

Prelude to etching: The surface interaction of chlorine on GaAs(110)

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The interaction of Cl₂ with GaAs(110) was studied with photoelectron spectroscopy at 300 K. The results show that Cl₂ dissociates and prefers Ga¹⁺ bonding at low coverage and chemically distinct states can be correlated with structural information obtained from scanning tunneling microscopy. This Cl-Ga state was characterized by a distinct surface bonding configuration as Ga atoms lost charge, As atoms gained charge, and the surface bonds became less *sp*³-like. The result was a chemical shift for both Ga and As. Cl-Ga islands developed as the Cl coverage increased and subsequent adsorption of Cl within those islands enabled the formation of Cl-As bonds and an As¹⁺ state.

Dry etchants play an important role in the fabrication of integrated circuits, a role that must be continually refined to keep pace with shrinking device features. Intensive research on plasma etching has focused on the effects that processing variables such as pressure, gas species, and bias have on the specificity and directionality of etching.¹ These studies notwithstanding, relatively little is known about the details of the etching reactions that occur at the surface. These details are important because realistic modeling of etch rates and etch morphologies must consider adsorption, desorption, and reaction mechanisms. Even for the comparatively simple Cl₂-GaAs(110) or (100) systems,²⁻¹⁴ there has been controversy concerning the Cl adsorption sites. Early investigations^{8,9} suggested that Cl bonded only to As while recent studies of desorption products^{6,7} have concluded that Cl bonds to both As and Ga. Scanning tunneling microscopy (STM) results by Patrin *et al.*^{15,16} have shown the formation of two-dimensional islands and chain structures for halogens bonded on GaAs(110).

In this paper, we use high resolution synchrotron radiation photoemission to investigate bonding changes at the Cl-GaAs(110) interface as a function of Cl₂ exposure. These studies were undertaken at 300 K for direct comparison to our STM results. We show that Cl₂ dissociates and bonds with both As and Ga to produce As¹⁺ and Ga¹⁺ states, with a preference for Ga bonding at low coverages, and we correlate these spectroscopic observations with the adsorbate sites obtained by STM. In addition, we deduce that ordered Cl bonding to Ga affects the distribution of charge of surface atoms and reduces the *sp*³ character of the surface bonds. This is reflected by a new As core level feature that is evident in the photoemission spectra.

The photoemission measurements were done using the Minnesota-Argonne Extended Range Grasshopper monochromator and beamline at the Wisconsin Synchrotron Radiation Center. Core-level and valence-band energy distribution curves (EDC's) were collected using a double pass cylindrical mirror analyzer in a vacuum chamber with a base pressure of $\sim 5 \times 10^{-11}$ Torr. The overall instrumental resolution for the Ga and As 3*d* core-level spectra was ~ 100 and ~ 160 meV using photon energies of 65 and 90 eV, respectively. The EDC's were analyzed using a nonlinear least-squares minimiza-

tion curve-fitting routine.¹⁷ Spectra were evaluated using convolved Lorentzian and Gaussian functions that represent chemically-inequivalent components evident in the EDC's. The intensities and positions of these components were simultaneously optimized against a background represented by a cubic polynomial. Fitting parameters determined from clean surface spectra included the spin-orbit splitting, the branching ratio, Lorentzian and Gaussian widths, and the energy position of the surface components. For Cl-modified surfaces, only the Gaussian widths were allowed to vary when physically justifiable to account for inequivalent bonding configurations.

Unpinned mirrorlike (110) surfaces of *n*-type (Si-doped at 1×10^{17} cm⁻³) and *p*-type (Zn-doped at 1×10^{18} cm⁻³) GaAs were prepared *in situ* by cleaving $2 \times 4 \times 20$ mm³ posts. Cl₂ was supplied by a AgCl electrochemical cell¹⁸ operated at 400 K and 10 μ A. The samples, located 4 cm from the source, were exposed to Cl₂ at 1×10^{-10} Torr after the cell had been operated for ~ 10 min to stabilize the flux. Under these conditions, the flux impinging on the surface was $\sim 5 \times 10^{13}$ molecules/cm² per minute. The Cl coverages were determined independently from (1) the calculated flux from the electrochemical cell, using Faraday's Law with a geometric correction; (2) the ratio of the intensities of the intrinsic surface-shifted components to the Cl-induced core-level components; and (3) the ratio of the intensities of the Cl 2*p* to the As 3*s* core-level emission.

Figure 1 shows the 3*d* core-level emission of Ga and As for GaAs(110) before and after the addition of 0.3 monolayers (ML) of Cl at 300 K. The data points are presented following background subtraction and the lines through the points correspond to the sum of the individual components. Normalization to constant height emphasizes line-shape changes. The spectra are referenced in energy to the bulk Ga and As components to compensate for changes in the surface Fermi-level position induced during adsorption. For submonolayer Cl coverages, we find that the Fermi level was pinned near the valence band maximum for both *n*- and *p*-doped samples, in agreement with reports in the literature.⁶ Analysis of clean surface spectra reveals the familiar surface and bulk components, as labeled in the lower panels. The surface component shifts with respect to the bulk components

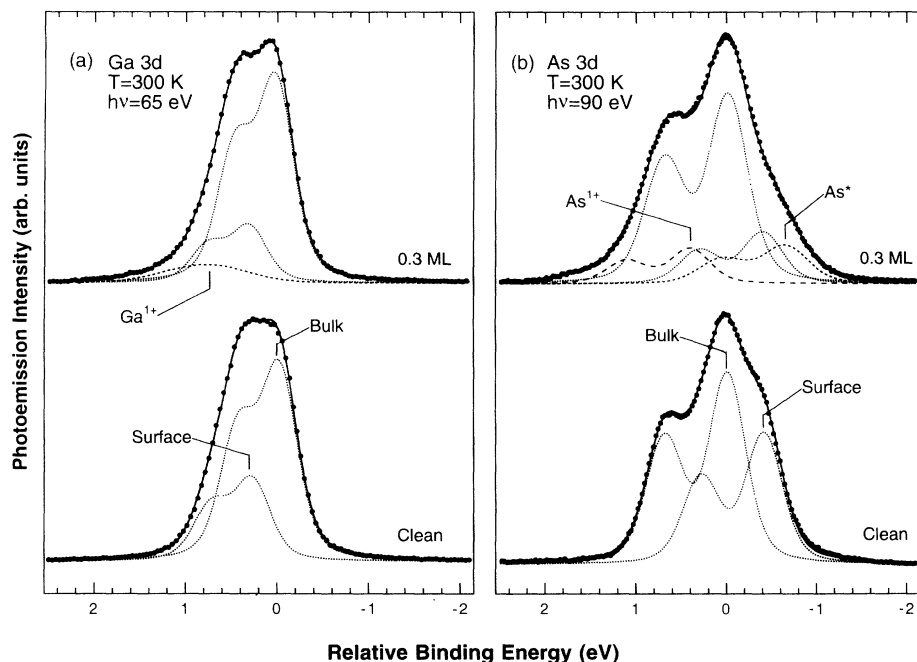


FIG. 1. $3d$ core level EDC's of (a) Ga and (b) As for GaAs(110) before and following adsorption of 0.3 ML of Cl at 300 K. Cl bonding to Ga is favored at low exposure and produces the Ga^{1+} state. As a result, there is a modification of the surface geometry and charge distribution so that the As^* feature is observed. In this regime, islands characterized by Cl-Ga bonding are predominant. Subsequent chemisorption of Cl to As atoms within these islands produces the As^{1+} state at the expense of As^* .

are -0.39 and $+0.31$ eV for As and Ga, respectively.

The Ga EDC's in Fig. 1(a) show a Cl-induced adsorbate peak, labeled Ga^{1+} , that is shifted $+0.61$ eV relative to the bulk component. This feature can be distinguished for coverages as low as 0.03 ML and it grows in intensity at the expense of the intrinsic surface component. The displacement of 0.3 eV between the Cl-Ga bonding peak and the intrinsic surface component reflects a redistribution of charge in the Ga-As bonds. Detailed line-shape analysis for Cl-exposed surfaces indicates that the bulk and surface components derived from the clean surface were not broadened for low coverages, implying that there was little surface disruption at room temperature. In comparison, spectra obtained after significant etching indicate surface disruption since the intrinsic components required an additional 50% broadening factor. We note that the Ga^{1+} peak evident for 0.3 ML in Fig. 1 is very broad because it reflects inequivalent bonding configurations associated with the Cl-derived islands observed with STM.^{15,16} A model of Cl adsorption sites on GaAs(110) derived from the results of Patrin *et al.*^{15,16} is shown in Fig. 2. The upper left portion of the figure depicts two-dimensional islands composed of Cl atoms adsorbed to the surface Ga. We associate these features that dominate at low coverage with the Ga^{1+} species observed spectroscopically.

The As $3d$ core level of Fig. 1(b) shows a loss in intensity of the intrinsic surface-shifted As component with Cl adsorption and the development of *two* Cl-induced peaks. The feature shifted $+0.43$ eV is attributed to an As^{1+} bonding state, as has been deduced by Schnell *et al.*⁹ and Shuh *et al.*¹⁹ As noted for the Ga^{1+} component, the As^{1+} component is broader than the clean components. These As-bonded species are depicted as defectlike sites in the ordered Cl-Ga island in Fig. 2, and STM measurements showed that As-Cl sites decorate the Ga-Cl islands

but do not produce a closely packed structure. This difference in packing is reflected in the improved resolution of the As^{1+} feature when compared with the Ga^{1+} feature since the Ga^{1+} peak incorporates contributions from both the interior and exterior of the Cl-induced islands.

The intrinsic surface components in the $3d$ core levels of Ga and As are the result of a relaxation of the (110) surface whereby As atoms gain charge and Ga atoms lose

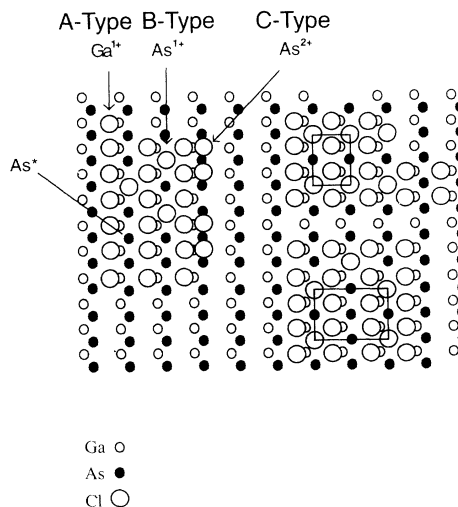


FIG. 2. Surface depiction from Ref. 16 of Cl adsorption sites on GaAs(110) at 300 K. The A-type Ga-bonded features are localized within the rectangle formed by four As atoms while B-type As-bonded features are centered directly over As atoms. C-type features occur only in pairs between As atoms along the edges of A islands. Local B-type $(2 \times 1)/c(2 \times 2)$ adsorbate structures are outlined at upper right.

charge relative to the bulk. This lowers the surface energy. The formation of Ga^{1+} and As^{1+} oxidation states upon Cl adsorption reflects the greater electron affinity of Cl. Hence, as shown in Fig. 1, the Cl-Ga, Cl-As, and intrinsic Ga surface components are electron poor while the intrinsic As surface component is electron rich in comparison to the bulk. While accounting for most of the observed effects, this picture offers no explanation for the As^* spectral feature in Fig. 1(b) since it appears at lower binding energy and, in this simple chemical model, it should be electron rich. As^* has not been previously identified because emission at a lower binding energy than the As bulk component was attributed to a broadened surface component. We discuss its origin below.

The STM-derived structures depicted in Fig. 2 are dominated by features labeled *A* and *B* that are associated with Ga-Cl (Ga^{1+}) and As-Cl (As^{1+}) bonding, respectively. *A*-type features appear offset with respect to Ga atoms, centered within the rectangle defined by four As atoms. Patrino *et al.* showed that patches of *A*-type features formed on the surface at room temperature and that these patches grew with exposure. We associate them with the Ga^{1+} spectral features of Fig. 1. These patches result in a local (1×1) structure. *B*-type features were observed that were located directly above surface As atoms and are associated with the As^{1+} spectral features. They form mixed $(2 \times 1)/c(2 \times 2)$ adsorbate structures at higher halogen coverage,¹⁶ as depicted to the right of Fig. 2. Constraints on the line-shapes for the bulk and intrinsic surface components and on the accompanying intensities for Ga and As supported the STM results for Br and Cl on GaAs(110) and indicate that Cl produces complex chemisorption bonding sites.

Core-level intensity analysis makes it possible to deduce the relative behaviors of each of the components as a function of Cl exposure. Figure 3 summarizes such results, where $\ln[I(\theta)/I(0)]$ is plotted as a function of Cl coverage. Here $I(0)$ is the total integrated intensity of the Ga $3d$ or As $3d$ core-level emission at zero coverage, $I(\theta)$ is the intensity of each component at a coverage θ , and $\theta=1$ corresponds to the Ga and As surface atom density of $8.85 \times 10^{14} \text{ cm}^{-2}$. Figure 3 shows that Ga and As have nearly identical attenuation curves for the total and intrinsic surface contributions and each decays exponentially. The surface components decay at a faster rate than the total emission, as expected for the growth of an adsorbate monolayer. After the adsorption of 0.4 ML of Cl, for example, the surface components are reduced to $\sim 27\%$ of the starting value.

Figure 3 also shows the normalized intensities for each Cl-induced Ga and As component. Ga^{1+} and As^* appear by 0.03 ML coverages and they exhibit comparable growth rates to ~ 0.2 ML. For $\theta < 0.06$ the normalized intensity of As^* actually is greater than Ga^{1+} . While this may indicate that each Ga^{1+} can generate more than one As^* , we note that the differences in intensity are smaller than the errors in the fitting procedures at these low coverages. From Fig. 3, the relative amount of As^{1+} initially lags the other Cl-induced components. The intensity of As^* reaches a maximum at ~ 0.25 ML and then de-

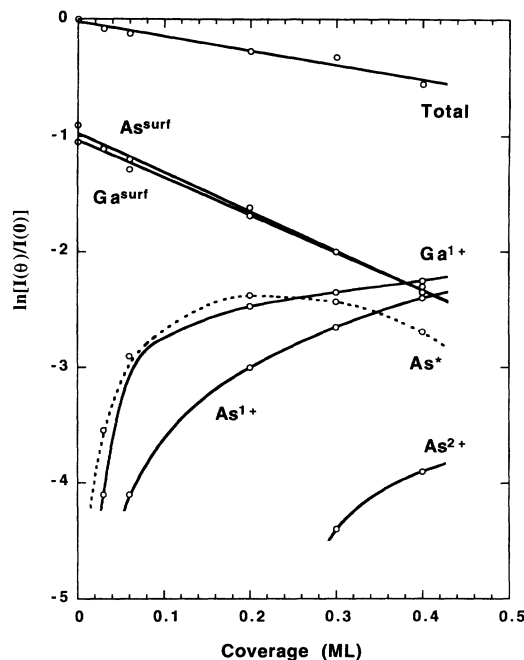


FIG. 3. Attenuation curves at 300 K for the Ga and As $3d$ core emission, $\ln[I(\theta)/I(0)]$, plotted versus Cl coverage, θ . Ga^{1+} formation dominates at low coverage and induces the formation of the As^* species, as depicted in Fig. 2. As^{1+} formation is associated with Cl adsorption to As atoms that are contained within Cl-Ga islands. Hence, As^{1+} forms at the expense of As^* . The similar reduction in the Ga and As surface components reveals that Ga^{1+} formation is balanced by As^* at low (< 0.2 ML) coverage, As^* and As^{1+} at moderate (0.15–0.35 ML) coverage, and As^{1+} at high (0.4 ML) coverage.

creases at a rate equal to the intrinsic surface components. Another Cl-induced As component, As^{2+} , is detected for coverages greater than 0.3 ML. As shown in Fig. 2, we associate this As^{2+} species with *C*-type features observed as a minor constituent in the *A*- and *B*-type STM structures. The formation of As^{2+} necessitates breaking the surface As back bonds and serves as a precursor state for further halogen attack. For coverages beyond ~ 0.5 ML, the surface becomes more complicated as a Ga^{3+} component develops and the intensity of As^{2+} grows significantly, as will be discussed elsewhere.²⁰ in Refs. 15 and 16.

The results of Fig. 3 indicate that Ga^{1+} formation is favored over As^{1+} at very low exposures as the ratio of Ga^{1+} to As^{1+} emission is ~ 2.7 at 0.06 ML. This ratio drops to ~ 1.2 by 0.4 ML. Inspection of the Cl $2p$ core level emission²⁰ demonstrates that there are two components corresponding to Cl-Ga and Cl-As with interactions that are consistent with the Ga^{1+} and As^{1+} states. Supporting evidence that Cl bonds to both surface sites comes from thermodynamic arguments^{21,22} since the bond strengths of Cl to Ga (4.9 eV) and to As (4.6 eV) are similar. Both are much stronger than the bond between Ga and As (2.2 eV).

An adsorption model where *B*-type As^{1+} features form

only when Cl is added to an *A*-type island gives a qualitative description of both STM and photoemission results. This argument suggests that Ga-Cl bonds are favored on the defect-free GaAs surface and that As-Cl bonds (*B*-type features) are only stable in the vicinity of Ga-Cl bonds (*A*-type features). The As^{1+} features first appear as defects in the (1×1) Ga-Cl structure, as depicted in Fig. 2, but continued Cl dosing gives the $(2 \times 1)/c(2 \times 2)$ structures. Although STM can discern the ordering of the As^{1+} sites, photoemission can make no distinction between random and ordered As^{1+} adsorption sites in the Ga^{1+} islands. This insensitivity to ordering of the As^{1+} sites becomes more evident when comparisons are made of photoemission and STM results obtained for chemisorbed surfaces prepared at 300 K and then heated to 475 K. Heating has the effect of converting the islands to linear chains derived of *A* and *B* features elongated along $[001]$.¹⁶ Spectroscopically, there is no difference between islands formed at 300 K with *B*-type defects and the linear chains produced by annealing. Although the chain structures observed with STM are dominated by *B*-type features due to their greater displacement relative to the surface, photoemission confirms that the chains are composed of both As- and Ga-Cl bonds. This suggests that the *B*-*B* interaction that favors the local $(2 \times 1)/c(2 \times 2)$ construction and chain formation is small. A small interaction energy between Cl adatoms is reasonable in light of the low transition temperature and the fact that the minimum separation between *A* and *B* features, 3.46 Å, is much greater than the bond length of Cl_2 molecule, 1.99 Å.

The As^* feature observed spectroscopically is particularly intriguing because it is shifted 0.65 eV to lower binding energy relative to the bulk component. At first sight, such a shift appears perplexing since Cl is more electronegative than As and Cl would not be expected to produce a transfer of electron density to As. Thus, As^* is not likely the result of a direct As-Cl bond interaction, and STM offers no configuration distinct from the *A*-, *B*-, and *C*-type features that are accounted for above. Instead, the development of the As^* feature can be understood by considering the As surface sites that are free of Cl adatoms but are associated with the Ga-Cl islands of Fig. 2, as labeled. Such As^* structures are produced when Ga-Cl islands form. The condensation of Cl on these islands gives As^{1+} at the expense of the As^* configuration. This accounts for the evolution of spectral component intensities evident in Fig. 3. Note that the loss in intensity of the Ga surface component corresponds entirely to the growth of the Ga^{1+} state. In contrast, the reduction in the As surface component is due to

Cl-Ga induced As^* growth for low Cl coverages and then converts to As^{1+} formation for $\theta > 0.1$. The similar behavior in the slope of each surface component suggests that Ga^{1+} and As^* form in a 1:1 ratio at low Cl exposures, while the ratio of Ga^{1+} to As^{1+} approaches 1 at higher halogen coverages.

The existence of the As^* component suggests that Cl-Ga bonding is stabilized by neighboring As atoms. The observed increase in average charge density of the surface As atoms may then simply reflect a bonding resonance from Cl to Ga to As. Charge transfer to As could also occur by a Cl-induced depletion of the Ga dangling bond relative to the relaxed (110) surface. A change in the surface bonds would add strain to the lattice because the Ga sp^2 -like bonds are nearly planar. We speculate that this increased surface buckling may allow a more complete transformation of As atoms from sp^3 - to s^2p^3 -like bonding, gaining electron density in the process. It will remain for calculations to resolve the details of the charge redistribution induced by chemisorption, and such calculations are under way.^{23,24}

Alternative explanations for the existence of As^* would include a shift and broadening of the original surface component due to inequivalent surface configurations or introduction of a component derived from As atoms released from the substrate. Both arguments appeal to adsorbate-induced surface disorder. However, at these coverages the STM results show very little disruption with halogen exposure at room temperature and the shape of the bulk and surface core levels are largely unaffected by Cl adsorption. If As^* were associated with surface disruption, then we would expect the As^* peak to increase with Cl coverage. In contrast, As^* reaches an intensity maximum at ~ 0.25 ML and then diminishes as the As^{1+} component grows, consistent with our picture.

In summary, Cl bonds dissociatively to both Ga and As surface atoms on GaAs(110) at 300 K with a preference for the former at low coverage and the appearance of the latter when Cl bonds to As within Cl-Ga islands. We have observed an As bonding configuration that is a consequence of Cl-Ga bonding since there is a depletion of charge from the Ga atoms.

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¹See, for example, R. J. Schutz, in *VLSI Technology*, 2nd ed., edited by S. M. Sze (McGraw-Hill, New York, 1988), Chap. 5, pp. 184–233; or the excellent review by H. F. Winters and J. W. Coburn, *Surf. Sci. Rep.* **14**, 161 (1992), and references therein.

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