Effect of Ion Bombardment on the Chemical Reactivity of Gallium Arsenide(100)

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The interaction of O_2 and H_2O, over the exposure range 10^7–10^{13} langmuirs, with chemically cleaned (1:1 HCl/H_2O) and Ar^+-ion-bombarded (0.5–3 keV) GaAs surfaces has been studied by X-ray photoelectron spectroscopy. Ion-bombarded GaAs shows an increased chemical reactivity compared to that of chemically cleaned GaAs when exposed to O_2 and H_2O. Ion-bombarded GaAs exposed to O_2 yields Ga_2O_3, As_2O_3, and As_2O_5; Ga_2O_3 being the major component. Exposure of chemically cleaned and ion-bombarded GaAs to H_2O produces only peak broadening on the high binding energy side of the Ga 3d core level photopeak, indicating GaO(OH) formation at an exposure $<10^{11}$ langmuirs and both GaO(OH) and $Ga(OH)_3$ species at exposures greater than 10^{11} langmuirs. However, the reactivity of the ion-bombarded material is greater than that of the chemically cleaned material. The results obtained in this study are compared with those for cleaved and annealed GaAs.

Introduction

Low-energy ion bombardment is used to prepare atomically clean surfaces for surface analysis and for device manufacturing. Ion-bombardment energies as low as 500 eV cause a disordered surface layer in GaAs that is As deficient.[1-3] After being cleaned, these ion-bombarded surfaces are often exposed to reactant gases and eventually exposed to air. Ion-bombarded (or disordered) GaAs has been shown to have a reactivity toward oxygen different from cleaved GaAs.[4-6] Ion bombardment has been shown to induce changes in breakdown voltages, barrier heights, trapping levels, and the optical properties of GaAs.[7,8] Ion bombardment also changes the surface structure so that the chemical surface reactivity could be altered.[4] In this study the effect of Ar^+ ion bombardment on the reactivity of O_2 and H_2O with GaAs will be compared with the reactivity of O_2 and H_2O on chemically cleaned GaAs.

Experimental Section

In this study n-type GaAs(100) with a Si doping density of $4 \times 10^{17}/cm^3$ was used. All specimens were cleaned in 1:1 HCl/H_2O at room temperature for 10 min to remove surface oxides. The samples were rinsed in deionized water and transferred in air to the XPS chamber. A cleaning procedure developed by Oelhafen et al.[9] to obtain clean, well-ordered surfaces of GaAs(100) was followed to aid in the effort to compare chemically cleaned and ion-bombarded GaAs.

The Ar^+ ion bombardments and surface analyses were carried out using a Perkin-Elmer PHI Model 5300 XPS system equipped with a Model 04-300 differentially pumped ion gun, mounted at 45° with respect to a line perpendicular to the specimen surface. Ar^+ ion bombardment was carried out at energies of 500, 1000, 2000, and 3000 eV using a 1-cm^2 rastered beam with ion currents in the range of 0.2–40 μA. The time of ion bombardment was adjusted to give fluences in the range of 2×10^{16}–9×10^{17} ions/cm^2. The samples were oriented such that ion bombardment was in the (111) direction.

Following ion bombardment, the sample was transferred under vacuum into a stainless steel ultrahigh-vacuum reaction chamber attached to the XPS system where exposures either to O_2 or to H_2O vapor were carried out. O_2 exposures ranged from 10^7 to 10^{13} langmuirs, and H_2O exposures were in the range 10^9–10^{12} langmuirs (1 langmuir = 1.3×10^{-4} Pa s). Care was taken to avoid exposure of the sample to excited oxygen.

The surfaces were analyzed by XPS using Mg Kα radiation ($h\nu$ = 1253.6 eV) as the excitation source and with a chamber pressure of less than 4×10^{-6} Pa. Spectra were obtained immediately following ion bombardment and also following reactant gas exposure at both 90° and 15° takeoff angles (toa) measured as the angle between the sample normal and the photoelectron analyzer. The photopeaks were analyzed by subtracting the X-ray source line width, smoothing, and curve resolving the data by using the software routines available with the PHI 5300 system. The atomic concentrations were evaluated from photopeak areas by using the appropriate sensitivity factors.

Ninety-five percent of the observed photoelectron signal comes from a layer $3\lambda \sin \theta$ thick, where θ is the takeoff angle and λ is the mean free path of the photoelectron.[10] For the Ga 3d and As 3d core levels λ is approximately 22 Å; therefore, the analysis depths are approximately 66 and 17 Å for 90° and 15° toa's, respectively. Spectra in this paper were acquired at 15° toa to enhance surface sensitivity.

Spectra for model compounds, Ga_2O_3 (Alfa, 99.99%), As_2O_3 (Aldrich, 99.999%), As_2O_5 (Fisher, 99.2%), and GaO(OH) (synthesized), were obtained for the determination of binding energies, full widths at half-maxima (fwhm), and atomic ratios. The oxides were dried at 110 °C prior to XPS analysis, and the powders were mounted on a stainless steel probe for analysis by using double-stick tape. The binding energies were determined by sputtering a thin layer of gold onto the sample and referencing the binding energies to the Au $4f_{7/2}$ level at 83.8 eV. The fwhm's and atomic concentrations were determined from spectra obtained before the deposition of Au onto the sample. The measured binding energies agreed with literature values.[11,12]

GaO(OH) was prepared by dissolving Ga metal in concentrated HCl. The hydroxide was precipitated by the addition of NH_4OH

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Table I. XPS Results for Chemically Cleaned and Ar^+-Ion-Bombarded GaAs

treatment			at. %							
	ion bombarded		toa = 15°			toa = 90°			Ga/As (±0.05)	
	ion energy, eV	fluence	Ga	As	O	Ga	As	O	toa = 15°	toa = 90°
chemically cleaned			28.0	35.9	36.1	39.5	44.4	16.1	0.78	0.89
	500	$(2 \pm 1) \times 10^{16}$	36.8	49.5	13.7	48.2	47.9	3.9	0.74	1.01
	1000	$(2 \pm 3) \times 10^{16}$	53.3	42.2	4.8	55.3	43.4	1.3	1.26	1.27
	2000	$(9 \pm 3) \times 10^{17}$	60.1	39.9	<2.0	58.7	41.3	<2.0	1.49	1.43
	3000	$(9 \pm 4) \times 10^{17}$	60.4	39.6	<2.0	60.8	39.2	<2.0	1.52	1.55

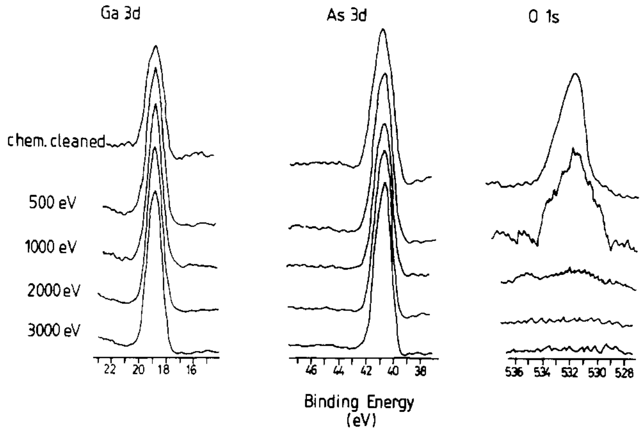

Figure 1. Representative spectra taken at 15° toa for chemically cleaned and ion-bombarded GaAs.

to attain pH 8. The precipitate was digested at 78 °C for 1 h, washed with deionized H_2O to remove most cations and anions from solution, and left to age overnight in deionized H_2O. The precipitate was then centrifuged, rinsed until the wash water measured pH 7 and there were no detectable traces of Cl^-, washed with acetone, and dried under vacuum. X-ray diffraction measurements confirmed the preparation of crystalline GaO(OH).

Results and Discussion

Chemically Cleaned and Ion-Bombarded GaAs. The surface atomic composition and the relative amounts of Ga(GaAs) and As(GaAs) on the surface of GaAs following chemical cleaning and Ar^+ ion bombardment determined from XPS measurements taken at both 15° and 90° toa's are summarized in Table I. Representative spectra for chemically cleaned and ion-bombarded GaAs are shown in Figure 1.

Following chemical cleaning the surface is arsenic rich (Table I), and no chemical shifts are detected in the Ga 3d or As 3d photopeaks that would indicate the presence of oxides on the surface. However, oxygen is detected on the surface (BE 532.0 eV) that is most likely due to adsorbed oxygen.[13-15] No evidence for contamination from the HCl solution was detected. These observations are similar to those obtained by Bertrand[13] for HCl-treated GaAs(100).

Ion bombardment of GaAs removes residual oxygen from the chemically cleaned surface, more oxygen being removed with increasing ion bombardment energy. Ion bombardment also results in the preferential sputtering of arsenic from the surface, as indicated by the increasing Ga/As atomic ratio, which is consistent with the results obtained by others for ion-bombarded GaAs.[1,3,16] It should be noted that the oxygen content also decreases with increasing ion bombardment time up to a point where a steady state is reached (the fluences used in this study) such that no change in either residual oxygen content or the Ga/As atomic ratio was obtained.

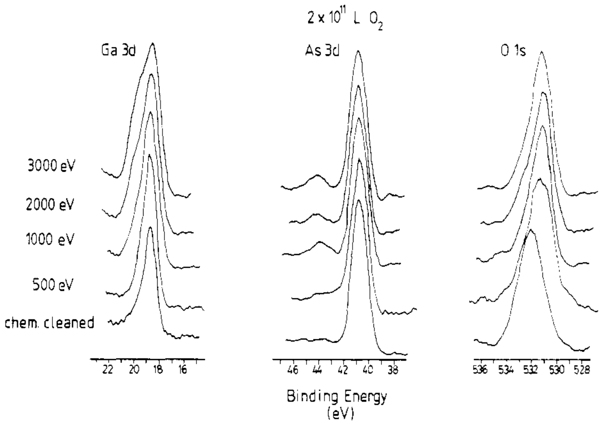

Figure 2. XPS spectra for 2×10^{11} langmuirs of O_2 exposure.

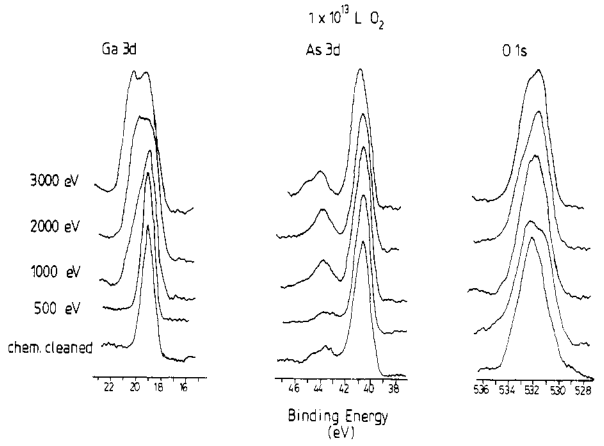

Figure 3. XPS spectra for 1×10^{13} langmuirs of O_2 exposure.

The Ga/As atomic ratios for the samples at different toa's can be used to evaluate the depth of damage caused by ion bombardment. The Ga/As atomic ratio for chemically cleaned GaAs is less than 1.0 at both toa's, indicating that an As-rich surface extends to at least 60 Å into the surface. For the lowest ion bombardment energy, 500 eV, the As-rich layer is being sputtered away by ion bombardment. This is noted by the 15° Ga/As atomic ratio that is As-rich (<1.0). The underlying substrate composition for the 500-eV ion-bombarded material is stoichiometric GaAs as noted by the 90° Ga/As atomic ratio of 1.0. For 3-, 2-, and 1-keV Ar^+-ion-bombarded samples, the Ga/As values at both 15° and 90° toa's for the respective ion energies are equivalent within the experimental error, indicating that an As-depleted layer extends to a depth of at least 60 Å. The results of McGuire[3] and Holloway et al.[17] state that the surface composition is dependent on both the energy and mass of the incident bombarding ion.

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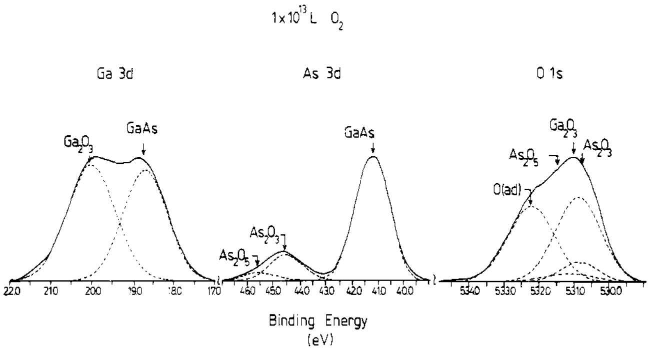

Figure 4. Curve-resolved spectra for 3-keV Ar^+-ion-bombarded GaAs exposed to 1 × 10^{13} langmuirs of O_2.

Recent results for GaAs bombarded with He^+, Ne^+, and Xe^+ at the same energy support some of these results.[18] However, in the present study focus is only on the dependence of the surface reactivity of Ar^+-ion-bombarded GaAs as a function on ion bombardment energy.

O_2 Exposure. The XPS spectra obtained at a 15° toa are presented for the Ga 3d, As 3d, and O 1s levels for chemically cleaned and Ar^+-ion-bombarded GaAs following O_2 exposure at 2×10^{11} (Figure 2) and 10^{13} langmuirs (Figure 3). The Ga 3d and As 3d photopeaks both exhibit evidence for the formation of oxides on the surface by the appearance of photopeaks on the high binding energy sides of the respective substrate photopeaks. The determination of chemical species in the photopeaks was accomplished by curve resolution. The curve resolution was carried out by using Gaussian-type peaks. The peak positions and the fwhm's used in curve resolution were determined by measuring XPS spectra for standard oxide compounds. The fwhm and peak positions for the Ga 3d and As 3d due to GaAs were determined from the spectra for ion-bombarded GaAs. Oxygen peak intensities were selected on the basis of knowledge of the oxygen/gallium or oxygen/arsenic ratio for the respective gallium (Ga_2O_3) and arsenic (As_2O_3, As_2O_5) oxides.

Typical curve-resolved spectra are shown in Figure 4 for 3-keV Ar^+-ion-bombarded GaAs exposed to 10^{13} langmuirs of O_2. These spectra are characterized by the photopeaks due to Ga(GaAs), As(GaAs), Ga(Ga_2O_3), As(As_2O_3, As_2O_5), O(Ga_2O_3, As_2O_3, As_2O_5), and O(ad). Table II summarizes the binding energies obtained for the surface oxides on GaAs following O_2 exposure.

The relative amounts of gallium and arsenic oxides produced as a result of O_2 exposure are shown in Figure 5 following 2×10^{11} and 1×10^{13} langmuirs of O_2 exposure. The quantities of gallium or arsenic oxide produced are represented as

$$\mathrm{Ga(Ga_2O_3)\ or\ [As(As_2O_3 + As_2O_5)]/[Ga(total) + As(total)]}$$

The zero point corresponds to the results obtained for chemically cleaned GaAs. It can be seen from the relative amounts of oxides formed (Figure 5) and the changes in the XPS spectra (Figures 2 and 3) that the reactivity of ion-bombarded GaAs is quite different from that of chemically cleaned GaAs.

Exposure of chemically cleaned GaAs to O_2 produces only Ga_2O_3 and As_2O_3. On the chemically cleaned surface the relative amounts of arsenic and gallium oxide are nearly equivalent. This is consistent with the results obtained by others for reaction on cleaved and atomically clean GaAs.[4,12] Exposure of Ar^+-ion-bombarded GaAs to O_2 produces Ga_2O_3, As_2O_3, and As_2O_5 with preferential formation of Ga_2O_3. The relative amount of Ga_2O_3 on the surface increases with increasing Ar^+ ion bombardment energy up to 2 keV. On the other hand, the reaction of O_2 with ion-bombarded surfaces produces approximately the same quantity of arsenic oxides as found for chemically cleaned GaAs.

Tabel II. Binding Energies for Surface Components

component	BE, eV	fwhm, eV	standards,[a] eV	lit., eV
Ga(GaAs)	18.8 ± 0.2	1.2 ± 0.2		19.0 ± 0.4[b]
As(GaAs)	40.8 ± 0.2	1.5 ± 0.2		41.0 ± 0.4[b]
Ga(Ga_2O_3)	20.0 ± 0.2	1.4 ± 0.2	20.0 ± 0.2	20.4 ± 0.2[b]
As(As_2O_3)	44.2 ± 0.3	1.5 ± 0.2	43.9 ± 0.2	44.6 ± 0.3[b]
As(As_2O_5)	45.5 ± 0.3	1.6 ± 0.2	45.5 ± 0.2	45.7 ± 0.1[b]
O(Ga_2O_3)	531.3 ± 0.4	1.5 ± 0.2	530.6 ± 0.2	531.4 ± 0.2[b]
O(As_2O_3)	530.3 ± 0.4	1.3 ± 0.2	530.6 ± 0.2	531.6 ± 0.2[b]
O(As_2O_5)	530.8 ± 0.4	1.6 ± 0.2	531.1 ± 0.2	531.6 ± 0.1[b]
O(ad)	532.6 ± 0.4	1.6 ± 0.2		
Ga(GaO(OH))	19.9 ± 0.2	1.7 ± 0.2	19.8 ± 0.4	
Ga($Ga(OH)_3$)	20.9 ± 0.2[d]	1.6 ± 0.2		
O(GaO*(OH))	530.8 ± 0.5	1.7 ± 0.2	530.3 ± 0.3	
O(GaO(O*H))	531.8 ± 0.5	1.7 ± 0.2	531.6 ± 0.3	
O($Ga(OH)_3$)	531.8 ± 0.5[d]	1.7 ± 0.2		
O(H_2O)(ad))	532.6 ± 0.5	2.0 ± 0.3		~533[c]

[a] This study. [b] From ref. 11. [c] From ref 19. [d] No standard compound was measured for this. The binding energy is assumed to be nearly equivalent to that for –OH in GaO(OH) as explained in the text.

The preferential formation of Ga_2O_3 on the ion-bombarded material could be due to the larger amount of Ga(GaAs) at higher ion bombardment energies. More Ga_2O_3 forms because more gallium is present on the surface. It has been suggested by Chye et al.[4] that once the surface becomes disordered by ion bombardment, bulk thermodynamics take precedent, forming gallium oxides more readily than arsenic oxides; the free energy of formation of Ga_2O_3 is −1004 kJ/mol and of As_2O_3 is −661 kJ/mol.[20] Chye et al.[4] note that Mark et al.[6] suggested that oxidation takes place first on residual defect sites and that additional disorder occurs by the exothermic release of adsorption energy. Chye et al.[4] argue that if O_2 adsorbs on native defect sites and subsequently generated defect sites, one would expect to observe roughly equal amounts of arsenic and gallium oxides on both ordered and disordered surfaces. They did not take into account the fact that the disordered surface produced by ion bombardment has a different surface Ga/As ratio than an ordered (cleaved) surface, a result of preferential sputtering of arsenic. Therefore, Chye et al.[4] should observe more Ga_2O_3 than As_2O_3 formation due to the presence of more gallium on the surface. Mark et al.'s[6] proposal of increased disorder to produce more defect sites would still influence the reactivity, but the ratio of Ga/As would also be expected to play a role in the final amount of gallium and arsenic oxides produced. However, taking into account the increasing Ga/As ratio and bulk thermodynamics or the ideas of Mark et al.[6] to explain the increased amount of Ga_2O_3 formed on ion-bombarded material does not entirely account for all the results obtained in this study. It will be shown in the following paragraphs that ion bombardment and the resulting defect sites play a significant role in changing the reactivity of the GaAs surface.

To determine what role the Ga/As ratio plays in the formation of oxides, a GaAs surface was prepared by a method other than chemical cleaning and ion bombard-

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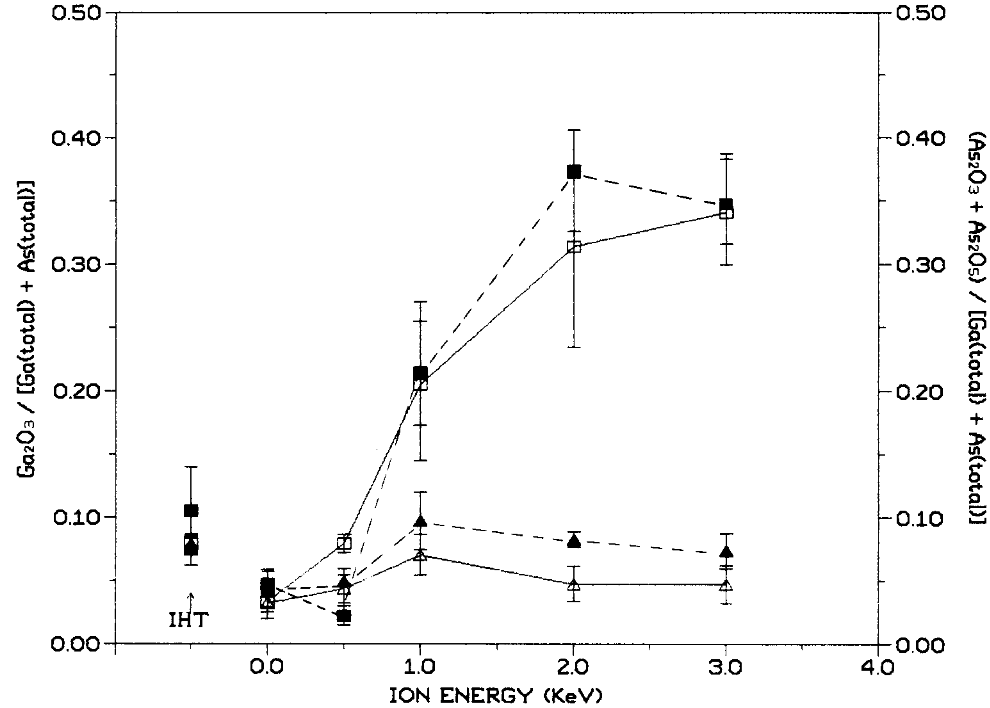

Figure 5. Relative amounts of gallium and arsenic oxides for O_2 exposure at 2 × 10^{11} langmuirs: gallium oxide (□), arsenic oxide (△); 1 × 10^{13} langmuirs: gallium oxide (■), arsenic oxide (▲). IHT GaAs was prepared according to the procedure given by Oelhafen et al.[9] and was exposed to 2 × 10^{11} and 1 × 10^{13} langmuirs of O_2.

ment, using the procedure outlined by Oelhafen et al.,[9] and is subsequently referred to as IHT-treated GaAs in this paper. An IHT-treated GaAs surface was obtained containing only Ga(GaAs) and As(GaAs) with a Ga/As of 1.23 ± 0.07 and with <10 at. % adsorbed oxygen on the surface. The IHT treated GaAs was exposed to 2 × 10^{11} and 1 × 10^{13} langmuirs of O_2, and the relative amounts of gallium and arsenic oxides were approximately equal (see Figure 5). If the Ga/As ratio were to determine solely the amount of gallium and arsenic oxides formed following O_2 exposure, one would expect results similar to that for 1-keV Ar^+-ion-bombarded GaAs exposed to O_2, where the Ga/As ratio before exposure was 1.26 (15° toa). However, the results for IHT-treated GaAs are similar to those for chemically cleaned GaAs (Ga/As = 0.6). The result that less gallium oxide forms on a surface rich in Ga but which was not ion bombarded demonstrates that ion bombardment influences the reaction chemistry of GaAs. It is reasonable that ion bombardment produces defects and/or disordered GaAs as the ion bombardment energy increases and that reaction takes place at defect sites.[4-6,15,21-27] Goddard et al.[21] suggest that defect sites with broken Ga–As bonds are needed to form a strong bond to molecular O_2 and that the defect sites catalyze the dissociation of O_2 into chemisorbed O atoms, which can then attack nearby Ga or As atoms to form oxides. For ion-bombarded GaAs, greater production of Ga_2O_3 would occur with increasing ion-bombardment energy, a result of the generation of disordered sites around Ga atoms since As is preferentially removed by sputtering.

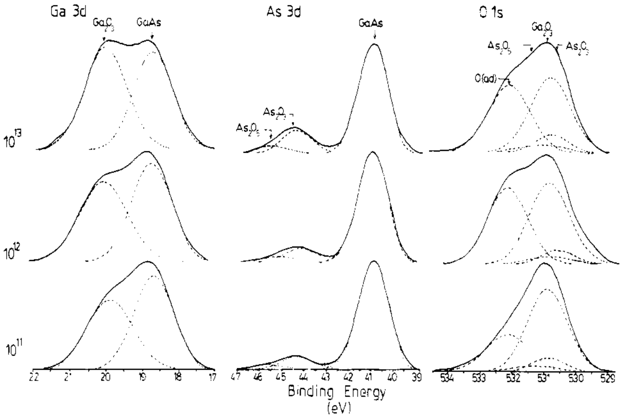

Figure 6. Curve-resolved spectra for 3-keV Ar^+-ion-bombarded GaAs exposed to 2 × 10^{11}, 1 × 10^{12}, and 1 × 10^{13} langmuirs of O_2.

The adsorption of O_2 on chemically cleaned and ion-bombarded materials produces both dissociatively adsorbed and chemisorbed molecular oxygen. Brundle et al.[15] discussed the reaction of O_2 with cleaved GaAs(110) over the exposure range 10^5–10^{14} langmuirs and noted that only dissociatively adsorbed oxygen forms gallium and arsenic oxides directly. In the XPS study of O 1s photopeaks, Brundle et al.[15] observed only oxygen with a binding energy near that for Ga_2O_3 and As_2O_3 ($\approx$531 eV). However, in this study (see curve fits in Figure 4) the oxygen photopeak is composed of species due to oxides and an additional photopeak at higher binding energy, 532.6 eV, which is attributed to chemisorbed molecular oxygen.[15,27] The amount of chemisorbed molecular oxygen increases with increasing O_2 exposure. A likely process is that dissociative adsorption takes place first to form the oxides and then molecular oxygen is adsorbed onto the oxide layer. That this process occurs is more apparent for 3-keV ion-bombarded GaAs exposed to O_2 (see Figure 6). An increase in the amount of oxides (both Ga and As) is evident by the increased intensity of higher binding energy Ga and As photopeaks relative to Ga(GaAs) and As(GaAs) peaks.

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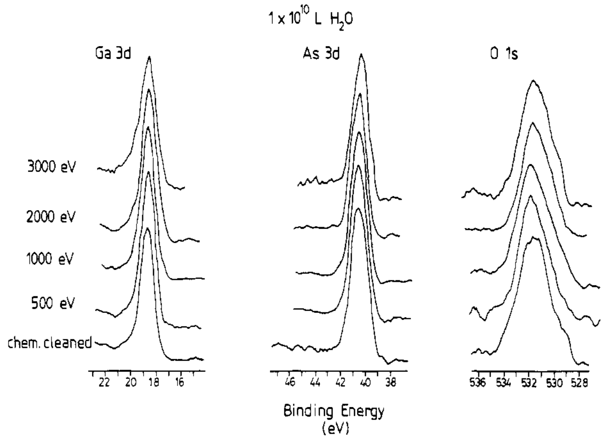

Figure 7. XPS spectra for 1 × 10^{10} langmuirs of H_2O exposure.

At the same time the O 1s peak intensity at higher binding energy increases more significantly with increasing exposure. This indicates that the majority of oxide formation takes place up to 10^{11} langmuirs and increased exposure does not significantly increase the amount formed. The initial exposure to oxygen probably forms a protective layer of a mixture of Ga_2O_3 (the major component), As_2O_3, and As_2O_5. Any further oxide formation would depend either upon the inward diffusion of oxygen through the oxide layer to oxidize underlying GaAs or by the outward diffusion of either As or Ga where the breaking of crystal bonds would be the limiting step in the oxidation process.[28] One should note that outward diffusion in group III–V compounds is very low compared to that of metal alloys being oxidized.[28] Thus, only an increase in molecularly adsorbed O_2 relative to chemisorbed oxygen is noted in the O 1s photopeak for O_2 exposures above 10^{11} langmuirs.

H_2O Exposure. The XPS spectra are presented in Figure 7 for the Ga 3d, As 3d, and O 1s levels for chemically cleaned and Ar^+-ion-bombarded GaAs following H_2O exposure at 10^{10} langmuirs. After H_2O exposure, a broadening occurs on the higher binding energy side of the Ga 3d photopeak while no change is observed for the As 3d photopeak. Broadening of the Ga 3d photopeak was also observed by Webb and Lichtensteiger[29] for GaAs exposed to H_2O.

Curve resolved XPS spectra for the Ga 3d and O 1s photopeaks for the 3-keV Ar^+-ion-bombarded GaAs as a function of H_2O exposure are shown in Figure 8. For H_2O exposures of 10^{10} langmuirs, the fwhm of the higher binding energy photopeak in the Ga 3d region was slightly broader than what had been previously observed for the same peak following the O_2 exposures (the photopeak due to Ga_2O_3). The fwhm of the Ga 3d photopeak for GaO(OH) is generally broader than that for Ga_2O_3, 1.7 ± 0.2 and 1.4 ± 0.2, respectively. For this reason the Ga 3d and O 1s photopeaks (10^{10} langmuirs of H_2O) were curve resolved to include Ga_2O_3, GaO(OH), or different combinations of each. From the results of these curve resolutions, the best possible fits were obtained when GaO(OH) was assumed to be the species present following H_2O exposure. The spectra shown in figure 8 are characterized by photopeaks due to Ga(GaAs), Ga(GaO(OH)), O(GaO*(OH)), O(GaO(O*H)), and O(H_2O(ad)) using the peak positions and fwhm that were determined from measurements on standard materials. The experimental peak positions as well as those obtained for the standard materials are summarized in Table II. For exposures above 10^{10} langmuirs of H_2O, indicating a single photopeak in the Ga 3d region for GaO(OH) is no longer sufficient. A new photopeak shifted 0.7–1.0 eV higher than that for GaO(OH) is needed to complete the curve fit as shown in Figure 8. This broadening may indicate the formation of another gallium-containing species, possibly $Ga(OH)_3$.[29,30] For 10^{10}-langmuir H_2O exposures described above, the photopeaks were first curve resolved by including Ga_2O_3, GaO(OH), or $Ga(OH)_3$ as well as possible combinations of all three species. The best possible results were obtained by using combinations of GaO(OH) and $Ga(OH)_3$. Therefore, the photopeaks in Figure 8 for exposures above 10^{10} langmuirs are curve fit to include GaO(OH) and $Ga(OH)_3$ as well as the respective contributions to the O 1s photopeaks for these species. The –OH of $Ga(OH)_3$ was assumed to have an O 1s peak position similar to the –OH in GaO(OH). The O(H_2O(ad)) peak position was taken from the literature[19] and from that obtained for hydrated oxides.

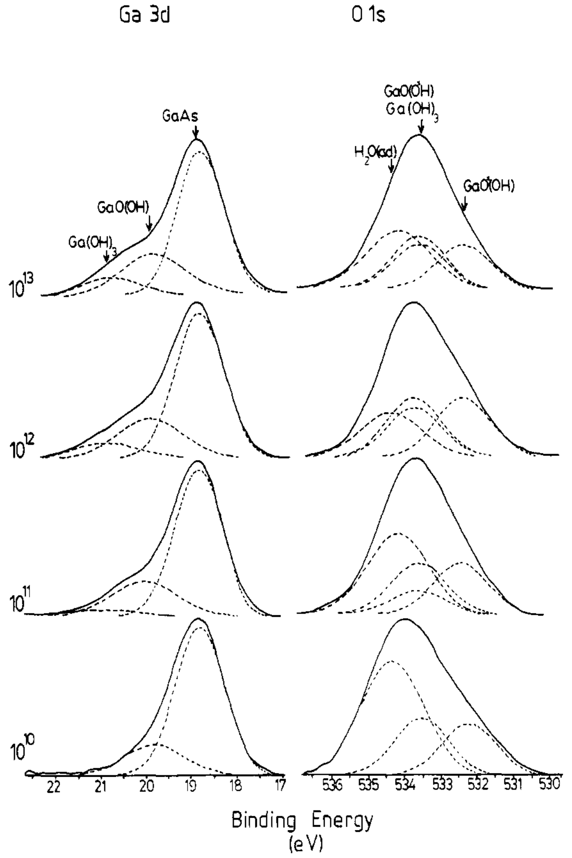

Figure 8. Curve-resolved spectra for 3-keV Ar^+-ion-bombarded GaAs exposed to 10^{10}, 10^{11}, 10^{12}, and 10^{13} langmuirs of H_2O.

The formation of $Ga(OH)_3$ occurs only for 2- and 3-keV ion-bombarded GaAs exposed to H_2O above 10^{10} langmuirs, and the amount of $Ga(OH)_3$ produced increases with increasing H_2O exposure. The relative amount of GaO(OH) and $Ga(OH)_3$ formed following H_2O exposure is presented in Figure 9 for exposures of 10^{10} and 10^{11} langmuirs as a function of Ar^+-ion-bombardment energy. The trend is similar to that found for GaAs exposed to O_2 in that the relative amount of oxidized Ga increases with increasing ion bombardment energy up to 2 keV and the reaction of ion-bombarded material is greater than that of the chemically cleaned GaAs. The adsorption of H_2O onto ion-bombarded GaAs also produces peaks in the O

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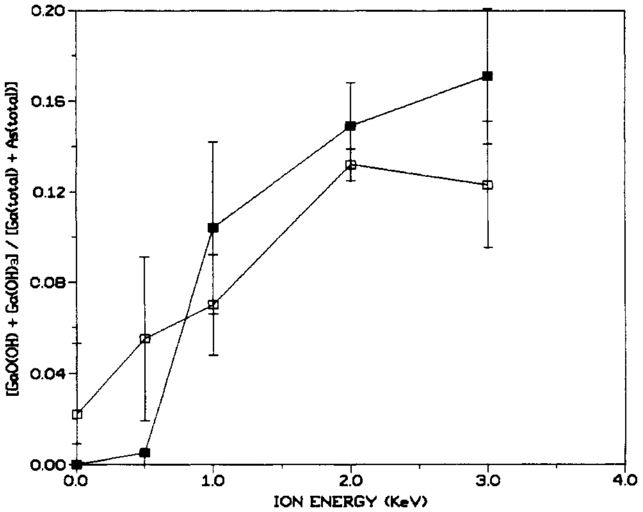

Figure 9. Relative amounts of GaO(OH) and $Ga(OH)_3$ for H_2O exposure at 10^{10} (□) and 10^{11} langmuirs (■).

1s region due to O from GaO(OH) and $Ga(OH)_3$ and that due to adsorbed H_2O.

These results are similar to those of Webb and Lichtensteiger[29] and Childs et al.,[24] who found that H_2O predominantly bonds to Ga sites. Webb and Lichtensteiger[29] also observed the dissociative adsorption of H_2O in the formation of Ga–OH bonds for exposures above 10^9 langmuirs (from UPS and SIMS results). GaAs exposed to H_2O has been shown to adsorb H_2O in a two-step process: an initial step of molecular adsorption onto Ga sites[29,31,32] followed by a physisorbed or condensed H_2O layer[29,32] for exposures greater than 10^6 langmuirs. Above those exposures the H_2O dissociates to form $Ga(OH)_x$ species. The results of this study show both dissociated H_2O in the form of GaO(OH) and $Ga(OH)_3$ and molecularly adsorbed H_2O present on the surface for ion-bombarded GaAs exposed to H_2O. GaO(OH) is the predominant species for exposures below 10^{11} langmuirs of H_2O. Above 10^{11} langmuirs of exposure, further broadening of the Ga 3d photopeak is observed and is attributed to $Ga(OH)_3$. These two different species have not been observed on chemically cleaned or annealed GaAs exposed to H_2O.[29]

Conclusions

In this study it has been shown that Ar^+-ion-bombarded GaAs shows an increased chemical reactivity compared to that of chemically cleaned GaAs, cleaved GaAs,[4] or sputter annealed GaAs[29] over the exposure ranges 10^7–10^{13} langmuirs of O_2 and 10^9–10^{12} langmuirs of H_2O. O_2 exposure of ion-bombarded GaAs produces Ga_2O_3, As_2O_3, and As_2O_5 with Ga_2O_3 being the major component on the surface. Chemically cleaned GaAs reacts to yield very small but equivalent amounts of Ga_2O_3 and As_2O_3. H_2O exposure of both chemically cleaned and ion-bombarded GaAs produces only a broadening on the higher binding energy side of the Ga 3d photopeak which has been attributed to GaO(OH) formation. For 2- and 3-keV ion-bombarded GaAs exposed to H_2O above 10^{10} langmuirs, the Ga 3d photopeak shows additional broadening to the higher binding energy side, possibly indicating the formation of $Ga(OH)_3$.

For both O_2 and H_2O exposures, the reactivity increases with increasing ion bombardment energy up to 2 keV. GaAs samples, Ar^+-ion-bombarded at 2 or 3 keV, show nearly identical quantities and distributions of chemical species following O_2 exposure; exposure of similarly bombarded materials to H_2O results in the formation of GaO(OH) and $Ga(OH)_3$. The increasing reactivity with increasing ion-bombardment energy reported in this study supports the conclusions of others (Goddard,[21] Mark,[6] Chye,[4] and Brundle[15]) that the reaction of gases takes place at defect sites on the GaAs surface. In conclusion, ion bombardment of GaAs affects the surface reactivity of GaAs and the magnitude of the effect is related to the ion bombardment energy.

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