ga oxide shows a very different behavior: The relative amount of Ga oxide increases with increasing annealing temperature up to about 500 °C, and shows a sharp drop between 550 and 580 °C. It is evident from Fig. 2 that the relatively high stability of Ga oxide is responsible for the required cleaning temperature of (580 ± 10) °C. The increase of the amount of Ga oxide with increasing temperature in the range $150 < T < 500$ °C indicates that the As oxide gets at least partially reduced by the Ga. The annealing behavior of the carbon content is shown in Fig. 3. In contrast to the oxygen content [Figure 2(a)], the C 1s intensity is decreasing continuously with increasing annealing temperature, and for $T_a > 550$ °C, is below the limit of detection by means of XPS (which is of the order of 4 at. % for carbon).

The UPS ($h\nu = 21.2$ eV) spectrum of a heat-cleaned p-GaAs(100) surface after 10 min at 600 °C is shown in Fig. 4(a). The corresponding spectrum of a GaAs layer grown by MBE (Molecular Beam Epitaxy) is shown for comparison in Fig. 4(b). The higher background at energies around -8 eV and the different relative intensities of the three peaks in the energy range between -5 eV and the Fermi level E_F in the spectrum 4(a) compared with that of 4(b) indicate that the 600 °C heat cleaning did not provide a perfect substrate surface. The distinct differences in these two spectra must be explained by a nondetectable amount of contaminants on the heat-cleaned surface, and/or defects in the surface structure of the heat-cleaned surface. In fact, the LEED patterns of the heat-cleaned substrate surface show diffuse spots with relatively high background, and no patterns could be observed with primary energies below 110 eV. The spectrum 4(c) was obtained after a combined simultaneous low energy ion etching and heat treatment. This cleaning procedure will be discussed in the next section.

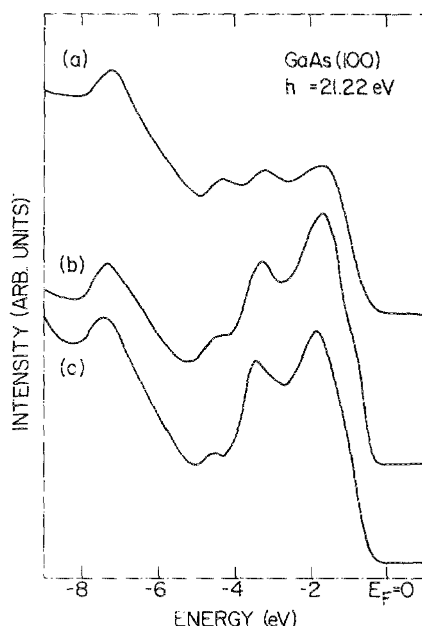

FIG. 4. UPS ($h\nu = 21.2$ eV) valence band spectra of GaAs(10) measured at normal emission and an angle of 45° for the incident light. (a) Heat cleaned substrate at 600 °C for 10 min. (b) Spectrum of a layer grown by MBE. (c) Spectrum of a substrate cleaned by a simultaneous low energy ion etching and heat treatment (150 eV Ar-ion bombardment at $T = 450$ °C for 30 min). Note the similarity of spectra (b) and (c).

B. Simultaneous ion etching and annealing

A great variety of different IHT's have been performed on GaAs(100) and (110) substrates. Three parameters have been varied: The Ar ion energy E_i, the substrate temperature T and the time t during which the IHT was applied. The lowest possible ion energy has been applied in our experiments. There seems to be a lower limit for E_i to remove the Ga oxide. A IHT procedure with $E_i = 100$ eV at 310 °C and a sample ion current of 2μA did remove the As oxide entirely (no oxide-related peak in the As 3d XPS core line) but the Ga 3d core line still showed a very high asymmetry parameter $a/b = 1.6$, which is characteristic for an "as introduced" surface. In addition, the ion current usually dropped below 1 μA at $E_i < 150$ eV, and therefore sputtering had to be performed over very long periods to achieve a given dose.

The results of a few cleaning procedures are summarized in Table I. All samples were cleaned in several steps, since the outgassing of the ion gun in the first run sometimes caused additional contamination of the substrate surfaces. Table I contains the Ga/As ratios as determined by XPS Ga and As 3d core level intensities calibrated with the experimentally obtained ratio from a GaAs overlayer grown by MBE. The oxygen and carbon contents are given in at. % of a surface layer of ≈ 20 Å from which the photoelectrons originate (determined from the O 1s, C 1s, GA 3d, and As 3d intensities, using atomic photionization cross sections[6] and correcting for the retard voltage dependence of the analyzer acceptance area).

The following points in Table I should be emphasized:

(i) The sample GaAs(100) (sample #3) was cleaned by a 600 °C heat treatment. Though the O and C contamination content after this treatment is relatively low, the UPS spectra [see Fig. 4(a)] show distant differences from that obtained from MBE grown overlayers [Fig. 4(b)] and the LEED patterns show blurred spots and a relatively high background.

(ii) A two step IHT cleaning procedure (sample #1) performed at medium temperatures (≈ 300 °C) yield a similarly low contamination content to the heat-cleaned sample, but a much better UPS spectrum [Fig. 4(c)], very similar to that obtained from the MBE grown overlayer [Fig. 4(b)], and a Ga/As ratio close to 1.0.[7] In addition, the LEED pattern shows sharp spots (1×1 surface) and a lower background. Therefore, the IHT-cleaned surface at ≈ 300 °C has a superior quality to that of the 600° heat-cleaned surface.

(iii) At higher temperatures (450–500 °C) the IHT cleaning procedure is able to produce in one cleaning step substrate surfaces with low contamination contents and high quality sharp (1×1) LEED patterns (sample #2).

(iv) A weak $c(8 \times 2)$Ga surface reconstruction has been found after a 500 °C IHT cleaning procedure, which became very clear after a post-annealing at 520 °C (sample #3).

(v) The relevance of the combined **simultaneous** low ener-

TABLE I. Ga/As ratios as determined from XPS Ga and As 3d core level intensities before and after different substrate cleaning procedures. The oxygen and carbon amounts are given in at. % and have been determined by using O 1s and C 1s XPS intensities taking into account the atomic photoionization cross sections, the spectrometer transmission, and the energy dependence of the photoelectron escape depth. The LEED patterns are summarized as follows: + (1×1) surface, blurred spots with relatively high background. + + (1×1) surface, sharp spots, low background.

	As introduced			IHT params			After IHT			
Sample	Ga/As ratio	O (at. %)	C (at. %)	E_i (eV)	T (°C)	t (min)	Ga/As ratio	O (at. %)	C (at. %)	LEED
#1	0.86	35	27	150	260	30	1.06	<9.0	...	+
(110)				100	310	46	1.01	<4.6	...	+ +
				100	310	46	1.01	<4	...	+ +
#2	0.90	45	12	150	460	35	0.99	<4.3	...	+ +
(100)				150	460	16	0.99	<3.5	...	
					500	15				+ + (8×2)
#3	0.91	34	34	...	600	10	1.0	<4.5	...	+
(100)				150	500	120	1.09	<3.3	<8.6	+ +
				250	500	70	1.06	<3.0	...	+ + (8×2) weak
				...	520	38	...	...	...	+ + (8×2)
				250	20	60				+ weak
				...	240	18	...	...	...	+
				...	330	25	...	...	...	+
				...	520	55	...	...	...	+ + (no reconst.)

gy ion bombardment and annealing was checked with another GaAs(100) sample; after a IHT cleaning procedure, the sample was sputtered at room temperature, after which LEED spots were barely visible. Post-annealing in several steps improved the LEED patterns substantially, and a high quality (1×1) pattern was obtained after a 520 °C anneal. In contrast to the IHT treatments, we were unable to achieve a reconstructed by annealing alone (sample #3).

IV. CONCLUSIONS

The present study has shown that the combined simultaneous low energy ion etching and annealing of GaAs substrates is a very efficient cleaning procedure. The IHT cleaned surfaces at medium temperatures ($\approx$300 °C) are superior in quality to the thermally cleaned substrates after a 600 °C heat treatment, as characterized by means of UPS and LEED. Discrepancies between the present work and earlier discussions of surface reconstructions achieved by thermal treatment alone may be due to differences in temperature calibration, HEED versus LEED sensitivities, and/or treatment prior to insertion of the substrates into the vacuum system.

Thermal cleaning cycles have proven apparently more than adequate for GaAs substrate cleaning for MBE growth of overlayers—at least as long as the active interfaces are well removed from the substrate–overlayer interface—but it is not clear that such procedures will be applicable to other possible substrate materials. For example, Al_2O_3 requires substantially higher temperatures than does Ga_2O_3 to achieve similar evaporation rates.[8] Furthermore, we achieve better sample order and cleanliness at lower temperatures than does the thermal cleaning process.

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