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Br_2 adsorption on GaAs(110) and surface etching at low temperature

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The adsorption and reactivity of Br_2 on GaAs (110) was studied in the temperature range of $25 \leq T \leq 300$ K with photoemission spectroscopy. Initial Br_2 adsorption was dissociative at all temperatures with Br bonding to both As and Ga. Thermally activated etching was observed after warming up a surface with condensed Br_2 multilayers. $AsBr_3$ formation was evident at 50–100 K but this species desorbed for $T \geq 150$ K. $GaBr_3$ formation also occurred and this species remained on the surface until ~250 K. Br-Ga and Br-As surface species were evident for all temperatures. The erosion of the (110) surface was nearly stoichiometric.

The halogens play an important role in etching processes employed in device fabrication, and the techniques of surface science have been used to advantage to elucidate surface bonding and reactions.[1–7] Chlorine was used as a prototype in the early photoemission studies of halogen adsorption on semiconductor surfaces.[3–5] For Cl_2-GaAs(110), photoemission valence-band[3] and Ga and As 3*d* core-level[4] measurements have indicated dissociative adsorption with Cl bonded exclusively with As on the surface at 300 K. However, a recent study on Br_2GaAs(110) by Cierocki *et al.*[6] has identified Br-As and Br-Ga valence states at 300 K. Surface etching was not observed in these studies. McLean, Terminello, and McFeely[7] have studied XeF_2 adsorption on GaAs(110), and observed the formation of AsF, GaF, and GaF_3 on the surface at 300 K. These results indicate substantial differences in halogen bonding and reaction on GaAs(110).

In this paper, we explore monolayer and multilayer Br_2 adsorption on GaAs(110) as a function of temperature ($25 \leq 300$ K) using photoemission in order to observe surface etching and to establish its relation with surface bonding. Bromine initially adsorbs on GaAs(110) dissociatively at all temperatures with Br-As and Br-Ga bond configurations. Further bromine exposure induces GaAs erosion at $T \geq 50$ K and surface etching with $AsBr_3$-like and $GaBr_3$-like species volatized. Core-level analyses indicate bonding between Br atoms and the GaAs surface is an important intermediate stage for the etching processes at low temperature.

The photoemission experiments were conducted at the Wisconsin Synchrotron Radiation Center. GaAs bars [Si-doped *n* type at $(0.5-1)\times 10^{17}$ cm^{-3}] were cleaved at a base pressure of 5×10^{-11} Torr. The sample was cooled by a closed-cycle He refrigerator and warmed by a heater attached to the cold head. A thermocouple was used to monitor the temperature. The Br_2 source was a homemade doser based on that described in Ref. 8. The main component, a AgBr electrochemical cell, was operated at 400 K with Br_2 release controlled by passing a current of 20 μA through the cell. The chamber pressure remained below 1×10^{-10} Torr during dosing. The advantage of this source is that it was possible to dose a small sample with a well-controlled and localized flux, minimizing the total exposure of the system to bromine. Angle-integrated As and Ga 3*d* core-level spectra were acquired with 90 and 65-eV photons, respectively, under conditions that gave a combined energy resolution (photons and electrons) of 170–220 meV. Br 3*d* levels were measured with 115-eV photons at a total resolution of 370 meV. The photon energies were chosen to give approximately the same inelastic scattering lengths. Since the Br_2 sticking probability at 25 K is close to unity and the electron inelastic mean free path was known from the emission of As and Ga surface core-level components,[9] the Br_2 exposure can be calibrated by measuring the intensity attenuation of the substrate As and Ga 3*d* levels and the emission from the Br 3*d* level. For our experiments, the Br_2 flux was $(4.0\pm 0.6)\times 10^{13}$ molecules/cm^2 per minute.

An overview of the effects of temperature on Br_2GaAs(110) surface interactions was obtained by exposing the surface to 11×10^{14} Br_2/cm^2 at 25 K and then warming the sample incrementally to 300 K. This exposure corresponds to 2.5 Br_2 molecules per surface Ga or As atom, producing a Br-derived multilayer at low temperature. (Br_2 exposure exceeding about 3×10^{14} Br_2/cm^2 at 25 K resulted in solid Br_2 on the surface, as can be clearly identified in the valence bands[10]). In Fig. 1, the curves labeled *A* and *A'* show the familiar As 3*d* and Ga 3*d* core-level emission for clean GaAs(110) at 25 K, with fits that show both the bulk and the surface-shifted components.[11] Bromine adsorption produced a dramatic change in the As 3*d* surface component as the feature originally at lower binding energy (-0.40 eV) was converted to one at higher binding energy ($+0.7$ eV). In contrast, the Ga 3*d* level showed only a slight increase on the higher binding-energy side (spectrum *B'*). Warming to 50–100 K produced a new As-Br species, as indicated by the As 3*d* doublet at about $+2$ eV (curves *C* and *D*). We assign the Br-induced As surface component at $+0.7$ eV to As^{1+} and attribute the As doublet at $+2$ eV to As^{3+} or $AsBr_3$-like bonding configurations. These assignments are consistent with earlier observations of a nearly linear relation between semiconductor oxide and fluoride states and the core-level shifts.[12,13] When the sample was warmed to 150 K, this As^{3+} signature disappeared (curve *E*), but a broad Br-induced Ga component grew at about -1.2 eV relative to the main line (curve *E'*). We associate this new peak with Ga^{3+} or $GaBr_3$-like species, noting that GaAs oxidation also yields Ga^{3+} species with a smaller energy shift (~ 1 eV) than As^{3+} (~ 3 eV).[14,15] By 150 K, valence-band and Br 3*d* core-level measurements indicated that all unreacted Br_2 had desorbed form the surface. Finally, warming to 300 K led to the disappearance of the Ga^{3+} emission and broadening of the As 3*d* line shape on both sides.

The changes in the As 3*d* surface component at 25 K indicate that Br bonds with surface atoms with charge transfer from As to Br. Reaction by 50 K produced $AsBr_3$-like and $GaBr_3$-like species, but the amount of As^{3+} and Ga^{3+} was less than one monolayer for a surface originally dosed with 11×10^{14} Br_2/cm^2. The disappearance of the As^{3+} and Ga^{3+} species at elevated temperatures raises the question as to whether they desorb, thereby etching the surface.

Figure 2 summarizes As 3*d* spectra taken as a function of Br_2 exposure for GaAs(110) at 75 K. This temperature was chosen because distinctive As-Br and Ga-Br species were produced and because the intensity changes in the As and Ga emission were easily observed. Bromine adsorption produced As^{1+} (curve *B*) at $+0.73$ eV, similar to that observed at 25 K. Extensive bromination is evident from the growth of the As^{3+} species with dosage. Another state that is probably As^{5+}-like emerged at 4.1 eV after exposure to 18×10^{14} Br_2/cm^2 (curve *D*). This species remained small while the $AsBr_3$ product continued to grow. Line-shape analysis shows the persistence of the As^{1+} feature throughout. Ga 3*d* spectra indicate significant Ga^{3+} growth in parallel with As^{3+}. Similar Ga^{3+} formation was also observed at 180 K, as discussed below. These results demonstrate the release of As and Ga atoms from the surface to form the higher bromides that are retained at 75 K and Br bonding to the surface to form As^{1+} and Ga^{1+}.

The inset of Fig. 2 shows the As to Ga 3*d* intensity ratio as a function of Br_2 exposure, normalized to the emission for the clean surface. At 75 K, the total As intensity relative to Ga gradually decreases, an affect we attribute to slow As bromide evaporation. Warming to 150 K following exposure to 30×10^{14} Br_2/cm^2 produced a significant change as the As to Ga intensity ratio dropped

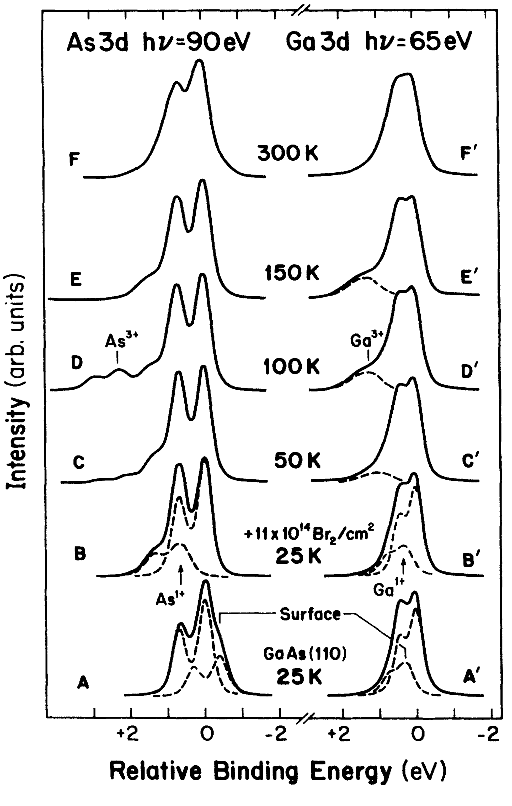

FIG. 1. As and Ga 3*d* core-level spectra taken before and after the condensation of 11×10^{14} Br_2/cm^2 on GaAs(110) at 25 K. The solid curves are traces of raw data and the dashed lines are the fitting components. The surface was warmed up incrementally to 300 K. All spectra were aligned with the bulk components. The surface bromination and the sequential disappearance of As^{3+} and Ga^{3+} below 300 K are clearly illustrated.

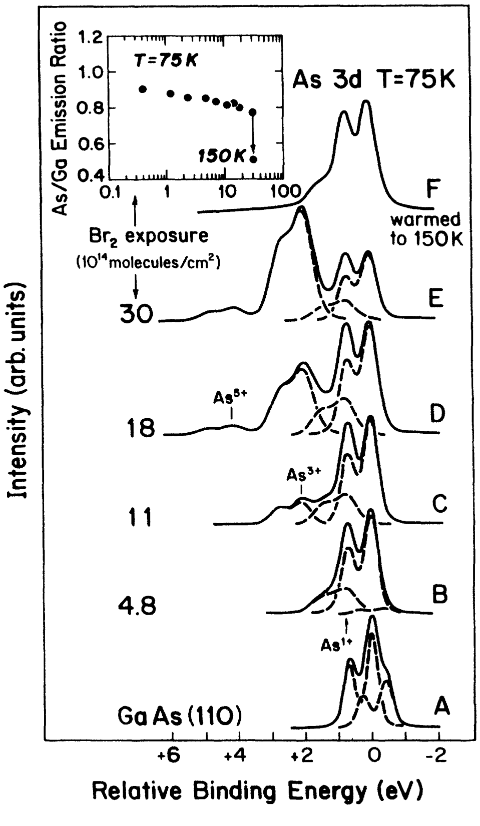

FIG. 2. As 3*d* levels showing the formation of As bromides as GaAs(110) was exposed to Br_2 at 75 K. The inset shows the As/Ga core-level intensity ratio, which is normalized to that on clean GaAs(110). As^{5+} disappeared at 125 K and As^{3+} evaporated by 150 K (curve *F*), causing a large drop in the As/Ga intensity ratio.

to about one half of the value on the clean surface. The As^{5+} emission disappeared at 125 K and the $AsBr_3$-like species desorbed by 150 K, producing curve *F* in Fig. 2. As^{5+} is probably unstable, as bulk $AsBr_5$ cannot be produced.[16] The loss of As-Br molecular species in vacuum can be understood qualitatively by noting that $AsBr_3$ has relatively low melting and boiling temperatures (306 and 494 K at 1 atm). From Fig. 2 it is evident that $AsBr_3$ is the primary species responsible for As etching at low temperature.

The exposure of GaAs(110) to Br_2 at 180 K yields a surface that is quite different from that formed at 75 K, as summarized in Fig. 3. During early stages of bromine exposure, the Ga 3*d* emission increases slightly on the high binding-energy side due to Br-Ga bonding. The existence of surface Br-Ga bonding is indicated by valence-band measurements[5] as well as Br 3*d* results discussed below. When the Ga^{3+} component appeared in Fig. 3, curve *B*, the Ga 3*d* spectrum contained a component at +0.32 eV, which can be assigned to a formal Ga^{1+} configuration. This Ga^{1+} component is very close to the original surface peak (+0.28 eV). The minimal chemical shift between the Ga 3*d* surface component of GaAs(110) and Ga^{1+} in the early stages of surface bromination suggests little net charge redistribution for the surface Ga atoms. The Ga^{3+} component is quite broad [~0.9-eV full width at half maximum (FWHM) for each spin-orbit split component], presumably due to surface inhomogeneity. Similar broadening has been observed for GaF_3.[7] Figure 3 shows that the Ga^{3+} peak increases continuously as a function of Br_2 exposure at 180 K. In contrast, the initial Br_2 exposure converted the As 3*d* surface component to the As^{1+} configuration, but there was little change thereafter at 180 K. The inset in Fig. 3 illustrates the steady decline of the As/Ga relative intensity as the Br_2 exposure increases, leading to the conclusion that the As bromides formed at 180 K were lost to the gas phase. The persistence of $GaBr_3$-like species reflects the higher melting and boiling temperatures of bulk $GaBr_3$ (394 and 552 K) compared to $AsBr_3$. After a total exposure of 54×10^{14} Br_2/cm^2 at 180 K, the sample was warmed to 300 K. As observed from curve *E* in Fig. 3, the $GaBr_3$ species evaporated from the surface and intensity analysis showed that the As/Ga emission ratios recovered to nearly unity (inset Fig. 3). It was also possible to estimate the amount of $GaBr_3$ that had accumulated on the surface at 180 K because any residual Br_2 or $AsBr_3$ had desorbed. From the relative Ga^{3+} intensity in curve *D* and an electron inelastic mean free path of 13 Å for $GaBr_3$, we determined that at least one monolayer of GaAs was etched away by a total bromine exposure

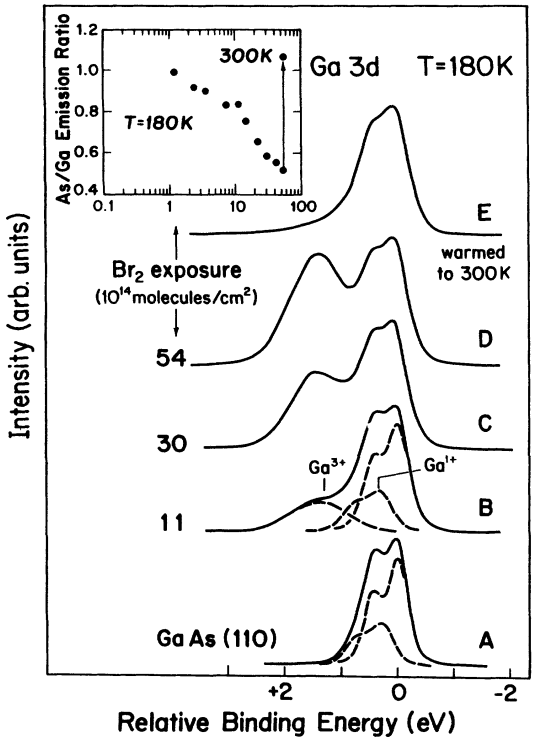

FIG. 3. Ga 3*d* levels for exposure to Br_2 at 180 K. The peak growing at 1.1–1.3 eV is related to Ga^{3+}. The inset shows the renormalized As/Ga core-level intensity ratio. For exposure to 180 K, there was no accumulation of the As^{3+} or As^{5+} species. When the sample was warmed to 300 K, the $GaBr_3$ species desorbed and the surface became approximately stoichiometric.

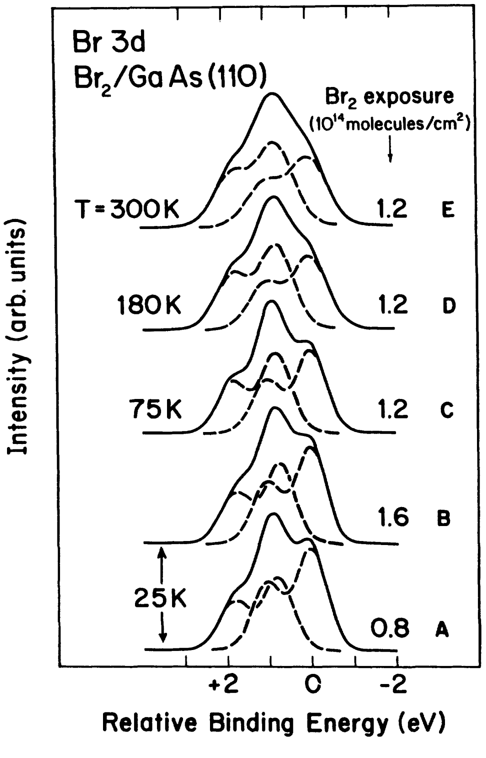

FIG. 4. Br 3*d* core levels showing two components after small amounts of Br_2 exposure at $25 \leq T \leq 300$ K. A quadratic background was removed from each spectrum. The spin-orbit splitting is 1.03 eV and the linewidths of the two components were restrained to be the same in each fit. The energy reference is taken to be the lower binding-energy peak, which is attributed to Br-As bonding. The second component at ~0.8 eV higher binding energy is related to Br-Ga bonding. A new GaAs(110) sample was used for Br_2 exposure at each specified temperature.

that was equivalent to about 12 Br_2 molecules for each Ga and As surface atom.

Etching of GaAs(110) must involve breaking of Ga and As back bonds. Bond breaking via Br in-diffusion is probably suppressed by the large energy barrier against embedding of the Br anion ($r = 1.95$ Å). The formation of Ga and As tribromides at temperatures as low as 50 K also implies an activation energy that is not associated with in-diffusion. Instead, the Br-derived surface bonding and the associated electronic structure reconfiguration play key roles in the weakening of back bonds.[17] The immediate appearance of the As^{1+} feature and its nearly constant emission relative to the bulk during erosion imply that As atoms in the topmost layer of GaAs always bond with Br. Surface Br-Ga bonding also exists and is favored by thermochemistry since diatomic halogen-Ga molecules generally have higher heats of formation than halogen-As molecules.[18] The fact that As^{3+} and Ga^{3+} appear simultaneously during erosion (see Fig. 1) indicates the Br affects both As and Ga surface bonds. As shown in Fig. 4, Br 3*d* core-level spectra measured after submonolayer exposures exhibit two components separated by 0.8 eV, regardless of substrate temperature during exposure. The one at lower binding energy is related to Br-As bonding, consistent with the significant charge transfer indicated in the As 3*d* levels. The higher binding-energy component involves Br-Ga bonding, in analogy to the O 1*s* results for O/GaAs(110).[19] We conclude the bromine adsorption is dissociative, even at 25 K. (Solid Br_2 condensation was observed at 25 K only for exposures exceeding $\sim 3\times 10^{14}$ Br_2/cm^2, as indicated by the bromine molecular orbitals in the valence bands[11] and a new Br 3*d* component at ~ 0.6 eV, deeper than the high binding-energy component in Fig. 4). The Br 3*d* results are consistent with the valence-band observation of Br-As and Br-Ga states at 300 K (Ref. 10), but in contrast to earlier conclusions for Cl_2-GaAs(110) where Cl was found to bind only to surface As.[3-4]

Finally, we have examined the room-temperature reactivity of Br with GaAs(110). As at low temperature, the initial Br sticking probability is close to unity. In this case, the Br 3*d* intensity saturated after exposure to $\sim 3\times 10^{14}$ Br_2/cm^2. The As and Ga 3*d* levels showed broadening toward higher binding energy but no new high bromides could be detected, in contrast to the low-temperature measurements where there was obvious As^{3+} or Ga^{3+} accumulation on the surface. We attribute the difference to desorption kinetics and the fact that our measurements involved dosing and subsequent measurement over a time frame of 10–40 min. We also note that the As and Ga 3*d* line shapes after a total exposure of 54×10^{14} Br_2/cm^2 were identical to those obtained after equivalent exposure at 180 K, followed by warming to 300 K where surface etching was obvious. Undoubtedly, the core-level broadening reflects the production of steps and surface irregularities, as well as disordered regions with As^{1+} and Ga^{1+} bonding to residual Br.

In conclusion, we have observed the dissociative chemisorption of Br_2 on GaAs(110) with Br-Ga and Br-As bonding configurations formed at all temperatures between 25 and 300 K. By studying the evolving surface character as a function of temperature and exposure, we were able to directly observe the thermally activated formation of Ga^{3+} and As^{3+}, As $^{5+}$ states and then their desorption below 300 K. We found the erosion of GaAs(110) to be nearly stoichiometric.

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